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THE PRINCIPLES AND PRACTICE
OF
TEXTILE PRINTING.

BY

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AND

JAMES BEST FOTHERGILL,
TECHNICAL CHEMIST AND COLOURIST.

With 13 Plates, many Patterns, and 80 Illustrations in the Text.

LONDON:
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1912.

PREFACE.

It is now many years since a comprehensive manual of textile printing has appeared in this country. In the interval, radical changes have taken place in this industry, which apply to some extent to plant and mechanical appliances, but chiefly to the introduction of new and important processes. New styles have been introduced, of which those in which the colouring matters (*e.g.* insoluble Azo dyes, Nitroso blue, Paramine brown) are produced in the fibres are of paramount importance. On the other hand, the industry owes to the incessant activity and ingenuity of the colour manufacturers the introduction of whole classes of new colouring matters, many of which are eminently suited to meet the requirements of the trade. Again, many reagents which were then quite out of the reach of the colourist at the time (*e.g.* formaldehyde, formic, lactic, and glycolic acids, hydrosulphite of soda, chlorate of soda, titanium salts, paranitraniline), on account of their expense, are now available in unlimited quantities at prices which allow of their universal application.

During the past few years, several of the colour manufacturers have issued to their customers some excellent literature on textile printing, but it is only natural that the information which these publications contain is more or less strongly biassed in favour of the special products of the particular firm from which it has emanated. The authors, feeling that an impartially written modern work on textile printing would be favourably received, undertook some three years ago to collate the requisite information, and to present it as a sequel to *A Manual of Dyeing*. It has thus been possible to considerably reduce the size of the new volume, in that repetition of such information as is essential to dyeing and printing alike has been avoided as much as possible. Thus, in the new volume, such subjects as a description of the colouring matters, their composition and properties, are entirely omitted, while others like bleaching, Indigo, Paranitraniline red and Turkey red dyeing are only dealt with as far as they are actually carried out in print works. Most of the processes described are taken from actual practice, and where it has been deemed desirable, a printed pattern has been introduced in the text, to illustrate the effect obtained.

The authors desire to acknowledge their indebtedness to the following firms for having kindly supplied patterns for illustrating the work:—Messrs The Calico Printers' Association, Ltd., Messrs Horridge & Cornall, Messrs Blakeley & Beving, Messrs Meister, Lucius & Brüning, Messrs The Badische Anilin- und Soda-Fabrik, Messrs F. Bayer & Co., Messrs The Society of Chemical Industry, Basle, Messrs J. R. Geigy, Basle, Messrs The Lancashire Ultramarine Co., and Messrs L. Cassella & Co. They also desire to acknowledge their thanks to Messrs Mather & Platt for numerous figures representing machines employed in the industry.

All the standard works on the subject, as well as patent and current literature, have been consulted.

E. K.
J. B. F.

June 1912.

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PART I.

INTRODUCTION.

INTRODUCTION.

The term "textile printing" is used to signify the production, by various means, of coloured patterns or designs upon all sorts of textile fabrics—cotton, wool, silk, jute, linen, and various mixtures of these and other fibres.

Textile printing is really a form of dyeing, but differs from that art in that the cloth, instead of being uniformly coloured throughout by immersion in a solution of dyestuff, has one or more thickened colours or mordants applied to it locally, the colour being developed by steaming, etc., or by dyeing. The close relationship existing, however, between the two is emphasized by the fact that although it is quite possible to print on cloth almost any form of colour capable of being converted into a viscous fluid—as, for example, paint, coloured wax, etc.—yet, broadly speaking, the whole of the colouring matters employed in the one industry are identical with those employed in the other.

HISTORICAL.

The beginnings of the art of ornamenting textile fabrics by the stamping or printing on of coloured designs are lost in antiquity. They are usually assumed to have originated in the Far East, where the Hindoos and Chinese are known to have practised hand printing with wood blocks from the earliest times, but recent discoveries in the Pyramids, and other Egyptian tombs, of fragments of cloth undoubtedly decorated by some process other than dyeing alone prove pretty conclusively that the ancient Egyptians also were acquainted with some form of the art. Textile printing was also practised by the Peruvians before the Spanish conquest in 1531–1532, but whether they discovered the process for themselves or derived their knowledge of it from outside sources (which is not likely, considering the limited means of communication they possessed at that date) is not known. Taken altogether, then, it is probable that the art of printing on textile fabrics was discovered independently and at different times by each of these nations.

On historical grounds, it would appear that the Chinese and Hindoos are about equally justified in claiming credit for the invention of *block printing*; for, while Pliny the Elder (A.D. 23 to A.D. 79) certainly alludes to some unknown process whereby the Egyptians of his time produced patterns on dyed cloth, it is on record that letterpress printing from *engraved wood blocks* was extensively practised in China nearly two thousand years ago, and, further, that valuable Indian fabrics *printed in colours* were known to, and esteemed by, the Romans in the days of the Empire. From this latter circumstance, which shows that the Hindoos had already gained a world-wide reputation for the excellence of their printed cottons, it may, not unreasonably, be inferred (*a*) that block printing, even at this early date, was an old-established industry in India; and (*b*) that any contemporary work produced in Egypt was either not executed by the process used by the Hindoos, or was still in the experimental stage, from which it seems never thoroughly to have emerged. Leaving, therefore, the

Peruvians out of the discussion—for no information relating to their work is available earlier than 1532—the question of the priority of discovery is narrowed down to the consideration of the rival claims of China and India. If we except the Assyrians, who employed carved wooden stamps for impressing cuneiform symbols on wet clay tablets and bricks, the Chinese, so far as is known, were the first to make use of engraved wood blocks for any kind of real printing. It is not unlikely, therefore, that they were the original discoverers of calico printing, for it is quite possible that the idea which led up to their invention of letterpress printing would suggest the feasibility of applying the same process to the ornamentation of textiles. That they produced block-printed fabrics in very remote times is unquestionable, but whether or not they anticipated the Hindoos in this respect is still a matter of conjecture, and even now, after a century or more of controversy, appears to be as far from settlement as ever. In fact, the rival claims of China and India to the honour of priority are based upon pure circumstantial evidence alone. Without going into detail, it may be interesting to note the main line of argument followed in each case.

Taking China first:—In the absence of direct proof to the contrary, it has been postulated by those who hold that textile printing originated in China, that because the Chinese were the first to practise letterpress printing, they would naturally be the first also to practise textile printing. This plausible argument, which depends entirely, for any value it may possess, upon the assumption that the highly civilised, ingenious, and technically skilful Chinese *would be certain to recognise almost immediately* the possibility of applying the principle of their newly invented letterpress process to the decoration of textiles, is pertinent enough to account in some measure for the rise of textile printing in China; but, as a factor in the determination of the probable *date* of that rise, it loses most, if not all, of its specious importance when submitted to analysis. Considering, for instance, that letterpress printing and dyeing are two very different crafts, with nothing in common; that in early times, in China, each craft was a "mystery," the processes of which were only known to and practised by those who had been duly initiated; and that, until comparatively recently, all new discoveries and methods were jealously guarded and kept secret as long as possible, it is in the highest degree improbable that—in the days when letterpress printing was a new invention, and dyeing a purely empirical process—either Chinese printers or dyers would know anything of the technicalities of each other's crafts; or, at least, would be sufficiently conversant with their practice to realise at once the possibility of combining them for the purpose of producing decorative effects hitherto unknown on textiles. In that unscientific age the development of an industry was necessarily a very slow process, and it is not unreasonable to suppose, therefore, that a considerable interval of time elapsed between the introduction of letterpress printing and that of textile printing: for, on the one hand, the printers, for a long time, would naturally confine themselves to, and be fully occupied in, perfecting and working their own particular invention, while, on the other hand, the contemporary dyers, following their occupation on "rule of thumb" lines, would be scarcely likely to conceive *at once* the idea of extending the scope of their craft by the application of an entirely new invention (the object, appliances, processes, and materials of which were so totally different from anything to which they were accustomed), especially as no mode or style of textile decoration then existed capable of giving them a lead in that direction. In any case, the assumption that the invention of letterpress printing involved that of textile printing, and that the two were practically coeval, is nothing more than a mere conjecture, based on possibilities which, though plausible enough on the surface, are found to be rather too subtle and too remote to be unhesitatingly accepted as probabilities when contrasted with the actual course along which the development of letterpress and woodcut printing proceeded in Europe during the Renaissance. To trace the successive steps in this development is both needless and beyond the scope of the present work; but it may be noted that, although block printing was extensively employed in the fifteenth, sixteenth, and seventeenth centuries for the ornamentation and illustration of books and for the reproduction of works of art, it never once suggested itself to the printers and dyers of those times as suitable for application to the ornamentation of textiles.

It thus appears that block printing *on paper* was not so inherently suggestive of textile printing as some seem to have imagined. Had it been so, it is inconceivable that such an important feature, which is assumed, for the purposes of argument, to have been patent to the early Chinese, should have escaped entirely, in analogous circumstances, the keen observation of mighty minds like Albrecht Dürer, Hans Holbein, Lucas van Leyden, and all the other great exponents of wood engraving; and that, too, in an age when craftsmen were no less expert, no less ingenious, no less civilised, and, if anything, more alert to seize upon any means of extending their trade, than were the Chinese of fifteen hundred years before. As a matter of fact, "calico printing" was an unknown art in Europe until the latter part of the seventeenth century—two hundred and fifty years after the first introduction of letterpress and "woodcut" printing; and even then it was not evolved from the latter, but was imported as a "workable process," both directly and indirectly, from India. On the whole, then, while granting that the relationship between the two processes is sufficiently close to afford a certain amount of presumptive evidence in support of the view that "textile printing" in China was derived, in the first instance, from letterpress printing, it cannot be said that any real grounds exist for the broad assumption that their respective inventions were coeval, and consequently it is safer not to assign the invention of the former (in China) to any definite period.

Secondly, as regards India:—Unfortunately, up to the present, no record has been discovered indicating, in the slightest degree, the approximate date at which block printing was first practised in India. But the simple fact of the beginnings of an industry, common to two countries, being put on record in the one and allowed to pass unnoticed in the other, is not of itself any proof that that industry was originated in the first, or that it was introduced into the second from outside. Other considerations must be taken into account before the evidential value of a mere record can be properly estimated; and so, curiously enough, in the case of India, the lack of historical data relating to the rise of textile printing, so far from prejudicing the Hindoo claim to priority in invention, tends rather to substantiate it. In this connection the following points are especially worthy of notice:—

(1) During the period in which textile printing is supposed to have been invented in China, the government of India was in the hands of the Brahmins, who, besides being the priests, scientists, philosophers, and lawgivers, were also the actual administrators of the country, and the sole custodians and interpreters of the Vedas—a series of Sanskrit writings revered as sacred by the Hindoos. According to the Vedic story, which was invented about 1200 B.C. by the Brahmins to justify their own claims to power, "Brahma—the Creator of all the World"—created four classes or "castes" of men from his own body, namely, from his head the *Brahmins*; from his arms the *Kshatriyas* (warriors); from his thighs the *Vaisyars* (tradesmen, craftsmen, and farmers); and from his feet the *Sudras* (menials). Further, it declares that the Veda was miraculously produced from Brahma's mouth at the same time as the Brahmins; that it was to be committed to their charge alone; and that it was to be taught and expounded by them only. Thus invested with divine authority, the Brahmins were regarded as beings of peculiar sanctity, and were held in high honour throughout India. In order to maintain their social, political, and religious supremacy, they adopted

the policy of attributing the *origin* of every branch of art, science, and manufacture to the Veda, adding to it as they thought fit. They instituted the laws of Manu which not only defined exactly the social and religious status of each caste, but regulated everything relating to the daily life of its members—food, clothing, occupation, education, and marriage,—and severe penalties were exacted for the slightest violation of their stringent ordinances. Moreover, they compiled a series of works, known as the Sutras, which, although not asserted to have been directly inspired by the god Brahma himself, were alleged to be based upon the sacred Vedas, and consequently had divine sanction for the statements they contained. In these Sutras they not merely elaborated their religious system, but insisted upon the recognition of their claim to be considered as a sacred, independent, and superior caste, supreme alike over kings, princes, and people.

By these and other means the Brahmins, little by little, extended their sphere of influence, and gradually, but not without some opposition, succeeded in forming practically the whole mass of the mixed population of India into one great social and religious Brahminical organisation—Hindooism—with themselves as its acknowledged leaders and sole directors. Notwithstanding the fact that Buddhism was in the ascendant from about 200 B.C. to 600 A.D., the Brahmins never lost their prestige, nor relinquished their policy of ascribing all new knowledge to the Vedas, for which purpose they kept themselves *au fait* with current developments in all branches of work that they considered of any importance. Neither did they cease from advocating a return to their own particular tenets, which were never entirely superseded by those of Buddha; and as they (the Brahmins) still retained the monopoly of Vedic learning, and were by far the most highly educated section of the Hindoo population, they continued to exercise considerable influence throughout the whole of the above period upon the secular affairs of the people, in whose minds the idea of "caste" was too firmly rooted to be easily eradicated, by a new and wholly ethical religious system, the central principle of which was that future well-being could only be obtained by those who lived a virtuous and charitable life on earth. To a people steeped in ignorance and superstition, such a doctrine was both incomprehensible and much less acceptable than the Brahminical teaching of expiation by propitiatory sacrifices to the gods—an easy way of atonement, and one which afforded a sense of comfort to those who believed in its efficacy. Again, the restrictions placed by Buddha upon indulgence in pleasure, and the observance of the moral precepts he enjoined, proved in practice too rigid and austere to find favour with the mass of the people, and consequently, although Buddhism was nominally the chief religion for about a thousand years, it never displaced Brahminism in any considerable part of India. The two religions were coexistent during the whole of this time, and about equally popular, in many instances flourishing side by side in the same district.

In its highest form, Buddhism was essentially a religion for the devout few. The ideal of Buddha was too lofty and his rules of life too strict for whole-hearted acceptance by the rank and file of the people of his time, and after his death his teaching was, little by little, incorporated with a mass of pagan legend and superstition, until it finally became transformed into a system of idolatry, pure and simple, with Buddha as god. The priests, instead of living the poor, simple, and humble lives ordained for them by Buddha, became rich, luxurious, exacting, and arrogant, and this, together with the debased condition of Buddhism generally, probably contributed in no small measure to the retention by the Brahmins of their old-established temporal power.

(2) If, therefore, textile printing was brought into India from China, it is incredible that its introduction, as a *new foreign industry*, should have escaped the notice of the Brahmins, whose policy, as previously mentioned, was to assign the origin of all knowledge to the Vedas, and through them to Brahma.

Even granting that its first entry into the country may have been unobserved by the Brahmins, it is almost impossible that the *sudden* appearance of the entirely novel decorative effects obtained by its means could have failed to attract their attention and to excite their curiosity; so that, in any case, if textile printing really were of foreign origin, it is surprising that, so far as is known, no attempt was made in the Brahminical writings to attribute its inception to the Vedas.

(3) If, on the other hand, it be considered as an invention of the Hindoo dyers themselves, the absence of all historical evidence relating to its commencement in India is, in one way at least, easily explainable. For in this case the Brahmins would probably regard printing as a mere modification or a branch of the already old-established art of dyeing, and, as such, of too little importance to merit separate mention. Dyeing being one of the industries carried on by the lower castes (Vaisyars and Sudras), was, naturally, not at all interesting *technically* to the Brahmins, and consequently any improvements made in its methods and processes would not be likely to come under their notice, especially if they were effected gradually, as must have been the case with textile printing.

Apart from all questions of evidence or surmise, the fact that textile printing was an extensive and highly flourishing industry in India during the earliest centuries of the Christian era is of itself almost sufficient to dissipate the notion that the art was introduced from China. In view of the reasons already adduced for supposing that the development of textile printing in China proceeded at the usual slow rate of all ancient industries, it is probable that the earliest date at which it could possibly have been introduced into India approximated fairly closely to that at which the products of Hindoo block printers were already known and appreciated in imperial Rome—a fact which clearly demonstrates that even at that early date the industry in India was not merely firmly established, but was established on a more or less extensive commercial scale. Taken altogether, then, it would appear that the most reasonable conclusion to draw is, that textile printing in India was a native invention, and that its advanced state of development, and the high estimation in which Indian calico prints were held at the beginning of our own era, were the result, not of any improvements that may have been effected by the Hindoos in a comparatively recently imported foreign industry, but of their long practical experience of an indigenous craft—an experience probably extending backwards, through many generations, to a period long anterior to that at which letterpress printing was first practised in China.

It is quite possible, therefore, that the Chinese derived their knowledge of block printing from the Hindoos, instead of the reverse being the case, as is frequently argued. In this connection, however, nothing can be positively affirmed; and it is well to remember that, judging by the development of other industries, similar materials and methods would not be at all unlikely to suggest themselves as suitable for the decoration of textile fabrics, to dyers, quite independently, in countries and times widely separated. Be that as it may, the source of European textile printing can be traced easily and directly to India; and consequently, so far as Europe is concerned, India is undoubtedly the true birthplace of the modern industry. From India it spread slowly westwards, by land, through Persia, Asia Minor, and the Levant, until it finally reached Germany, France, and England towards the latter part of the seventeenth century. At about the same time, French trading vessels brought samples of Indian prints, together with full particulars of their manufacture, direct by sea, from the French possessions on the east coast of India, and probably, therefore, the French were the first to practise calico printing in Europe. If so, the art very rapidly became known in Germany, for towards the close of the seventeenth century Augsburg was celebrated throughout the Continent for the excellence of its printed linens. The first attempts to imitate Indian chintzes are, however, believed to have been made in Holland, where the Dutch East India Company introduced printed calicoes before they became generally known in France and England. Some support is lent to this view by the fact that certain authorities attribute the introduction of textile printing into England to Flemish workmen in 1676; but it is very uncertain as to where, when, and by whom the first attempts really were made, and it is probable that they took the form of painting rather than that of printing. Thompson of Clitheroe, an expert calico printer, and one of the greatest authorities of his time on the subject in all its bearings, assigns the beginning of the art in England to a somewhat later date, and asserts that we owe our knowledge of textile printing to a French refugee who established the first printworks *on record* at Richmond-on-Thames in 1690. It would appear, however, that some process of printing or ornamenting textile fabrics was already carried on in this country prior to this date, for, in a pamphlet published in 1677, Sir Joshua Child refers to cotton cloth imported from India for the express purpose of being printed in England in imitation of Indian chintz patterns. A patent taken out in 1619 shows that even at that early date Indian printed calicoes were known in England; and a petition presented to Parliament in 1627 bears evidence to the fact that their importation had by that time become sufficiently important to threaten the interests of English textile workers. The East India Company, however, was too powerful for its opponents, and in 1631 printed calicoes were scheduled, subject to an import duty, as legal articles of commerce. From this time forth English manufacturers sought to restrict their importation by (1) agitating for an increase in the duties, and (2) by doing their best to put competitive imitations on the market. In both of these objects they were eventually successful; but some of the earlier patents show how ignorant they were of the method, and how far letterpress printing failed to suggest to them the true principles of block printing on textiles. For instance, in 1634 a patent was granted for a process of applying patterns cut out in silk, wool, and other fabrics to cotton cloth, affixing them thereto by means of oil, gums, and other adhesives. Other patents dealt with methods of painting on dyestuffs and pigments, but none of them seem to have been successful in practice, and after 1690 block printing replaced them all. In 1689 a printworks was established at Neuchâtel by Jacques Deluze. The reputation attained by this works stimulated other countries to follow suit, and in a short time calico printing had spread rapidly in France, Germany, England, and Portugal, and was greatly extended in the Netherlands, which have always been celebrated for the imitation of "batticks," a style of decoration peculiar to Java and the East Indies generally.

After the closing of the Richmond Works by the death or return of its founder, a printworks was started at Bromley Hall, in Essex, and subsequently others were established in Surrey, to supply the demands of the London market.

Calico printing was first practised in Scotland in 1738, and twenty-six years later was introduced into Lancashire, where, in 1764, Messrs Clayton, of Bamber Bridge, near Preston, laid the foundations of what has since become one of the most important industries of the county.

Block printing being only suitable for comparatively coarse designs, Bell, a Scotchman, conceived the idea of printing calico in the same way that engravings are printed, viz. from engraved copper plates. This process was largely employed in London for many years; but technical difficulties in the way of making the successive impressions join up imperceptibly limited its application to certain styles of pattern, such as those suitable for handkerchiefs and designs made up of detached objects. These shortcomings were entirely overcome in 1783 by Bell's invention of the roller or cylinder printing machine—a machine which was not only capable of being applied to almost every known style of design, but revolutionised the industry by enabling large quantities to be produced at a cheap rate, thus bringing printed calicoes within the reach of the million, upon whose consumption alone depends the success of any great industry.

Oberkampf, of Jouy-en-Josas, was the first to introduce the roller machine into France, and he made such excellent use of it that for a long time he was looked upon by the French as its inventor. Bell's claim is now, however, generally admitted, for as the machine was unknown to Oberkampf before 1800, and was working in England in 1785, it stands to reason that it could not have been invented by the French printer.

With the exception of a few refinements of movement, and a few additions extending its range of usefulness, the machine in use at the present day is substantially the same as that invented by Bell one hundred and twenty-eight years ago—a fact which shows how successfully he overcame all the difficulties of the problem he set himself to solve.

But improvements in calico printing were by no means confined to the mechanical methods of its application; many processes were improved and new ones invented, and many new colours were gradually added to the palette, so to speak, of the calico printer's colourist.

Down to about the end of the eighteenth century dyers and printers were almost entirely restricted to the use of vegetable dyestuffs, especially in patterns containing several colours; but with the advance of chemical science all but the best of such colours have been replaced by artificial products. Amongst the earliest improvements in this direction may be mentioned the employment of mineral colours developed on the fibre—Iron buff, Prussian blue, Antimony orange, Manganese bronze, and the yellow and orange chromates of lead. The year 1856 marked the beginning of a new epoch in calico printing, for in that year W. H. Perkin opened up a new and vast field of chemical research by his great discovery of "Mauve"—a colouring matter derived from that apparently most unpromising material, coal-tar. Following the lead given by Perkin, Medlock prepared Magenta in 1860, Griess the diazo-compounds in 1864, and Graebe and Liebermann a method of producing artificial Alizarin, the essential colouring principle of madder root, in 1868. Within recent years artificial Indigo has also been prepared, and, as far as calico printing is concerned, it has already practically replaced the natural product, being specially suited for this purpose on account of its freedom from sand and other gritty particles, an advantage which ensures better and more regular results, besides effecting considerable economy in other directions.

The resources of the calico printer and dyer are constantly added to by the unceasing production of new and improved artificial dyestuffs, and the number at his disposal is now so enormous and their properties so diverse that he is enabled to introduce almost any shade demanded into styles of work that were formerly restricted to one or two colours only.

At present calico printing is carried on in almost every civilised state in the world, and its advance during the last two centuries has been so stupendous that the combined annual output of the numerous works is now, probably, many times greater than the sum-total of the production during the whole of the eighteen centuries preceding the invention of Bell's roller printing machine.

GENERAL CONSIDERATIONS.

A piece of printed calico is at once one of the most familiar, most useful, and perhaps the most wonderful of all the wonderful products resulting from the practical application of human ingenuity to the service of man. The decorative purposes to which printed goods can be put are so numerous and varied, and the needs they supply so universal and diverse, that they have become a household requisite in every class of society, and are so widely disseminated that a "bit of print" is now to be found in almost every palace, cottage, hut, and tent of every country with which commercial relations have been established.

In *first-rate* modern calico prints beauty and utility are united, and the result represents, to a degree hitherto unapproached by any other article of domestic use, the combination of some of the most splendid achievements of mechanical genius, scientific research, and artistic skill. And yet, despite all this, even the finest of these fine examples of applied science and art evoke but little real interest, and are nowadays looked upon by the public as very commonplace things indeed. The wealth of thought, expert knowledge, and skilled labour brought to bear upon their production (not to mention the vast expenditure entailed, and the imposing, yet delicate and exact, machinery employed) is only equalled by the stolid, matter-of-fact indifference with which the result is regarded. It is true that printed goods are immensely popular, but their popularity is independent of any artistic merit they possess, and is due rather to their affording a cheap, clean, and convenient means of introducing *colour* and *pattern* into the wardrobe and the decoration of the home, than to the facts that they are the outcome of centuries of experiment, and the concrete realisation of the devoted study of generations of artists, chemists, and engineers. To the great majority of purchasers a calico print is purely and simply a calico print—pretty, maybe, and useful, but beyond that nothing more than a piece of coloured cotton, a thing of little value and of less interest; and it rarely or never occurs to them that any process at all is involved in its production. Perhaps this is not to be wondered at, for the very abundance and the cheapness of printed fabrics have brought them within the reach of all, even the poorest; and now that they are common objects in every household, they are no longer novelties, and have ceased to attract any particular attention. In short, if familiarity has not exactly bred contempt, it has at least bred apathy; and yet, if the purchaser were only able to realise that in high-class calico printing many of our most talented designers find almost constant employment for their inventive faculties in the creation of new and artistic patterns, and that their ideas are, more or less, adequately expressed in practical form through the medium of the most perfect application of the latest discoveries in tinctorial chemistry and the most recent improvements in machinery, he would appraise the result at a very much higher figure than its price per yard, and would probably find that a calico print of the best quality possessed artistic merit and scientific interest far beyond what he had imagined.

Although calico printing, on an industrial scale, is not perhaps the form of applied art best suited to display the individuality of any one man, it is nevertheless capable of yielding results the artistic and decorative qualities of which entitle it to a prominent place in the ranks of those influences which make for true beauty in our immediate surroundings. The ingenuity of the artist and chemist has a scope in calico printing such as no other industry devoted to the decoration of textiles affords. The vast variety of effects obtainable—ranging from the most bewildering intricacy of fine pattern and the utmost delicacy of ornament, to the broadest effects of heavy line and mass,—the possibility of presenting the same pattern in numerous and diverse combinations of rich permanent colours, and the adaptability of the process to ornament of every style and to fabrics of every kind, give a freedom to fancy and an impulse to originality in the selection and treatment of suitable ornamental material that are not to be found in any other direction. With its wide range of possibilities, calico printing affords the chemist almost unlimited opportunities for introducing new, improved, and elegant "effects" of all descriptions, and offers to the designer, amongst other things, a means of conveying to the masses, for whom he largely works, new, clear, and truthful impressions of many of the subtler features of plant forms which are too delicate for reproduction by any other method of textile decoration. The result is that, at the present time, a collection of the best examples of the work of the best calico printing firms exhibits fertility of invention, beauty of form and colour, wealth and variety of incident, and a rare discriminative faculty in the selection of just those features of natural plants best suited to the work in hand, and in their adaptation to the embellishment of the fabric in question—all of which qualities stamp the goods which possess them as artistic productions. Of course, no one would contend for a moment that calico printing can equal the richness of either tapestry or silk-weaving, in both of which crafts the variety of surface obtainable, and the texture and lustrous sheen of the materials employed, add considerably to the resources of the designer, and impart to the work a beauty quite distinct from that of its pattern and colour alone; but for cheaper work, within the reach of everybody, calico printing offers a ready and reliable means of producing pleasing coloured patterns on a variety of fabrics—patterns which, from an artistic point of view, leave nothing to be desired, and in many cases are superior in artistic merit to those commonly employed for even the most costly and sumptuous goods in woven wool and silk.

A *first-rate* example of calico printing is, therefore, worthy of much more consideration than it usually receives, and, so far from being a mere commonplace article, it is "a thing of beauty," and if not exactly a "joy for ever," is at least, so long as it lasts, a source of pleasure to those who can intelligently appreciate its excellences. Unfortunately a vast amount of modern machine-printed work, although *perfectly executed*, is undoubtedly *artistically bad*, inasmuch as the facilities of the process have been grossly misapplied in stupid and nugatory attempts to imitate deceptively the conventional treatments of ornament peculiar to, only suitable for, and characteristic of quite other methods of textile decoration. Printed imitations of woven "effects"—embroidery, patchwork, appliqué, lace work, tapestry and chenille hangings, etc.—are artistic barbarisms, whose only claims to notice are (1) that they exemplify what ought to be avoided in calico printing design; (2) that they are typical of what consummate technique, unrestrained by a sense of "fitness," is capable of perpetrating in way of "catchpennies"; and (3) that they seriously hamper a rightful appreciation of better work, in that those who purchase them (and there are thousands who do) have the impression that their superb execution must needs, in some unexplained way, imply equally superb design. To a cultivated eye, however, such productions represent the acme of perverted taste; and as they are palpably the work of the mere slavish imitator, ignorant, or wilfully disregardful, of the wonderful artistic possibilities of his craft, they scarcely merit more than mention and dismissal. The same remarks apply to those attempts at the literal transcription of Nature which are made to do duty as "designs" in so many of our modern cretonnes. They, too, are imitations—pretentious imitations—all the more to be deprecated because they convey entirely erroneous impressions of what they are supposed to represent, namely, the actual appearance and habits of growth of natural plants. Moreover, they are obviously inconsistent in treatment, some parts of them being "naturalesque" and others "conventional." This cannot, of course, be avoided; for the conditions of calico printing absolutely require the pattern to repeat itself exactly at frequent and regular intervals; and consequently, while it is possible to imitate deceptively certain parts of a plant or flower, it is altogether impossible to represent its natural appearance as a whole, for Nature never repeats herself. "Realistic" or "naturalistic" design involves no effort of the imagination, and requires no more invention than is entailed in twisting about ready-made ornament until it fits a given space without leaving unsightly gaps. Natural flowers, if well drawn, may be an *adornment*, but they are certainly not *ornament* in the proper sense of the word, for, strictly speaking, pure ornament implies, not the servile copying of Nature, but the adaptation of modified natural forms to the enhancement of useful articles. The modifications or changes which are effected in natural forms during their transformation into "ornament" constitute what is known as "conventional treatment"; and as each material and method employed in the "applied arts" possesses characteristic qualities and distinctive limitations, which must (in practice) be taken into account in designing for it, this conventional treatment takes various forms according to the circumstances under which it is to be applied. It follows, therefore, that no definite rules can be formulated as to the extent to which the process of conventionalisation may be safely carried: it is largely a matter of good taste, guided and controlled by constant reference to Nature, and to the conditions of execution or manufacture. Without going into the subject of design, which is beyond the scope of the present work, and will only be touched upon lightly in the following pages where required to explain certain technical necessities, it may be said that "conventionalisation" consists (1) in simplifying, emphasising, or exaggerating the salient features of natural forms so that their ornamental significance is perfectly clear; (2) in arranging them on definite lines, thus reducing their waywardness to order; and (3) in so treating them that their luxuriousness and infinite variety are capable of being expressed in the easiest, most rational, most suggestive, and most effective way in the material and by the process for which they are "designed." To do this properly demands much more of the designer than a well-trained eye and consummate draughtsmanship. Both are necessary to him; but if he is to originate anything new, he must, in addition, be a profound student of Nature and of the history of his art; must learn to understand that natural forms, while eminently adapted to Nature's purposes, are unsuited to the very different purposes of ornament; he must further possess the rare faculty of selecting, and restricting himself to, just those natural features best suited to the work he is engaged upon; and he must be sufficiently conversant with the capabilities and peculiarities of the materials and processes with which he has to deal to enable him, by appropriateness of treatment, in conjunction with an artistic perception of colour and form, to utilise their characteristic qualities to the utmost advantage, and at the same time to keep well within their limitations. Other things being equal, the degree to which the possibilities and limitations of material and means are honestly recognised and respected by a designer is a measure of his technical proficiency and of his power of interpreting Nature in the best possible way; for only by a wholesome and intelligent appreciation of the influence of material upon design can he hope to add to the beauties of form and colour in his work, that "beauty of fitness" which is an absolutely essential element in all decorative work that claims to be artistic. To attempt to get more out of materials and processes than they are naturally capable of expressing is to repudiate their characteristic qualities, and, consequently, to depreciate the value of and to enfeeble the resulting work by depriving it of, perhaps, its greatest charm, viz. the evidence that it ought to bear to its ornament having been designed with direct reference to the conditions of its execution. In calico printing, as in all applied arts, technique governs design. To one sufficiently acquainted with the capabilities of the various methods of printing, it suggests in no uncertain manner the most appropriate treatment and the best kind of conventionality to adopt in a given case, and its limitations, so far from restricting the play of a clever designer's fancy, and slackening his invention thereby, are an incentive to further effort, and become in his hands sources of fresh beauty.

This brief review of some of the more important *general* principles underlying all good design whatsoever will give the reader some idea of the vital necessity of adapting design to process, and may perhaps help him to realise that a well-designed, well-executed calico print is not merely a useful article, but one capable of appealing to the most refined taste in matters artistic, and full of interest to the scientist, and to the craftsman and designer, who, whilst naturally finding their chief delight in certain superior qualities of the best hand-printed work, are yet sufficiently broad-minded to appreciate fully the value of the enormous resources placed at their disposal by modern machinery and methods.

Of many calico printing firms, both at home and abroad, it can be said with truth that in their best work they apply perfectly the true principles of ornament, and, by calling in the aid of the best artist-designers who thoroughly understand the exigencies of manufacture, and by carefully avoiding the meretricious imitative and "naturalistic" effects which brought about the decadence of calico printing in the nineteenth century prior to the advent of William Morris, they succeed in producing work of artistic distinction and fitness; work which ought to become—and will become when its merits are more generally recognised and acknowledged—an important factor in educating the public to a fuller appreciation of all that is best in "applied art."

A first-rate calico print, apart from its useful and decorative qualities, and its charm as an expression of human thought and invention, is a wonderful example of what can be achieved when art, science, and commerce work harmoniously together, and it illustrates very aptly one of the most important chapters in the history of our industrial development. It brings many and varied activities to a focus; and, whether the result of their co-operation prove artistically pleasing or otherwise, no one, except the grossly ignorant, can, after a moment's consideration, honestly describe it as either inartistic, uninteresting, or commonplace.

PART II.

METHODS OF PRINTING.

METHODS OF PRINTING.

Apart from weaving, embroidery, painting, and appliqué, etc., there are five distinct methods of producing coloured patterns or designs on various textile fabrics:—

(1) By hand block printing.
(2) By perrotine or machine block printing.
(3) By "stencilling."
(4) By flat-press printing from engraved copper plates.
(5) By machine or "cylinder" printing from engraved copper rollers.

Of these five methods, cylinder printing is by far the most important; but hand block printing is coming more and more into use again for certain styles of work, and the "perrotine" machine, although little used in England, still finds extensive and increasing employment on the Continent. Stencilling has up to the present found but little application on a large scale, and flat-press printing on textiles is practically obsolete except in Switzerland, where it is used to a slight extent, in conjunction with block printing, for the production of a special class of work. Occasionally machine or "cylinder" printed goods are "filled in" by hand block printing—notably in the case of certain brightly coloured handkerchiefs for the East, in which the red ground is printed by machine, and the brilliant pinks, yellows, blues, and greens are subsequently "put in" by hand printing; and it is quite possible that very fine decorative effects could be obtained on canvas and jute by combining block printing with stencilling, as is already done in coloured woodcuts and for friezes.

Each of the above five methods of printing possesses inherent advantages as well as disadvantages, so that no single one of them can either replace or be replaced by either of the other four without sacrificing some desirable and characteristic quality in the resulting work. The discussion of the æsthetic value of these various characteristic qualities does not fall within the purview of this book; but as they are functions of process, they determine, to a great extent, the choice of the particular method to be adopted for the execution of a given design, and consequently some mention must be made of their influence in practice, and of the causes from which they arise, in order to convey an adequate idea of the scope of the several methods of calico printing.

In the following descriptions, therefore, they will be dealt with from a strictly practical point of view, and as briefly as is consistent with a proper explanation of the points they are intended to illustrate.

(1) BLOCK PRINTING BY HAND.

The art or craft of block printing consists in cutting a design in relief upon blocks of wood, so that the raised parts when charged with colour will transfer the design to whatever fabric the block is stamped upon. It is the oldest, and generally considered to be the most artistic, of all methods of printing textiles, but it is a slow and somewhat expensive process, and is, moreover, in its practical application, more strictly limited to certain styles of design than is its modern competitor, the cylinder printing machine.

The subtle gradations of tint and stipple, the delicate cross-hatchings, the fine, sharp outlines, the clean cut edges of the masses, and the absolutely invisible joining-up of the repeats of even the smallest "cover" patterns—all features so characteristic of most designs printed by the cylinder machine—are altogether impossible to obtain by block printing of any kind.

On the other hand, a first-rate block print, whatever it may lack in mere mechanical neatness, is unsurpassed for its breadth of effect, its decorative value, its freedom from "finicking" detail and elaborate shading, and, above all, for the purity, richness, and transparent quality of its colour, which, in large masses, has the pleasing appearance of a water-colour wash. Compared, too, with perrotine, flat-press, and stencil printing, block printing by hand possesses many advantages. The perrotine is only capable of being applied to designs small in scale and containing not more than three colours; on the flat-press, continuous patterns are impracticable, and it is most difficult to print more than a single colour. By stencilling, unbroken outlines cannot be obtained except by exceeding the proper and natural limits of the process; but by hand block printing, patterns containing any number of colours and on any scale can be reproduced with ease and certainty, the only condition of success being that their ornament must be treated in a broadly conventional manner.

On the whole, then, hand block printing is, *after cylinder printing*, the most generally applicable, and, in consequence, the most important of all other methods, so much so in fact that cylinder printing is its only rival, and that solely in certain classes of work where mechanical precision is a feature of the design, or where cheapness (but not necessarily vulgarity) is a desideratum.

The principles of block printing differ entirely from those of cylinder printing, and it is to this difference that the distinctive character of the work produced by block is to be attributed. If, therefore, the fullest advantage is to be taken of the best qualities of either method, it is evident that the proposed design must be drawn up with due regard to the possibilities and limitations of the particular method which is selected for its reproduction. These possibilities and limitations arise from the nature of the processes and materials employed, and, so far as the two methods in question are concerned, their influence on design is best explained by comparing the fundamental principles of engraving, and of printing from, wood blocks and copper rollers respectively.

In wood engraving—or "block cutting," as it is termed technically—the design is cut or otherwise raised in *relief* on a thick, *flat* block of wood; colour is then applied to the *raised parts*, and the impression of the design obtained by stamping the block smartly by hand on the cloth to be printed. In copper roller engraving the opposite course is pursued, the design being cut out in *intaglio* on the *rounded* surface of the roller, and the impression taken by filling the *incisions* with colour and pressing the cloth into them, both these latter operations being effected by the machine. Further, in the case of block cutting, it is quite impracticable to leave either comparatively fine lines or minute spots in relief, since not only is the utmost skill required to cut them without breaking the grain of the wood, but because, even when successfully cut, they are too weak to withstand the wear and tear of printing. In copper roller engraving, on the contrary, all qualities of line and dot, from the coarsest to the finest possible, may be cut easily, safely, and without the slightest fear of their subsequent damage in printing.

Thus the restrictions imposed upon the treatment of ornament by the nature of "block cutting" limit the application of block printing to such designs as depend for their beauty upon breadth of effect and boldness of handling.

More delicate results can certainly be obtained by employing blocks upon which the design is "built up" in strips of metal (a method to be described later), but in no case can a block print, by whatever means it is produced, ever come up to the delicacy of line and stipple possible in roller printing. Appropriate treatment of ornament, therefore, is absolutely essential if the best qualities of block printing are to be brought out.

Another important point to be considered in connection with the limitations of block printing is the question of "repeat." This presents no difficulty at all in cylinder printing, where the pattern can be arranged to fit perfectly on the roller itself; but in block printing, where the cloth is printed by many separate impressions of the block, the pattern must be so arranged that each impression or "repeat" joins up on every side with the other impressions by which it is surrounded. The question of "repeat" belongs properly to the subject of design; but as it has such an important bearing upon the limitations of block printing, it may not be amiss at this point to give a brief description of what it really is, and to explain how it influences the planning of ornament.

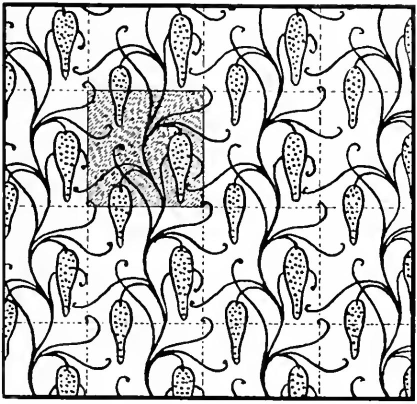

Fig. 1.—Example of a "repeating" pattern.

All patterns for calico printing are based upon a regular geometrical figure—square, oblong, diamond, or hexagon—and are so planned that when their opposite edges are brought together, or placed adjacent to each other, all the lines and masses that occur upon them "join up" exactly and complete the pattern, without leaving any unsightly space or showing any break in continuity of line. This may be achieved in several different ways, which call for no mention here, but the following rough sketches based on the square, and showing the ordinary vertical and side repeats, will sufficiently illustrate the point.

In fig. 2 (representing the darkened portion of fig. 1) that part of the design which falls, within the square ABCD, on the line CD must appear again or "repeat," outside the square, on the line AB; that which falls inside on AC must similarly repeat outside on BD, and *vice versâ* in both cases. Every element of the design is thus seen to occur *within the square ABCD*, and to be arranged in such a manner that when a series of similar squares are placed together with their opposite sides in contact—chess-board fashion—as occurs in block printing, they form a complete pattern (see fig. 1).

To prove whether a pattern will repeat properly or not, it is only necessary to cut it down the centres into four squares (1, 2, 3, and 4, in fig. 2), and then to transpose them as in figs. 3 and 4, when any defect in the fitting is at once apparent, and can be easily remedied before the pattern is cut on the block.

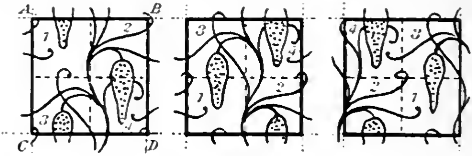

Fig. 2. Fig. 3. Fig. 4.

(Repeats of Fig. 1.)

When a continuous pattern, embodying long unbroken lines or masses of colour, is executed by block printing, these "joinings-up" at the repeats are always more or less perceptible—a defect due to the necessarily separate application of the block for each fresh portion of cloth printed, and the consequent difficulty of accurately adjusting the successive impressions to each other. They may, however, be rendered practically unnoticeable, in certain styles of pattern, by arranging the "repeats" so as to occur behind leaves, or at the junctions of stems and branches, etc., or by allowing some of the smaller objects to complete themselves beyond the limits of the square, as in fig. 5, where the design cut on the block appears, as shown at *a*, surrounded by the heavy line (which is, of course, not engraved). A good example of this latter method of working is to be seen at the Manchester School of Technology in a block printed reproduction of a Saracenic pattern executed at the works of, and presented by, the late Sir Thomas Wardle of Leek. To employ an irregularly shaped block of this kind entails a few extra impressions at each piece-end, but it ensures better work than could possibly be obtained by attempting to print the two halves of a solid object at separate times.

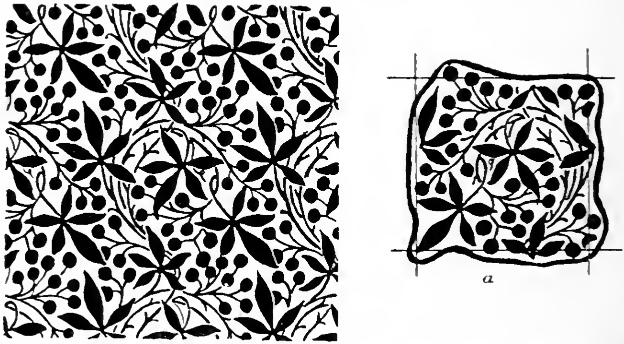

Fig. 5.—A repeating block pattern and sketch (*a*) of the repeat engraved.

In cylinder or "machine" printing—a continuous operation—faulty joints at the repeats never occur, being entirely avoided by engraving the required number of side repeats "to fit" along the length of the roller, and by making the vertical repeats to meet exactly on its circumference. This special facility of roller engraving enables the cylinder machine to be used not merely for patterns that are quite beyond the possibilities of block printing, but also for many others which could be executed perfectly by its means.

The nature of block printing precludes any possibility of very fine lines, softened edges, or delicately blended effects of shading over small spaces. A pattern intended for "blocking" should therefore be designed on broad conventional lines, with each mass of colour perfectly defined and distinct, and with its detail treated in a suggestive rather than an imitative manner. The number of colours that may be introduced into a block printing design is limited only by considerations of economy in block cutting—a separate block being usually required for each colour. In designs with very long or wide "repeats" two or more blocks are necessary for each colour, as it is impossible to obtain a uniform impression by hand from a very large block on account of its great weight, which prevents the printer manipulating it properly, and gives rise in consequence to irregular work. Such large-scale patterns are, however, rarely printed, and it is questionable whether the effect obtained is either better than that obtained in the ordinary way, or sufficiently good to justify the increased cost of production. Graduated and shaded effects may also be employed if desired, but as each tint must necessarily be of a distinct shape, easily possible to cut on the block, they are produced, not by the imperceptible merging of one colour into another, as in stipple work on copper rollers, but by placing in juxtaposition a series of suitably shaped patches of colour, which together give the effect of light and shade in a highly suggestive manner. (See fig. 6, a leaf in three shades of olive, copied from a cretonne pattern printed by block.)

FIG. 6.—Example of graduation in block printing.

When outlines or moderately fine details are designed to occur along with heavy solid masses in the same colour, it is advisable to "cut" them on a separate block, firstly, because if "cut" on the same block as the masses, a colour sufficiently thick to print the outlines and details properly would only yield bare and uneven impressions of the masses, which require much thinner colour; and secondly, because, in multicolour patterns, the employment of a separate outline block allows the colourist much greater latitude in arranging and balancing his various colour combinations—a point of no inconsiderable commercial, not to speak of artistic, value.

In cylinder printing, outline and mass are frequently printed from a single roller, good results being ensured by varying the scale and depth of engraving according to the circumstances; but even here the colour possibilities of the pattern are seriously crippled, and in most cases two rollers are engraved, especially if the masses are large and the outlines comparatively light.

Several other minor conditions govern the application of block printing, but from the foregoing brief consideration of its capabilities as compared with those of cylinder printing it will be seen that, irrespective of all other causes, its specific province is marked out, by the nature of the materials and processes employed in its practice, as that of dealing with patterns in which breadth of effect and purity of colour are of more importance than mechanical perfection in the execution of intricate and delicate detail,—in a word, patterns or designs mainly used for decorative purposes.

BLOCK CUTTING.

Formerly wood was used exclusively for the making of calico printing blocks, but as, from time to time, demands arose for more delicate patterns, metal was gradually introduced, for reasons and in ways that will be fully dealt with and explained in the description of each type of block.

1. **Block cutting on Wood.**—For this purpose use may be made of any fairly hard, close-grained wood, such as box, holly, lime, sycamore, plane, or pear. But as box, holly, and lime are only procurable in small planks and are expensive, a block of sycamore, plane, or pear wood is generally preferred in practice.

For large blocks it is customary to combine these woods with still cheaper ones by gluing one thickness of sycamore or other suitable wood to two thicknesses of deal or pine, taking care to see that the grain of each piece runs in a different direction. Before the glue sets, the block is placed under pressure, and is occasionally further strengthened afterwards by screws which pass through each of the three or more thicknesses or layers of which it is composed. The screws are, of course, put in after the pattern is "cut," otherwise they would interfere with that operation. Another and better method is to join the several thicknesses together by "tonguing and grooving" in conjunction with glue. Composite blocks made in either of these two ways, while being quite as efficient for printing purposes as those cut out of the solid, possess in addition three great advantages over them, viz.—(1) they are cheaper; (2) they are lighter in weight, and consequently easier to use; and (3) they are much less likely to warp in printing.

The shapes and sizes of blocks for hand printing vary according to the width of the cloth to be printed, the uses to which it is to be ultimately put, and the planning of the design as regards its vertical and side "repeats," with which, in cretonne patterns, the lengths and breadths of the blocks are usually made to correspond. If, for instance, cretonne cloth 30″ wide be employed, the side repeats of the pattern must naturally be some divisor of 30″ in order to allow of some whole number of "repeats" being fitted into its width exactly—a precaution it is necessary to take for the purpose of avoiding a waste of valuable material when two widths of it are required to be joined or sewn together without exhibiting any interruption in the "run" of the pattern. The blocks for such a cloth would therefore have a width of 5", 6", 7½", 10", or 15", which would permit of six, five, four, three, or two whole "side repeats" being fitted exactly into the 30 inches of width. The "vertical repeat" of a pattern is quite independent of the width of its "side repeat," and may be any convenient length desired; but it must be remembered that the larger the block, the more difficult is it for the printer to adjust the various impressions accurately, and therefore the more uncertain are the results of printing. For this reason block printing patterns rarely exceed 20 inches in vertical repeat, as otherwise the block would be too heavy for the printer to handle with any degree of comfort, speed, or precision. A usual size for cretonne patterns is 15" × 15"; sometimes 20" × 15" is used; but if the design is on a larger scale, say 30" × 15", or 30" × 30", two sets of blocks, each carrying half a "repeat," are usually necessary to ensure the best results.

As a general rule, blocks are either square or oblong, but sometimes they are diamond-shaped, and frequently take an irregular form, as shown at fig. 5, *a*. In any case, of whatever size and shape, and whether simple or composite, wood blocks for textile printing must always be between 2½" and 3½" thick, for the reason that the thicker they are, the less liable are they to warp, crack, or get twisted out of shape by the prolonged contact with wet colour to which they are subjected during the printing operation.

Although block cutting, generally speaking, is only a refinement of the primitive art of carving in "flat relief," its successful accomplishment for the purposes of textile printing (especially if the design be at all intricate) calls for the utmost care and attention on the part of the worker, and demands of him a sureness of eye and delicacy of hand that can only be attained by long practice and experience of the craft. Being one of the many distinct trades of which calico printing is made up, its full discussion here from a technical point of view would occupy too much space; but as some knowledge of the various practical methods of reproducing a design is essential to a proper understanding of their respective scopes, the following short description of the actual process of block cutting will perhaps help to make clearer what has already been said respecting the particular possibilities of hand printing from wood blocks.

A suitable piece of wood of fine, even grain, and free from all defects, such as knots, cracks, etc., having been chosen and cut to size, its working surface is first of all planed up to a dead level, and then, if necessary, further smoothed with fine sandpaper. Upon the perfect flatness of this surface depends entirely the evenness of the resulting print; for no amount of skill in printing can remedy the irregularities caused by low places on the face of the block. The next step in the process is the transference or "putting on," as it is termed, of the pattern. For this purpose a careful outline tracing of the design, made with a mixture of lampblack and linseed oil, on transparent tracing-paper, is laid face downwards upon the smooth, level surface of the block, and transferred thereto by rubbing it gently from the back with either the thumb-nail or an ivory burnisher. The "putting on" completed, those portions of the design to be preserved in relief are tinted with some water-resisting colour—an ammoniacal solution of cochineal is generally used, and is as good as anything—after which the block is given into the hands of the "cutter," whose work consists in removing the ground between the coloured parts. He commences by thoroughly damping the block (in which condition it must be kept until finished by being wrapped in damp cloths during the night), and then proceeds to cut away the untinted parts of the wood round about the larger objects, leaving the more delicate work until the last. The depth to which the ground is sunk varies considerably. For large objects it may be any depth from ¼" to ¾", but it decreases in proportion as the objects become smaller or are massed closer together, as, for instance, in the case of the petals of a small flower. Usually, too, the sides of the outstanding parts of the block, instead of being cut vertically downwards, slope outwards a little, in order to retain as much of the strength and original solidity of the block as is possible.

The tools used in "wood block cutting" are practically the same as those used in ordinary fine carving. They include various sizes and shapes of chisels, gouges, and drills, together with instruments something like surgical scalpels or penknife blades, which are employed chiefly for trimming up edges and cutting straight lines. When the whole of the uncoloured portions of the block have been cut out to the required depth, the pattern stands up in relief in the same way as letterpress type, only more so. It only remains now to verify the accuracy of the "repeats" by a practical trial and add the "pitch pins." These latter are small pins of brass driven in, at the corners of the block, down to the level of the printing surface, and so adjusted as to position that in printing, when those on the right-hand side of the block are placed over those on the left-hand side of the previous impression, the repeats of the pattern correspond exactly. Sometimes, to prevent the block from absorbing an unnecessary amount of moisture from the printing colour, the cut-out portions are varnished; but when this is done great care must be taken not to drop any varnish on the printing surface, as any difference in texture is apt to give rise to unevenness of colour in the resulting work.

It frequently happens in printing large, solid masses from wood blocks that either the edges are clumsy or that the colour is unevenly distributed. The first successful attempt to overcome these serious disadvantages was made by forming the outlines of such solid masses from strips of copper or brass hammered into the face of the block deeply enough to hold them securely in place, and at the same time leave them projecting sufficiently far for the purposes of printing; the spaces between the outlines thus formed were then filled in with felt, which, being more porous than wood, absorbed more colour, and consequently gave a fuller impression. The clumsiness of the edges was prevented by the narrow fillet of metal, which only took up a little colour—just sufficient to print the cloth, without spreading beyond its proper limits when the block was struck with the mallet of the printer. Later on, this process was replaced in many instances by the simpler and cheaper method of "flocking." In "flocking," the face of the block is first varnished and then dusted with finely divided woollen flocks or "fluff"; after thoroughly drying, the varnish is applied a second time by "dabbing," and the block placed face downwards on paper covered with the same "fluff," and left there until the varnish is perfectly dry and hard. It is then removed, the excess of fluff is dusted off, and after the edges of the design have been trimmed up with a sharp knife the block is ready for use. Both the "felting" and "flocking" of blocks are still in general use, but the former appears to be most favoured in England.

The number of blocks required to realise any ordinary design must correspond to the number of colours employed in that design. As each block, therefore, only represents one colour, separate tracings must be made of the portions of the design occupied by each colour, and transferred by the "putter-on" to separate blocks, which are then "cut" and treated as already described. Thus for a design containing red, pink, yellow, two greens, blue, and an outline, seven separate blocks would be required, and the cloth would require printing seven times—once for each colour. It is this which makes block-printed goods so expensive when compared with those printed by machine from copper rollers—a method in which all the colours are printed at a single operation, and at a speed some hundreds of times greater than that of hand block printing.

Some idea of the curious appearance presented by the separate colour blocks

Fig. 7.—Dark olive.

Fig. 8.—Medium olive.

Fig. 9.—Light olive.

Figs. 7, 8, and 9 show the three blocks employed in producing fig. 6.

of a multicolour pattern may be obtained by referring to the three rough sketches on page 25 (figs. 7, 8, and 9), which represent those portions of the three olive blocks used to produce the complete leaf shown in fig. 6.

Such, in brief, is the outline of "wood block cutting," a method eminently adapted to yield rich, broad, decorative effects, but, as previously pointed out, quite inapplicable to designs embodying fine outline and delicate detail. When patterns of this latter class are intended to be reproduced by block printing, recourse is had to the following method of "coppering."

II. **"Coppered" Blocks.**—In the process of "coppering," the design, instead of being cut out of the solid wood, is "built up" on the flat surface of the block in strips and rods or pins of copper or brass. By this means spots and lines, varying in width from $\frac{1}{64}''$ to $\frac{1}{16}''$, can be obtained easily, and of ample strength to withstand the shocks of printing. Moreover, many delicate little forms, which are either impracticable or too fine to cut on an ordinary wood block—such as ovals, rings, diamonds, stars, rosettes, etc.—are easily capable of realisation on a "coppered" block by simply inserting short pieces of rod or tubing corresponding in section to the shapes desired. For making these small objects, brass rod or tubing is drawn, in long lengths, through a steel draw-plate perforated with holes of the required shape; short pieces of the necessary length are then cut off, and when a number of these are driven into the face of the block they furnish a series of objects identical in shape, size, and height. For solid objects brass rod is used; for those in outline brass tubing.

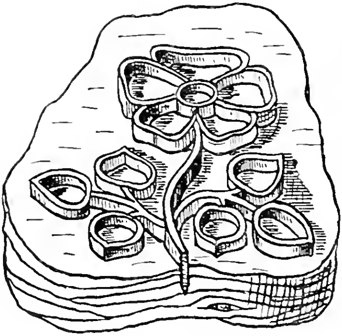

Fig. 10.—Portion of a "coppered" block.

In the making of a "coppered" block the pattern is transferred or "put on" in the usual way, but the "cutter," instead of removing the ground, as for wood blocks, only works on the outline, which he cuts out with suitable tools to a depth of about a quarter of an inch. The holes for the insertion of the pins, etc., for spots, etc., are drilled out at the same time. The pins and strips (or ribbons) of brass are then hammered edgewise into the cut-out lines until the necessary projection is attained—about $\frac{1}{4}''$ above the level of the block; the face of the block is then filed or ground on a flat stone table until every piece of brass stands at exactly the same height, after which any distortion of the lines or displacement of the smaller objects caused by the filing, grinding, or hammering is corrected with pliers of convenient shape. Finally, the whole working surface of the block is polished with fine emery-paper, and after the "pitch pins" are adjusted the block is ready for use. Fig. 10 shows a portion of a coppered block.

"Coppered" blocks, besides being capable of rendering much more delicate effects than are possible to obtain from wood blocks, possess three further advantages over them, viz.—(1) their working parts being entirely of metal, they neither swell nor warp out of shape under the action of wet colour; (2) they are more easily repaired, and consequently are more serviceable; and (3) the brass strips and pins of which the pattern is composed being of the same width throughout their substance, it is only necessary, when the block becomes uneven in surface from constant use, to file it level again, when it will give precisely the same impression as at first. This levelling-up cannot be done on wood blocks because, as a rule, the parts in relief increase in width as they recede from the surface (especially so in the case of lines and small objects); so that if it does become needful to level-up a wood block, the whole of its pattern will require to be re-cut at the edges to bring each object back to its original dimensions.

On the other hand, "coppered" blocks yield a more mechanical and harder effect than those of wood, mainly on account of the fact that the outline they give is of uniform thickness throughout its entire length. In the older process of "wood cutting" the quality of line can be varied at will (so long as it is kept thick enough), with the result that it offers to the designer greater opportunities of giving "expression" to his work. "Coppered" blocks, too, unless, of course, felted as well, are quite unsuited to the printing of heavy, solid masses of colour, and therefore they are only used for fine outlines and delicate touches, like the veining of leaves and similar light work.

III. **Cast-metal Blocks.**—In addition to the two methods of block making already described, a third is frequently employed for small patterns (and those made up of many similar detached objects), where it is necessary, on both technical and economical grounds, to put several "repeats" on the same block. In these cases a great reduction in the time and cost of making blocks has been effected by the introduction of stereotyping—a method whereby as many castings of the "repeat" of the pattern as may be required are made from one mould, and afterwards arranged to fit, and screwed securely in place on a plain block.

The first attempt in this direction was made by casting type-metal in plaster of Paris moulds or matrices taken from patterns cut on ordinary wood blocks; but it was soon abandoned on account of the expense incurred by having, almost invariably, to make a new mould for each casting required. This necessity arose from several causes: in the first place, the high relief of blocks for calico printing made it exceedingly difficult to completely fill all the interstices of the pattern with the plaster; secondly, it was almost impossible to separate the mould from the model without damaging the finer parts; thirdly, during the drying and heating of the moulds they were very liable to crack; and fourthly, when a casting was withdrawn from a satisfactory mould, it usually happened that the more delicate portions of the mould broke off and stuck in the corresponding parts of the casting. In addition to all these risks, the time occupied in "trimming" up defective castings, and the cost of plaster and of fuel for drying, were also heavy items in the cost of production. After many unsuccessful trials to overcome these various defects in plaster moulds, an ingenious means was eventually devised of making a modified wood block itself serve as a mould. The method of working is as follows:—

On a perfectly dry and well-seasoned block of lime or pear wood, sawn across the grain (so that the latter runs at right angles to the working surface), and rather larger in area than the casting required, the outline of the design, or rather one repeat of it, is "built up" in brass, just as in the "coppered" blocks described above. The strips may vary in thickness in different parts of the pattern according to the kind of line required, but each separate strip must be of uniform thickness, and all must be of exactly the same breadth. The design is now "put on" the block and the strips driven in to the predetermined depth, leaving at least $\frac{1}{8}''$ projecting above the surface of the wood. It need hardly be said that every strip of brass must penetrate the wood to exactly the same depth. The pattern completed in this way is then surrounded with a brass border screwed round the outside of the block, and slightly higher than the pattern itself. All the metal parts are then well cleaned and painted with zinc chloride, after which the block is placed face dowards in an iron tray containing a flat cake of previously melted and cooled solder, corresponding in thickness to the amount of the projection of the brass pattern on the block. Heat is now applied under the iron tray, and the solder, in melting and alloying itself with the *outstanding* portions of the brass, transmits at the same time sufficient heat to the *inserted* portions to carbonise the wood immediately in contact with them. On cooling, and taking out the border screws, the brass is found to be firmly embedded in the solder, and the two together can be readily detached from the block by a gentle tap on the back with a hammer, thus leaving a mould of the original pattern burnt in the wood. The mould is now well dusted with chalk or black-lead, and, after blowing away the excess of powder, is provided either with a cardboard or brass border about $\frac{1}{8}''$ high, which converts it into a shallow tray, with the pattern on the bottom burnt out in intaglio. The casting is effected by pouring in molten type-metal up to the level of the top of the border, taking care at the same time to tap the mould smartly once or twice before the metal commences to set, for the purpose of causing it to flow into and completely fill every part of the pattern. When cool, the casting is taken from the mould, and its edges, and such other parts as require it, sharpened up by filing or scraping. A sufficient number of "repeats" of a pattern made in this way are adjusted on a plain block of wood so that they join or fit to each other exactly, and are then permanently secured to it by means of screws or nails. Finally, the block is laid face downwards on a stone or iron slab and ground with emery or sand until all the castings are of exactly the same level.

When it is intended to print solid masses from this kind of block their outlines only are cast, the spaces between them being filled in with felt. If cast solid they would take colour very badly, and give a clumsy and uneven impression.

A simpler, cheaper, and more expeditious method of making wooden moulds was invented by Burch of Accrington, whose patent typing machine burns out the pattern directly, and thus dispenses with the necessity of inserting strips of brass, etc. The machine consists essentially of small steel punches, of various shapes and gauges, heated to the requisite temperature by the flame of a small gas blowpipe or a bunsen burner, and capable of being raised or lowered to any desired extent by means of a lever actuated by the foot of the worker. The whole is mounted in a framework similar to that of the ordinary drilling machine used by engineers—a machine which it resembles very closely, the only radical difference being that the punches do *not* revolve. To make the matrix or mould, the block, with the pattern previously drawn upon its surface, is first placed under the heated punch: this is then lowered and burns its way through the wood to the proper depth, the lines of the pattern being followed by steadily moving the block about by hand whilst in contact with the punch. When one part of the design is completed the punch is raised, and another part of the block then brought under it, ready to undergo the same operations, which are repeated until the whole mould is finished.

In a later development on these lines the heated steel punches are replaced by revolving drills; in all other respects the procedure of mould-making is the same.

THE OPERATIONS OF PRINTING BY HAND.

In addition to engraved blocks, two other pieces of apparatus are required for the printing of calico by hand, viz. the sieve which supplies colour to the block, and the printing table upon which the cloth to be printed is extended.

The sieve (fig. 11) is composed of three separate parts: (1) the sieve proper (*a*), consisting of a wooden drum, covered at one end with a head of fine woollen cloth stretched over it tightly and secured by nails; (2) a similar but rather larger drum (*b*), covered with waxed cloth or thin mackintosh; and (3) a tub (*c*), almost filled with old colour or flour paste—commonly known as the "swimming-tub"—and of sufficient size to allow of the second drum (*b*) floating freely on the surface of its contents without much lateral play. The object of the "swimming-tub" is to provide the elastic support necessary to enable the colour-charged woollen sieve (*a*), when placed upon it, to give up its colour evenly and regularly to the block. A separate woollen sieve is required for each colour, but the same "swimming-tub" may be used over and over again for as many sieves as will fit it. The sieves are not necessarily round, but may be either square or oblong if more convenient for working.

The printing table (fig. 12) is made of perfectly flat slabs of stone or iron (*a*) 2″ to 4″ thick, covered with a printer's tightly stretched woollen blanket (*b*), and supported on a strong and rigid framework of wood. Its dimensions vary considerably according to the cloth to be printed, but a usual size is 8 ft. long, 3 ft. broad, and 3 ft. high.

At one end the framework is provided with brackets (*c*) for carrying the rollers (*d*, *d*), on which are wound respectively the "sets" of the cloth for printing and of the "back grey"—a piece of unbleached calico used for protecting the blanket from the colour which penetrates through the white cloth during the printing. At the other end of the framework another bracket supports the roller (turned by hand) used for drawing forward the "back grey."

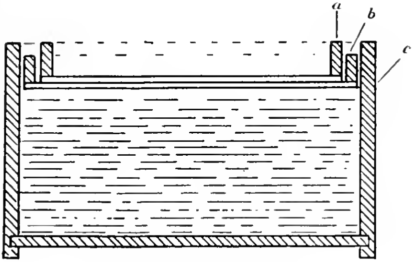

Fig. 11.—Sieve and swimming-tub.

Beyond and above the printing table a series of hanging rollers are suspended from the roof of an upper storey for drying purposes. Formerly the printed pieces were simply allowed to hang in loops from these rollers until sufficiently dry to be taken down, but at the present time many tables are furnished with steam-heated drying chests (*f*, *f*, *f*), situated between a double series of rollers (*e*, *e*, *e*), over which the cloth is drawn by hand. Any distortion of the partly printed pattern, due to the stretching of the cloth under excessive tension, is avoided by gearing several of the upper rollers with the "draw" rollers (*g*), and driving by means of a strap connecting the latter with the hand wheel (*h*) below.

The actual printing is performed as follows:—The woollen sieve, previously saturated with the suitably thickened colouring matter, is placed on the waxed cloth head of the drum (*b*) of the "swimming-tub," and is then again coated with colour, spread over it evenly with a flat brush by a boy called the "tearer." The printer now charges the face of the block evenly with colour by pressing it twice, in different directions each time, on the sieve, and then applies it to the cloth stretched on the table, ensuring a full impression of the pattern by striking the back of the block with a heavy wooden mallet. It is important that the first row of impressions across the width of the cloth should be exactly at right angles to the selvedges, otherwise the pattern, if properly fitted at the repeats, would gradually run off the edges of the cloth at one side, and tend to

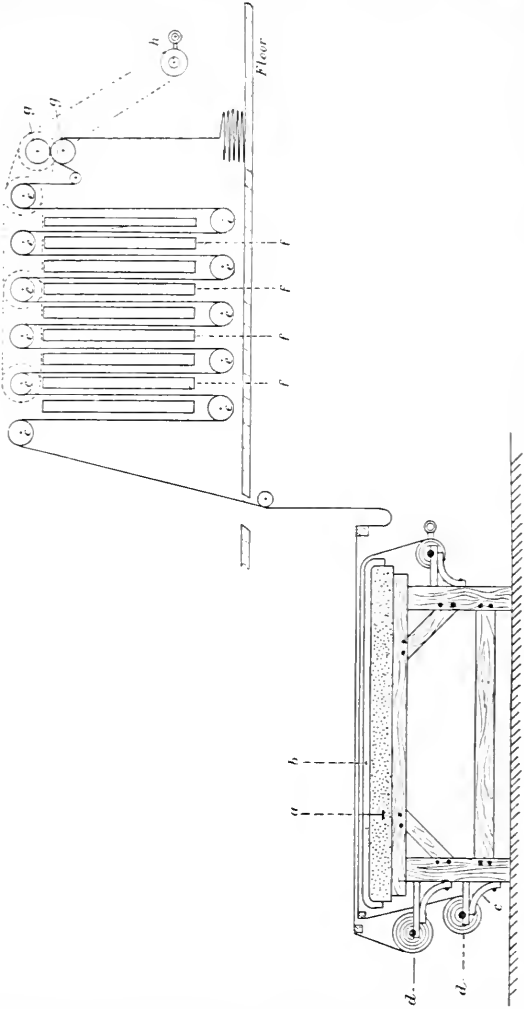

Fig. 12.—Printing-table and accessories.

approach the centre at the other; in short, it would be crooked, and would require extra impressions to fill the cloth. The printer therefore rules guiding lines on the cloth for the first and sometimes also for the second row of repeats, and thus avoids any mistakes he might make if he trusted to his eye alone. The first impression printed, the "tearer" re-charges the sieve with colour, and the printer proceeds with the second and succeeding impressions in precisely the same manner, taking care to make each "join up" or "repeat" properly by placing the "pitch pins" at the top and on one side of the block, exactly over those already printed, by the bottom and the opposite side at the previous impressions. When the two or three yards of cloth lying on the printing table have been printed, they are drawn over the hanging or drying rollers, and at the same time an equal length of fresh cloth is unwound from the roller at the end of the table and drawn forward over it, ready to undergo the same operations, which are repeated again and again until the whole of the cloth on the "set" or roller is fully printed.

In multicolour patterns containing superpositions—that is, the falling of two colours together to form a third—or where each colour in some part fits up closely to all the rest, it is usual, in order to prevent them spreading into each other whilst wet, first to print the cloth throughout with one block; then to dry it, re-wind it on the "set," and print it with the second, block fitting or "registering" the second colour accurately in place by means of the "pitch-pins," with which every separate block of a pattern is furnished, and without which it would be almost impossible to obtain correct "registration." The third colour is applied in the same way, the process being repeated as many times as there are colours in the pattern. Where, however, the various colours are distinctly separated from each other, as, for instance, in patterns made up of differently coloured spots or other detached patches of colour, they may, if desired, be printed immediately one after the other without removing the cloth from the table.

For the purpose of facilitating the correct "registration" of the "repeats" of a pattern, the cloth used in block printing is almost invariably stiffened a little to prevent it from wrinkling during the progress of the work. As a rule, a single run through a three-bowl calender is sufficient for this purpose, but very soft, lightly-woven goods often require to be further "assisted" by a run through a thin solution of gum or starch paste, followed, after drying, by "calendering."

The majority of patterns, as already pointed out, require as many blocks for their reproduction as they contain colours, but in certain classes of design, where the colour-masses are entirely separate or stand clear of each other, it is possible, by modifying the construction of the sieves and the method of supplying them with colour, to print several colours at once from *one* block, thereby effecting a considerable saving in time, labour, and the cost of block cutting.

"Toby" Printing.—Whenever, for example, the several colour-masses of a design are entirely detached from each other, and lie, moreover, at some little distance apart, they may be all "cut" on one block and printed at one operation from a divided or "tobying" sieve of the following ingenious construction:—Over a wooden block, hollowed out into shallow compartments (*a*, *a*, *a*, fig. 13, plan), varying in size, shape, and number according to the requirements of the design, a fine woollen sieve cloth (*d*, fig. 13, section) is stretched and cemented with a mixture of pitch and resin to the tops of the dividing walls of the compartments; a thick string *e*, *e*, *e*, *e*, well soaked in the same pitch-resin mixture, is then cemented *over* the cloth, along the outlines of the compartments, and by forming little ridges on the surface of the sieve, prevents the different colours from intermingling at their edges

The compartments are supplied with colour from below through the connecting-tubes *f*, *f*, *f*, *f*, which communicate with the colour boxes *b*, *b*, *b*, *b*, arranged at the sides of the sieve. With a sieve constructed as shown in fig. 13, it is evident that eight distinct colours could be printed from one block, but, for the sake of simplicity, only four colour boxes are shown. These colour boxes are filled to a height a little above that of the sieve itself, so as to exert a gentle pressure on its under side and help the colours to force their way to the surface. A constant level is maintained in practice by the simple expedient of filling the bottles *c*, *c*, *c*, *c* with colour, inverting them in the boxes, and finally adjusting them so that their mouths rest upon the surface of the colour at exactly the right height above the sieves. Their mode of action is obvious.

Printing from a "toby" sieve is performed as usual, except that, in order to ensure the correct colouring of every impression, the block must always be applied to the sieve in the same way; not dipped in two different directions, as required for ordinary block printing. To enable the printer to do this with certainty every time, and thus furnish every part of the pattern with its proper colour, the block is provided with projecting gauges, which fit into corresponding notches on the sides of the sieve, and will fit nowhere else.

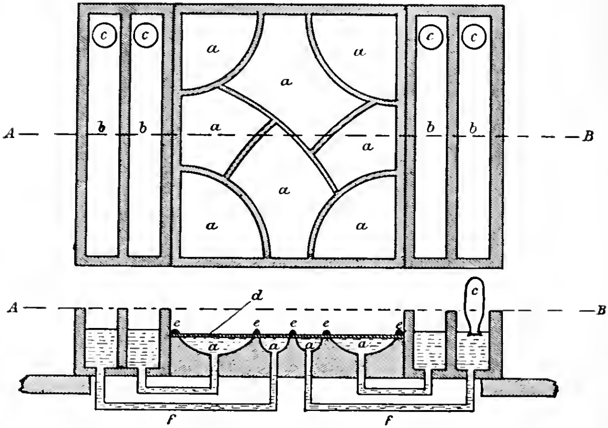

Fig. 13.—Tobying sieve.

The consistency of the colour used in "tobying" exercises considerable influence on the result. If it is too thick it will not pass through the sieve; if too thin, it "floods" the sieve and gives a clumsy impression. Natural gums of the gum Senegal class are usually preferred for thickening purposes, on account of the fact that in even comparatively thin solutions they still retain sufficient "body" to print well.

"**Rainbowing**" (Fr. *fondu*).—Another method of obtaining multicoloured effects from one block is known as "rainbowing," and is adopted when the colours are intended to melt gradually into one another. It differs only from ordinary block printing in the means employed for furnishing the sieve with colour. This is done by a special *colour lifter* that deposits the various colours in little pools across the width of the sieve, over which they are then spread lengthwise in the form of overlapping stripes with a "spreader"—a wooden roller or a half-round piece of wood. The colour lifter consists of a board of wood of the same area as the colour box, provided on one side with a handle and on the other with a series of adjustable pegs or brushes, so arranged that when they are dipped into a divided colour box each peg falls into a certain compartment and takes up its own particular colour. The sieve and "swimming-tub" are of the usual construction, but rectangular in shape; for convenience of working the latter is fitted at one end with a shelf, upon which the divided colour box is placed so as to be in close proximity to the sieve. As in "tobying," the block works against gauges to ensure that it is always dipped in the same place on the sieve. Fig. 14 will give some idea of the apparatus for "rainbowing" as it appears in plan and perspective.

If it be required to produce, say, a side-repeating spectrum or "rainbow" effect in six colours, the divisions of the colour box may be filled as follows:—In No. 1 is put red; in (2) orange; in (3) yellow; in (4) green; in (5) blue; and in (6) violet. The lifter, with its pegs placed in the holes indicated by the black dots in *d*, fig. 14, is then dipped two or three times in the colour box, and transferred quickly, after each dip, to the sieve, when the adhering colour drains off the pegs and is deposited on the sieve in the positions shown by the black spots at *a*, fig. 14. When a sufficient number of pools of the various colours have been transferred in this way, they are joined up into stripes with intermingling edges, and distributed over the entire length of the sieve, by moving the "spreader" backwards and forwards from end to end of *a*. The printing is done as usual, except that if the block is applied more than once to the sieve it must, of course, always fall on the same stripes, otherwise the effect would be spoiled.

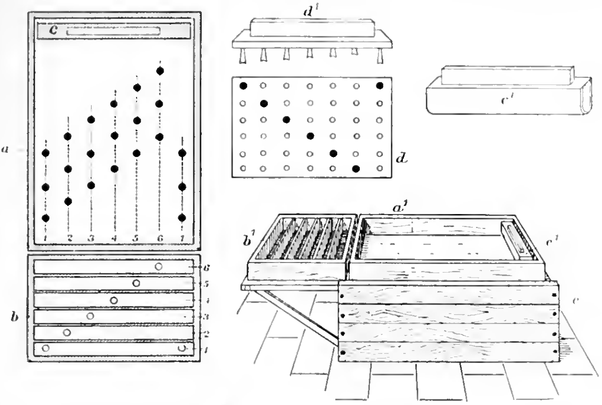

FIG. 14.—Rainbowing or "fondu" apparatus.
a, *a'*, the sieve; *b*, *b'*, the divided colour box; *c*, *c'*, the spreader, covered with cloth; *d*, *d'*, the colour lifter; *e*, the swimming-tub.

By altering the position and number of the pegs in the lifter and changing the colours in the box, it is obvious that many rich and beautiful shaded effects can be obtained readily by rainbowing; such, for instance, as printing each block of a multicolour pattern in gradated tints of its own particular colour, on either a flat or shaded ground; or producing from a plain block various stripes, differing in shade and distance apart according to the disposition of the colours on the sieve.

Notwithstanding that "rainbowing" is capable of yielding striking effects, it is very rarely used at the present time, much more regular results being obtained by machine, and at a tithe of the cost. "Toby" printing, on the other hand, is still employed for filling in the brightly coloured parts of certain styles of handkerchiefs, the grounds of which have been dyed; but it, too, has lost most of its former importance, and is now only used in conjunction with roller printing for a very small proportion of some of the coarser export work.

Many other additions to, and modifications of, the apparatus described in connection with the above methods of block printing have been suggested from time to time, and even made use of; but as they are quite obsolete and have no bearing on modern practice, they call for no special mention in a work of this sort.

(2) BLOCK PRINTING BY MACHINE.

It will be evident from the foregoing descriptions that the labour of hand printing from small blocks must be enormous, and that no high rate of output is possible. This latter disadvantage was recognised in the early days of calico printing, when, to supply the demand for a popular pattern, it frequently became necessary to cut three or four sets of blocks for it, and print them simultaneously by as many printers. The great expense thus incurred naturally set the problem of printing from large blocks by machinery, and finally led to the invention of the "surface" printing machine, and later the "perrotine."

The pioneers in this direction displayed a vast amount of ingenuity in trying to adapt the principle of the typographic machine to the conditions of calico printing; but of all the numerous attempts made on these lines only two achieved any degree of success, viz. the machines of Watt in England and of Depouilly in France.

As both machines are now of historical interest only, no further mention of them need be made beyond saying that they were only capable of printing one colour at a time, that they were only suited to coarse work, and that they foreshadowed most of the principles afterwards so ingeniously applied in the "perrotine"—a three-colour block printing machine, invented in 1834 by Perrot of Rouen, who, ten years later, further improved it to print four colours.

(*a*) **Perrotine Printing.**—Besides printing three or four colours at once, the "perrotine" also performs mechanically all the other operations connected with the actual process of printing, viz. the charging of the sieves with colour; the transferring of the colour from the sieves to the blocks; the stamping of the blocks on the cloth; and the moving forward of the cloth, after each impression, a distance equal to the width of the block, so that a fresh portion of the cloth is brought into such a position that when the next impression is made its repeats join up exactly with those of the previous one.

As compared with hand printing, the "perrotine" possesses the advantages of (1) printing the whole width of the cloth at one operation; (2) of giving an enormously increased rate of production—250 per cent., according to Persoz; (3) of yielding a superior quality of work as regards the accuracy of the fitting of the repeats and the registration of the different colours; and (4) of making it possible to print comparatively fine line patterns—such as open-line checks—with a certain degree of precision. On the other hand, the employment of the "perrotine" is restricted to patterns not exceeding 5½" in vertical repeat, and not containing more than three colours, or at most four, though it is questionable whether the four-colour machine was ever used to any extent. Such effects, too, as are obtained from the "toby" sieve are quite beyond the capabilities of the perrotine; but "rainbows" or *fondus* may be produced in several additional colours by suitably dividing the colour boxes which supply the sieves.

In designing for the perrotine, superposition of colour is also best avoided as much as possible, because in block printing, where the colour lies more or less on the surface of the cloth, if two wet colours fall together on the same spot they invariably spread out beyond their proper limits and result in a clumsy impression.

The blocks used in the perrotine machine are made in one or other of the ways already described, and are usually 30″ long by 3″ to 5½″ broad, according to the pattern and size of the machine. The machine itself is exceedingly complex in its construction and working, but the following description and the diagrammatic sketch will give some idea of its mode of action. It consists essentially of five separate parts, viz.—(1) the printing tables, which are stationary; (2) the sieves; (3) the mechanical "tearers," comprising a brush and colour boxes; (4) the block carriers, which are actuated by delicate machinery in such a way as to impart to them a motion very similar to that produced by the human hand when it presses the block on the cloth during the printing; and (5) an ingenious arrangement for drawing the cloth forward after each impression.

The tables *a*, *a*, *a* are of cast iron, 36″ long and 6¼″ broad, and are arranged, as in fig. 15, at right angles to each other, forming, in a sense, the three sides of an incomplete four-sided prism. At each corner of the square thus formed is situated a guide-roller, covered with pins to prevent the cloth from slipping, and around these four rollers R, R, R, R and the three tables the cloth to be printed, together with a blanket and a "back grey," circulates in a regular, though intermittent, way. The sieves *e*, *e*, *e* consist of a framework, over which is stretched a piece of stout woollen cloth free from nap, and each sieve is provided with a to-and-fro motion, which allows it to move away from between the block and the table as soon as the former has received its charge of colour. The colour boxes *c*, *c*, *c* are furnished with rollers—one partly immersed in the colour and the other above it, but in contact with it, and regulated so as to work against the sieve when it moves away from the block. The brushes *d*, *d*, *d* are for the purpose of distributing the colour over the sieve in a smooth, even coating; they may be either stationary or given a slight reciprocating motion for the better equalisation of the colour charge. The block carriers *b*, *b*, *b* are of cast iron, mounted in slides or guides which ensure their perfect parallelism of motion—a necessary condition if perfect fit and evenness of impression are to be obtained.

The working of the "perrotine" is somewhat as follows :—

The first block and its sieve being in the position shown in fig. 16, the first effect of setting the machine in motion is to cause the sieve to move upwards against the colour-furnishing roller in the box *c* and the brush *d* until it reaches the position shown in fig. 15. At this point the block is pushed forward and gently pressed against the colour-charged sieve, thereby receiving its own charge of colour; this is repeated, and then the sieve moves back again to its original position (fig. 16). Whilst the latter movement is in progress the cloth from the roll K, the "back grey" G, and the blanket H all advance on to the table, and immediately the sieve is quite clear of them the block advances and stamps the first impression on the cloth. The block now recedes, the sieve rises once again to the position in fig. 15, and the same cycle of operations is repeated on a fresh portion of the cloth, which has moved forward towards the second table after the first impression. The second impression of the *first* block being completed, the *second* block and its accessories are put into motion, with the result that as the third impression of the first block is made, its first impression comes on to the second table and receives the second colour of the design from the corresponding block. In exactly the same way the cloth passes under, and is printed by, the third block, so that as it emerges from the machine it is fully printed in three colours,

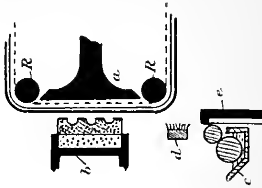

Fig. 16.

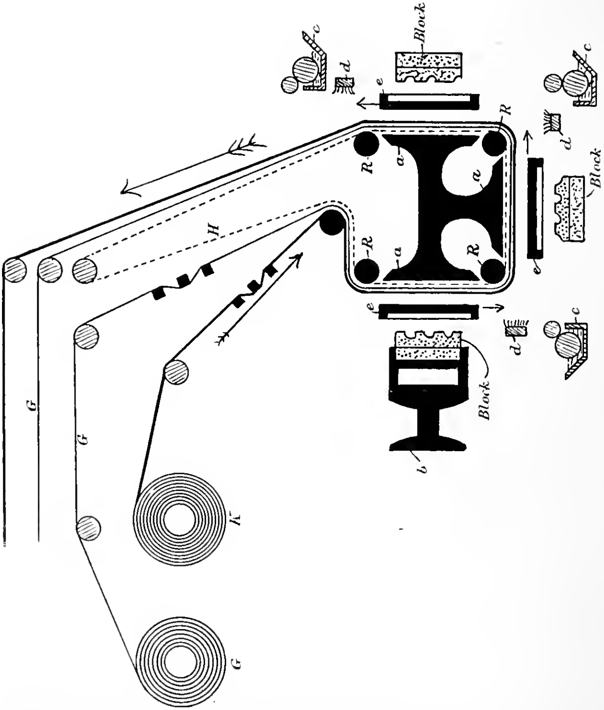

Fig. 15.

Diagrammatic sections of the "Perrotine."

and with a perfection and at a speed quite beyond the powers of a hand block printer.

It ought to be mentioned that each block may be worked independently of the others, and consequently, by stopping two blocks and the cloth, the third can be made to print twice on the same part of the cloth if it be thought that the first impression was too weak.

Continental calico printers were not slow to recognise the advantages offered by the "perrotine," and, in spite of its obvious limitations, it rapidly superseded to a considerable extent the hand printing of three-colour "block" patterns. For some reason or other it never found much favour with English printers—possibly because they may have thought that the days of block printing were numbered and, in consequence, have devoted all their energies to the development of the roller machine. In France and Italy, however, it is still in use, and at the present time many fine prints are produced either wholly or in part by its agency.

(*b*) **Surface Printing.**—Another and totally different system of block printing by machine—earlier in date than the "perrotine," but less important for textiles—is known in England as "surface printing" or "peg printing."

It is of French origin, and was invented by Ebinger in 1800 (thirty-four years before the "perrotine") for the purpose of imitating, as nearly as possible, English work printed on the cylinder machine from engraved copper rollers—a process unknown in France at that date. Ebinger was so far successful in his aim as to hit upon the correct principle of continuous printing, viz. by passing the cloth between a cylinder covered with a woollen blanket, which acted as the printing table, and an engraved roller furnished with colour from a plain one working in a colour box below; but in other respects his machine was of the most primitive description, and utterly failed to achieve the object of its invention. It was tried at both the Jouy and Beauvais printworks, but was eventually abandoned for the following reasons:—(1) the rollers being entirely of wood, rapidly got warped by the action of the wet colour and became quite useless, thus entailing considerable expense in block cutting; (2) the system of supplying the block with colour was defective, and resulted in uneven work; and (3) the impression made was inferior to that obtained from an ordinary flat block.

Some years later Burch, of Peel's Works, at Church, Lancashire, made experiments in surface or continuous relief printing; and after studying the causes of Ebinger's failure, finally succeeded in establishing the conditions essential to its practical application. The first defect of Ebinger's machine—warping—he overcame by applying to his pattern rollers the method of "coppering and felting" already described. The wooden foundations of the pattern rollers were further protected from dampness by a thick coating of waterproof varnish; the second he partly remedied by furnishing the pattern roller (a cylindrical block in reality) with colour from a short endless blanket, over which the colour was evenly distributed by two plain rollers—one, the furnisher, working partly immersed in the colour, and the other, the "distributor" or "spreader," simply pressing against the blanket. Further, by multiplying the number of rollers round the central bowl, he contrived to print several colours at once.

These and other of Burch's improvements made it possible not only to print "surface" rollers, with more or less success by themselves, but also to associate them with engraved copper rollers in the same machine, and thus print both styles at the same time—a combination of relief and intaglio printing largely practised at that period by Peel, of Church Works, and occasionally even to-day for special patterns.

With the exception of a few minor improvements—such as the introduction of stereotyped relief rollers and little matters relating to the adjustment of the various parts of the machine—Burch's principle is still in use for surface printing.

The following three diagrammatic sketches will sufficiently illustrate the principle of the different arrangements used by Ebinger, Burch, and Gadd & Hill respectively.

In fig. 17 (Ebinger's), A is the pressure cylinder wrapped with a woollen blanket E; B is the pattern roller or cylindrical block; C the colour furnisher wrapped with cloth; D the colour-box; and Z the cloth. All the parts are adjustable to each other. In fig. 18 (Burch's), A, B, C, and D refer to the corresponding parts in fig. 17; E and GG are carrying rollers for the colour-furnishing blanket I; F is the spreading-roller or distributor; X an endless blanket passing continuously round A; Y the "back grey" to preserve the blanket from colour; and Z the cloth to be printed. The rollers E, GG, and F are all adjustable by screws; E for regulating the quantity of colour supplied to I; GG for varying the area of contact and the pressure between B and I; and F for taking up the position best suited to its purpose when the other rollers are altered. Fig. 19 represents, in a somewhat exaggerated manner, the disposition of the rollers round the cylinder of an eight-colour surface printing machine made by Gadd & Hill of Salford. Only two rollers are shown fully fitted with their colour boxes, etc.; but the other six are arranged in practically the same way, with, of course, slight variations in detail, according to the different positions they occupy round the cylinder. Fig. 19 is, to all intents and purposes, identical with fig. 18, except that it displays more rollers, and that the "spreading-" or distributing-roller F in the latter is replaced in the former by a blade of metal (or of wood) called a "doctor," which rests very lightly upon the travelling colour blanket, and equalises the colour it brings forward from the "furnisher" by a slight lateral to-and-fro movement, the effect of which is to spread the colour across the width of the blanket as it escapes under the "doctor." By means of this combination of travelling

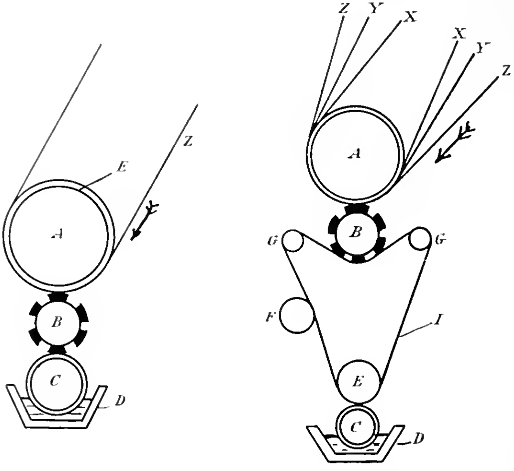

Fig. 17. Fig. 18.

Types of surface or "peg" printing machines.

blanket and traversing "doctor" it is very easy to produce rainbow, *ombré*, or *fondu* effects, similar to those obtained by the "rainbow" method of hand block printing. For this purpose it is only necessary to divide the colour box into as many compartments as there are colours desired, fill each one with its particular colour, and proceed as for ordinary printing; the movement of the "doctor" has sufficient amplitude to blend the edges of the several stripes of colour together into one continuous series of vari-tinted bands across the full width of the colour-furnishing blanket, so that no part of the printing roller is deprived of colour.

Notwithstanding the many improvements effected in the "surface" printing machine, it has never come into general use for textiles, nor has it even replaced, to any appreciable extent, other methods of block printing.

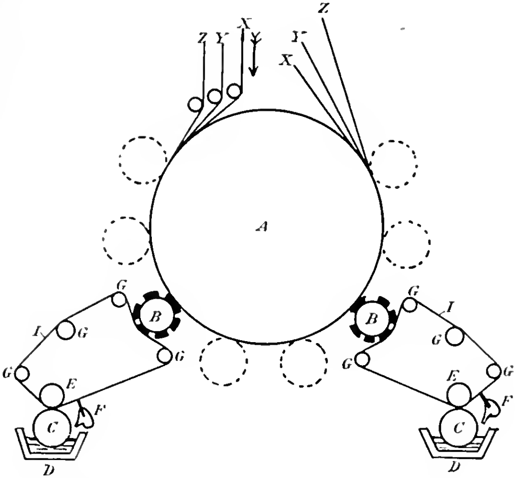

FIG. 19.—Another type of surface or "peg" printing machine.

The advantages it has, in being capable of printing multicolour patterns at one operation in a continuous maner, with perfect repetition of the design, and at the same time allowing of a high rate of production, are more than counterbalanced by the technical difficulties it gives rise to in practice. These may be summed up as follows:—

Firstly, being a complex machine, it requires much more than ordinary supervision on the part of the printer, and consequently the risks of faulty work are increased. Secondly, unlike ordinary block or perrotine printing, the surface roller can only receive one application of colour at each revolution, and therefore is more liable than they are to both take it up and transmit it unevenly; moreover, the constantly varying tension of the endless colour-carrying blankets exerts considerable influence on the regularity of the resulting print; and when it is considered that the adjustment of each blanket requires the alteration of either the "doctor" or one or more of five rollers, it is evident that the printer has his hands full. Thirdly, it is *impossible* to obtain from "surface" rollers a perfect impression of the pattern. This last is an inherent defect in the process, and is due to the fact that when colour is applied from a *rounded surface* to one not perfectly absorbent, it gets squeezed backwards into a little heap, which in "surface" printing spreads out somewhat beyond the lower boundaries of the engraved objects, and gives them the appearance of having been smeared. This is not always very noticeable, but it is always liable to occur, and it constitutes one of the greatest practical objections to the employment of "surface" printing for textiles.

At the present time "surface" printing machines seldom find application in the calico-printing industry except on rare occasions when special effects of solid, outstanding masses of opaque colour, otherwise unattainable, are desired. On the other hand, they occupy an important place in the printing of oilcloth, linoleum, yarns, and wall-papers, and are also used to some extent in the printing of certain classes of woollen goods. In each of these cases comparatively coarse, heavy patterns, large in scale, are for the most part used; and as crispness of definition is not essential to their success, the chief defect of surface printing is, within certain limits, of no account.

Up to fifty years ago an enormous number of inventions and improvements had been made in block printing, with the object of stemming the steadily increasing popularity of Bell's cylinder printing machine. Various schemes of multicolour printing were tried, in which use was made of travelling sieves, of ingeniously constructed mechanical blocks, capable of being enlarged or diminished in area, or of bringing forward in turn each of the separate parts of the design, and of numerous other modifications of the appliances and processes of hand printing. None, however, except the perrotine, the surface printing machine, and ordinary hand block printing have survived, except in rare instances, for the cheapest class of felt and carpet printing. All attempts to keep pace with the rapid development of cylinder printing from engraved rollers were in vain, and gradually block printing declined in importance, until by about 1870 it had fallen into almost complete disuse. But hand block printing was never entirely superseded by any form of machine for certain classes of work, and during the last quarter of a century the increased interest taken in all handicrafts, due primarily to the magnificent work of William Morris and his collaborators, has resulted in its revival, and in that of the patterns for which it is peculiarly adapted. At the present time many of our foremost artist-designers are engaged in designing patterns for block printing, and it is now no uncommon thing for the best and most celebrated house-furnishing establishments to devote a whole window to the display of fine specimens of block-printed cretonnes, chintzes, bedspreads, table-covers, curtains, and other articles of a decorative nature.

(3) STENCILLING.

Although stencilling on textiles is an old process—it was employed tentatively in the early days of calico printing in Europe—yet until a few years ago it was scarcely known in this connection, and was almost unrecognised as suitable for anything but the marking of bales, cart-sheets, and other work of a like rough nature. It is only within the last fifteen or twenty years that its possibilities as a mode of *decorating* textile fabrics have been fully revealed by the publication of works on Japanese art, and by the exhibition of specimens of Japanese work. Even yet it has not received from calico printers that amount of attention to which its merits would seem to entitle it: but this, perhaps, is not surprising, considering that for a long time by far the greater number of available examples of "stencilling" were the work of the ordinary "house decorator and plumber," in whose hands its finest qualities were lost, and who, instead of turning its limitations to account, emphasized them to the point of ugliness. It is not to be wondered at, therefore, that stencilling came to be generally regarded as a mere makeshift for the cheap ornamentation of wall spaces and dado borders, and that consequently it was, until recently, neglected by textile printers, whilst other methods of printing advanced. During the last few years, however, many of our best designers have recognised its capabilities, and have demonstrated by their excellent work that, properly employed, it affords a cheap, ready, and efficient means for the decorative treatment of almost every kind of textile material—cotton, linen, wool, jute, silk, and velvet. In England stencilling on these various fabrics is usually confined to hangings, curtains, bedspreads, table and cushion covers, and canvas for wall-coverings and friezes, etc. etc.; but that it is not restricted to the execution of these comparatively large-scale patterns is shown by the delicate designs stencilled by the Japanese on fine silk and cotton muslins, suitable for dress goods.

As compared with block printing, stencilling offers much greater latitude to the designer in the planning of his ornament. The pattern may be intricate or simple; delicate or broad; in fine line or mass, or both combined; and in either flat or gradated and broken tints. The facility with which fine line and mass can be produced from one stencil plate, and the ease with which two or more different colours can be blended in one object, constitute the chief technical advantages of stencilling over block printing. Against these must be put the impossibility of cutting a perfect circle or any other complete outline on a stencil plate. A spot merely requires a hole to be punched right through the plate, but if a complete circle were cut the inside would drop out at once, leaving a spot; similarly with all other uninterrupted outlines. To prevent this, the outlines of a pattern must be broken at convenient points, by being only partially cut, the uncut or "reserved" portions—known as *ties*—serving to support the inside parts by connecting them with the rest of the reserved portions, or the body of the plate—see fig. 20, *C*, where the circumferences of the circles are interrupted at every point of intersection.

Stencil plates are merely sheets of paper or thin metal, with perforations arranged to form a pattern. They are laid on the work, and colour is brushed through their cut-out parts on to whatever material shows beneath them, thus producing a coloured pattern corresponding to the shape of the perforations. Ties are not only used for outlines, but must be freely introduced, for strength, wherever long lines, extended spaces, or intricate patterns are cut, otherwise the plate will be too fragile, and apt to lie unevenly on the work, and thereby give rise to faulty execution. Although an unbroken outline cannot be *stencilled*, it may be *reserved* or left uncut in cases where both ground and pattern are cut out on one stencil, or where two or more plates are employed for the realisation of a multicoloured design—in which cases it (the outline) appears in the original colour of the material to be ornamented. This method of working is illustrated roughly in fig. 20, *B*, where a continuous white outline is obtained by cutting two separate stencil plates, one for the black parts and the other for the shaded parts.

In some of their best textile work the Japanese cut their paper stencils with such exceeding delicacy that the ties left are not, by themselves, sufficiently strong to hold the plate together. They therefore cut two identical stencils at the same time from a doubled sheet of paper, and afterwards glue them together with a layer of raw silk threads between them. These threads, which extend over both the cut and uncut parts of the plate, afford the necessary support to the pattern, and as they always lie a little distance above the surface to be decorated, and are so thin, they easily allow the colour to spread under them, and do not in any way affect the ultimate result, except to improve it. Marvellously delicate effects are obtained in this way, but it is open to question whether such refinements of process do not exceed the proper limits of stencilling.

The best modern designers, so far from being hampered by the necessity for "ties," frankly admit their limitations, and make effective use of them as integral parts of the design. They avoid the clumsy and arbitrary breaks of line, so common in older work, by ingeniously arranging the ties to suggest the veining and doubling over of leaves, the twisting of tendrils, the junction of flowers and leaves with stems, the folds of drapery, and a hundred and one other natural effects.

The character of a single-colour pattern may be varied in several different ways at very little cost. The background may be cut out, leaving the uncut portions of the plate to represent the pattern; conversely, the pattern may be cut out, leaving the ground in "reserve," when it will appear in the natural colour of the material under treatment; or by applying different colours separately, and blending them on the work, with a stroke of the brush, before the plate is removed, a great variety of broken or gradated colour effects may be easily obtained from one stencil—effects quite beyond the power of either block or machine printing to attain.

The same rules that govern the "repeats" of patterns in block printing apply equally in stencilling, and similar means may be employed to mask the prominence of awkward repeats. Generally speaking, every stencil plate must contain at least one full repeat of the design; but in the case of certain geometrical and all "turn-over" patterns only half a repeat need be cut, the other half being added on the work by reversing the plate. Unless the pattern be very large or intricate it is better, however, to cut the full "repeat"; for in reversing the plate it requires very careful cleaning, and frequently, too, the previous impression must be allowed to dry before the second half can be stencilled. The "turn-over" pattern is a device borrowed from the weaver. It is constructed on straight or waved parallel vertical lines, and being of necessity symmetrical, it is obvious that if the stencil plate contain only half the pattern, the whole can be completed by turning it over and stencilling through the back. The same principle can also be applied in stencilling to unsymmetrical patterns, as shown in fig. 20, *A*, where the shaded portion of the design represents the stencil plate used, the black parts being cut out.

In patterns of two or more colours a separate stencil plate is required for each distinct colour. It is possible, with care, to obtain a two- or even a three-colour pattern from one plate by applying the particular colours to certain parts of it, but it is a risky method, and one seldom resorted to in practice, separate plates for each colour being almost invariably preferred. In an elaborate pattern, requiring several plates for its realisation, one plate may be schemed to make good the "ties" of another; but, as a rule, the most artistic results are obtained by allowing the ties to be seen, and by utilising them for the twofold purpose of strengthening the plate and of serving as an essential feature of the design.

All stencilled patterns ought to be complete as stencilled; if they require any subsequent retouching by hand, the design is either unsuited to the process or its planning is defective.

Unlike other methods of textile decoration, stencil work permits of the pattern being carried out in almost any kind of colour. For heavy woollen goods, velvets, jute, and buckram, which are destined to serve as hangings, wall-coverings, and decorative panels, oil colours are frequently used, brushed lightly over the surface of the material, so as to retain its "clothy" appearance as much as possible. For cotton, linen, silk, and lighter goods generally, either water-colours or the ordinary dyestuffs may be employed, according to the purposes for which the work is required; the former in special cases, and the latter for such articles as tablecloths, curtains, bedspreads, and the like—all of which require to be "fast" to washing. Work executed in oil or water colours

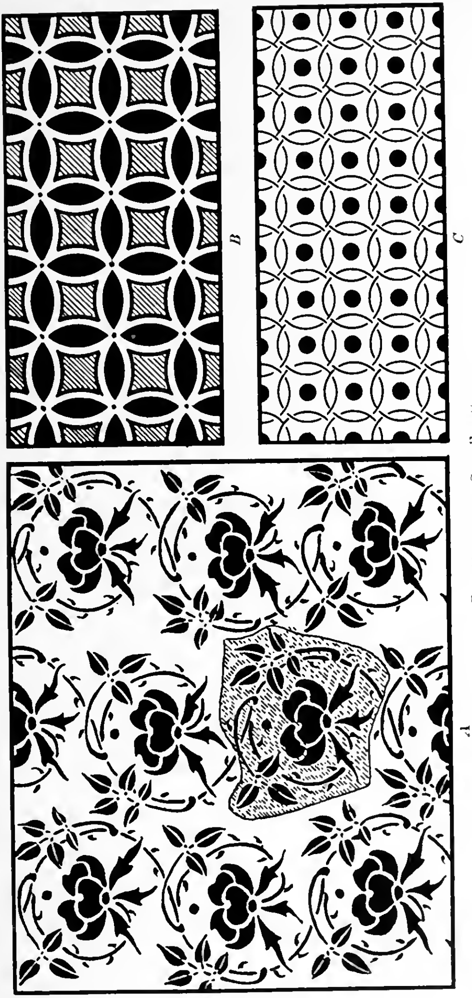

FIG. 20 A, B, C.—Stencil patterns.

is finished when dry, but when dyestuffs are made use of the goods must, of course, go through the usual operations necessary to their proper fixation.

A stencilled pattern, though quite different in character from, is quite equal in its way to, a block print. It possesses similar qualities of colour and breadth, and is subject in "all-over" patterns embodying long unbroken lines, or long stretches of unbroken colour, to the same misfitting of the "repeats." Whatever beauty some people may claim to find in such "misfits," a practical stenciller always tries his utmost to avoid them by arranging his design to repeat at the "ties." It is not always possible to do this, however; hence their occasional appearance in even the best work. On the whole, the most successful patterns for stencilling (and also for block printing) are those in which no tight-fitting joints are necessary, *i.e.* patterns made up of detached units—"powdered" patterns, with an unbroken space of background surrounding each "repeat."

Stencil plates cannot be manipulated quite so quickly as blocks, and, in consequence, for the commercial production of large quantities of printed textiles, stencilling is not cheaper than block printing. On the other hand, the low cost of the materials and the rapidity with which the plates can be "cut" enable it to be profitably employed in the execution of small orders, for which the expense of "block cutting" alone would be prohibitive, as, for instance, when, as frequently happens in high-class house furnishing, a small quantity only of a special pattern is required to complete a scheme of decoration.

The making and using of Stencil Plates.—As above noted, "stencilling" is not strictly speaking a printing process. Colour is applied to the material to be decorated, not by impression, as in printing, but by being brushed or sprayed[1] through the interstices of a pattern cut out in waterproof paper or thin sheet metal.

Stout cartridge paper or two-sheet Bristol board is usually preferred for stencil plates. Whichever is selected must be first of all thoroughly saturated with either boiled or raw linseed oil. When it has absorbed as much as it will hold it is wiped dry, and the last traces of superfluous oil removed by pressing it for some time between two sheets of similar paper. Freshly prepared in this way, cartridge paper is tough, supple, easy to cut, and sufficiently transparent to permit of a tracing of the design being made upon it directly; but if kept for any length of time it becomes hard, brittle, and opaque, and dark in colour.

The cutting out of the pattern is done with a sharp-pointed knife, and is best accomplished on a sheet of plate-glass, the hard, polished surface of which, by offering no obstruction to the passage of the knife, allows it to cut cleanly, smoothly, and regularly through the paper, and ensures not only more accurate work than could be obtained on a wooden table, but also effectually prevents the raising of "burrs" or rough back edges on the underside of the stencil. After cutting, the plate is made impermeable to moisture by coating it on both sides with a waterproof varnish. A solution of shellac, or the tougher resins, in methylated spirits or naphtha, answers this purpose; it dries quickly, leaving a hard, durable surface, easy to clean, and not readily affected by the colours.

Stencil plates may also be made of thin sheet copper or zinc, but they are dearer than those in paper, less easy to cut with accuracy, and, in any but small sizes, more difficult to handle in practice. Whilst they are superior to paper in so far as durability of material is concerned, their thinness has the disadvantage of rendering them more liable to damage in the course of working. The slightest blow or a fall is quite enough to cause dints or creases in a metal stencil—defects which, by preventing it from lying flat on the work, render it temporarily useless. Moreover, these defects, as is well known, are difficult to remedy, some experience of sheet-metal work being necessary to flatten out a

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[1] For spraying, a special apparatus is made by The Aerograph Co., Ltd., of Holborn Viaduct, London. The flow of colour from the nozzle is under perfect control and can be regulated at will so as to obtain any desired degree of gradation.

locally warped or creased plate without causing it to spring in some other part. Generally speaking, paper stencils are the best for all ordinary purposes. Their initial cost is very low, and they are very easy to duplicate if they happen to get torn. Another great advantage they possess is that, owing to their transparency, each of the separate colour parts of a multicolour pattern, together with the gauge or "pitch" marks, can be traced directly on to the stencil plates, thus obviating any mistakes that might arise in transferring separate tracings to separate plates, and making certain, without any preliminary trial, that every colour in the design will "register" perfectly.

The *modus operandi* of stencilling is very simple. The plate is laid perfectly flat on the material to be treated, and suitably thickened colour is then brushed through its perforations with a hog-hair brush. On lifting the plate the pattern appears on the cloth as a coloured silhouette, corresponding with the cut-out parts of the stencil. Different effects may be got according as the colour is brushed, dabbed, sponged, or sprayed through the stencil, and still others may be obtained by placing different colours on different parts of the stencil, and then blending them together with a sweep of the brush In this way each repeat of the pattern will vary in tone somewhat, but will still retain the general appearance of the others.

In stencilling patterns of two or more colours the same procedure as that adopted in hand block printing is followed. The cloth is stencilled throughout in one colour first, then dried, and the others added in like manner. If desired, it is obvious that every repeat may be coloured differently, and this variation is frequently made use of in stencilled wall-hangings and papers—that are executed for special schemes of house-decoration—for the express purpose of getting lighter colours in dark corners.

No definite rule can be laid down as to the consistency of the colour nor the amount to use, but it should be thick enough not to "run," and applied in sufficient quantity to cover the material well without spreading under the uncut or "reserved" portions of the stencil.

Stencilling Machines.—Only two stencilling machines have ever been used to any extent in calico printing,—one known in its final form as Monteith's Press, and now obsolete; the other a modern machine, invented a few years ago by S. H. Sharp for printing metallic powders, etc.

Monteith's press was used for the production of "bandanas," a peculiar kind of handkerchief, with a pattern consisting of spots and other simple objects in white or yellow on a dyed ground, generally of Turkey-red or of Indigo. Briefly described, the process was as follows:—Several pieces of cloth, folded to the requisite size, were tightly compressed in a modified hydraulic press between two leaden stencil plates pierced with identical patterns, and arranged so that their perforations lay exactly over each other; a liquid discharging agent—a solution of bleaching powder—was then forced through the whole by means of a hydraulic pump, and, following the line of least resistance in its passage through the cloth, it only destroyed the colour in those portions lying immediately between the perforations in the two stencil plates. A full description of Monteith's press may be found in Persoz's *Traité de l'impression des tissues*, but fig. 21 illustrates the principle made use of. The dotted lines indicate the direction taken by the discharging agent; the thin horizontal lines, the folds of the cloth; and the heavy broken lines at the top and bottom of these latter, a section of the two identical stencils, showing how their respective perforations must correspond.

Work done by this process was chiefly characterised by its coarseness of execution; and although it imitated native Indian "bandanas" fairly well, it was much inferior in all other respects to the work of contemporary block printers. Owing to the fact that no amount of pressure could entirely prevent the discharging agent from spreading by capillary attraction into the surrounding ground colour, it was impossible to employ anything but spots or the simplest clear cut masses in the designs, and even then the "raggedness" of their edges was always more or less in evidence. The whole process was exceedingly cumbersome, and its only resemblance to stencilling lay in the use of the pierced leaden plates—certainly not in the effects produced, which resembled poor block prints more than anything else.

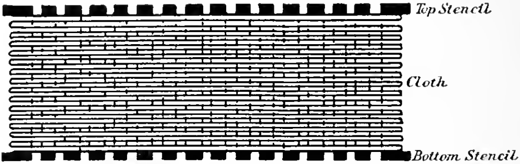

Fig. 21.—Illustrating the principle of Monteith's press.

The continuous stencilling machine, patented by S. H. Sharp in 1894, is entirely free from the defects of Monteith's press, and is applicable to a much wider range of designs, including stripes, which are impracticable in ordinary stencilling, on account of the difficulty of hitting off the repeats exactly. Sharp's machine consists essentially of the following parts, geared to work together by power, and arranged as shown in figs. 22 and 23:—

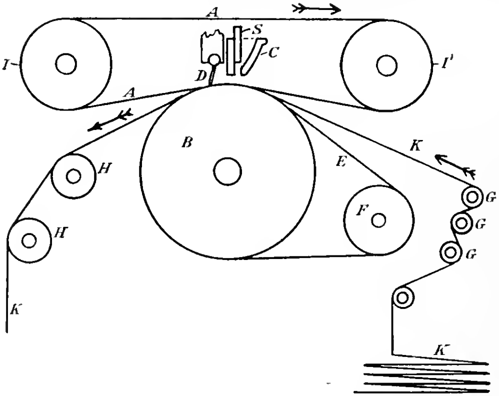

Fig. 22.—Section of Sharp's stencilling machine.

A is an endless metal stencil, carried by the plain rollers I, I', one of which (I') is adjustable; B an iron cylinder, also adjustable; C a fixed colour box, with a slotted opening at the bottom extending the full width of the machine, and capable of being opened or closed by the vertical slide S, for the purpose of regulating the flow of colour; D the "presser"—a brass or steel blade carried in brackets on the machine side, and caused to press on the stencil by springs or weighted levers. The "presser" serves both to force the colour through the holes in the stencil, and at the same time to prevent the excess from being carried forward. E is an endless woollen blanket circulating round the cylinder B and the adjustable roller F; G, G, G, tension rails for keeping the cloth K tight and free from creases; H, H, drawing rollers, covered with sandpaper, or fine pins, for carrying forward the cloth, after printing, to the drying chamber, where it is suspended on rails until dry.

The ordinary stencil used in this machine is simply a thin sheet of steel or brass, brazed at the ends to form an endless band, and perforated with any desired pattern made up of *detached* ornamental units; but for continuous stripe patterns a different arrangement is necessary. When stripes are to be printed the plain rollers I, I′ are replaced by corrugated ones (X, X′, fig. 23) made up by slipping large and small slotted iron discs on a tongued spindle, and tightening them up by means of a nut on the end of the latter. Guide rollers (Y, Y, fig. 23), similarly constructed and of the same "pitch," are also added, and, instead of the stencil, a series of endless steel bands or tapes are employed, varying in width according to the width of the sort of stripe required. The corrugations in the rollers must, of course, correspond in width to the width of the tapes which work in them, as otherwise the stripes printed would vary in thickness. By this ingenious modification of stencilling it is possible to print stripes showing absolutely no "repeat." The patterns may be varied by combining wide and narrow bands, the corresponding guide and bearing rollers being "built up" of discs of various thicknesses. In fig. 23 the colour-box C is not shown, but it occupies the same position as in fig. 22.

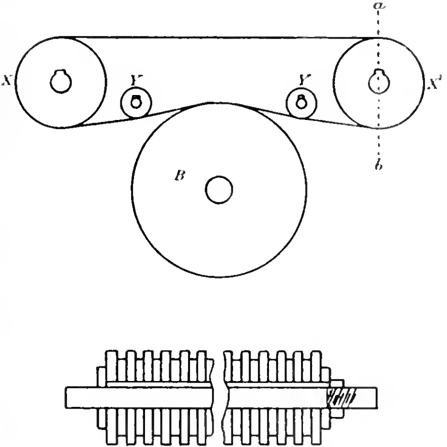

FIG. 23.—Section of Sharp's stencilling machine.

The operation of printing is carried out as follows:—First the end of the cloth (K) is inserted between the stencil (A) and the bowl (B); colour is then allowed to run on to the top of the stencil, and the machine is set in motion when stencil, bowl or cylinder, and cloth all move together in the direction indicated by the arrows. During this movement the colour is carried forward against the "presser" (D), which forces it through the pattern on to the cloth beneath, and at the same time scrapes off the excess from the plain or uncut portions of the stencil, leaving it quite clean. If this excess of colour were allowed to remain it would spread through the pattern to the underside of the stencil, and, at the next revolution of the machine, would be transferred to the cloth and produce faulty work. As the cloth emerges from beneath the stencil it is led over the "draw-rollers" (H, H), which continue to carry it forward into the drying chamber as long as the machine is in motion. The drying chamber is situated close to or below the machine, and consists of a steam-heated brick room, furnished near the top with wooden rails, over which the cloth is hung in long loops, so that its printed side never comes into contact with anything until it is perfectly dry.

The chief use to which this machine is put is for the printing of metallic powders. On an ordinary printing machine metallic powders are difficult to work, as they tend to fill up the engraving of the rollers and frequently give rise to thin, bare impressions; but in Sharp's machine neither of these defects is possible, and consequently the resulting print is full and rich in colour, and, after drying and calendering, exhibits a brilliant metallic pattern. The metal, being mixed with an oil-varnish, adheres tenaciously to the cloth, and is not only fast to washing, but also remains untarnished for a very long time, even when exposed to the action of town air.

(4) PLATE OR FLAT-PRESS PRINTING.

Before the introduction of the roller printing machine the only means available for the reproduction on textiles of the most delicate line and stipple designs was by printing them from flat copper plates, engraved by hand with a burin or steel graver in the ordinary well-known way.

Originally the process was carried out exactly as for the printing of engraved pictures, and, according to Girardin, was first practised on calico in 1770 by Bell, the inventor of roller printing. The plate, engraved with the pattern, was entirely coated with printer's ink, rubbed well into the engraving with a soft pad; the excess was then removed from its plain surface by first wiping several times with a cloth, and finally with the ball of the hand until no part of it except the engraved lines retained the slightest trace of ink. A piece of cloth was then laid over it and the two together passed through a heavy cylinder press, the pressure of the steel bowls of which forced the cloth into the engraving of the plate, and thus caused the pattern to be transferred to it. The process was slow, and, from its nature, it is obvious that only small articles—such as handkerchiefs—could be printed, as "repeats" were impossible to fit, and long lengths of cloth were impracticable to handle.

In the "flat-press" machine, which is constructed on similar lines to the modern lithographic machine, the latter defect is overcome, but the difficulty of the "repeats" is still such that continuous designs are never attempted, and consequently the flat-press is restricted to the printing of patterns that are either made up of detached objects or sprays, or that are complete in themselves without repeats, as for instance tablecovers, panels, or handkerchiefs. Practical difficulties also prevent the flat-press from being used for more than one colour, though it is possible that if the cloth were backed with a stout, waxed paper support to prevent it stretching, it might be printed in several colours, in the same way that posters are printed on Prebay's continuous lithographic machine.

In the flat-press machine the engraved copper or steel plate is mounted on a heavy iron carriage, which moves to and fro in such a way that the plate, when inked, passes under and in contact with a heavy woollen-covered iron cylinder, between which and the plate the cloth to be printed passes. As the carriage moves forward the cylinder revolves and presses the cloth into the engraved pattern on the plate, thus making the desired impression. On leaving the cylinder, and whilst still moving forward, the whole plate is re-inked automatically, the excess of ink being then removed from its surface by a steel "doctor" or blade, which is arranged to bear upon it during the return journey of the carriage to the back of the machine. During this return journey the plate re-passes under the cylinder, but out of contact with it. On regaining its original position a system of cams comes into play, and raises it sufficiently to make contact again with the cylinder at its second forward movement, and so print a second length of cloth.

In this way the machine works continuously, printing the cloth in an intermittent manner. As the cylinder remains stationary, except when in actual contact with the travelling plate, it allows of the second impression being commenced where the first leaves off; but as the exact junction of the repeats cannot be relied upon in delicate patterns, and as coarser patterns are better and more cheaply executed by block printing, the flat-press is still only made use of for those finely engraved "powdered" and bordered patterns which at the time of its invention it was impossible to execute by any other means.

At the present time "flat-press" printing is practically obsolete in most countries, except for, perhaps, a few fancy articles on satin, for which there is an occasional slight—very slight—demand. In Switzerland, however, it is still used to some extent for the production of a special style of handkerchief with a finely engraved border and a floral centre—the latter being filled in by block printing after the border has been printed on the flat-press.

(5) MACHINE, ROLLER, OR CYLINDER PRINTING.

"Machine printing" is the name generally applied to the process of printing from engraved copper rollers, as distinguished from hand block printing, perrotine printing, surface printing, and stencilling. It is at once the most important, most productive, and most comprehensive of all the various methods of ornamenting textiles; and by its means almost any style of design on almost any fabric can be rapidly reproduced in from one to sixteen colours at a single printing. Compared with stencilling, hand block, and perrotine printing, the output from a cylinder machine is enormous, under favourable conditions as much as 18,000 yards of cloth being printed in one colour, or 8000 to 9000 yards in twelve colours, per working day. Moreover, the technical excellence of the work so obtained is not in any way sacrificed to the high rate of production.

The Roller Printing Machine.

The invention of roller printing is generally attributed to Bell, a Scotchman, who patented it in 1783, and who first employed it with practical success at the works of Livesey, Hargreaves & Co., near Preston, in 1785.

It is an open question, however, as to whether or not he was the actual originator of the idea, for O'Neill quotes two previous patents which seem to prove that a considerable amount of work had been done on similar lines at a much earlier date. In 1743 Keen and Platt patented a three-colour machine with a separate pressure bowl to each roller; and in 1772 Aitkin patented a single-colour machine in which three bowls or rollers of sycamore worked one above the other, in slots in the sides of the oaken framework. The top and bottom bowls were smooth, whilst the middle one was engraved to a depth of $\frac{1}{8}$-inch; the cloth passed between the top and middle bowls, and was printed by the latter, which received its supply of colour from the bottom one working presumably in a colour box beneath. No mention is made in either patent of copper rollers, of "doctors," or of the method of applying pressure to the several bowls, so that it is impossible to say with any certainty what these early machines really were, or whether they embodied the principles upon which Bell subsequently worked in perfecting his own invention. From the depth of the engraving ($\frac{1}{8}$-inch) mentioned in Aitkin's patent, it is fairly safe to assume that his machine was intended for cylindrical block or "surface" printing, and it is very probable, too, that Keen and Platt's patent related to the same process; for if an important innovation, such as the continuous printing of calico from the incised lines of a pattern cut on a metal roller, had been introduced by either patentee, it would have attracted too much contemporary attention to have passed unrecorded. In the absence of positive proof to the contrary, then, Bell's claim to priority in the invention of continuous printing from engraved copper rollers cannot well be disallowed. At any rate, whatever uncertainty may exist as to the true origin of the process, it is beyond all doubt that to Bell, and to Bell alone, belongs the credit of having been the first to make a practical success of it.

In its simplest form a modern printing machine consists of the following parts, arranged as shown in the two diagrammatic sections, figs. 24 and 25:—(A) is a hollow copper roller, engraved with the pattern and carried by a steel shaft or mandril (B), which works in bearings on the machine side. It (the roller A) revolves in contact with a cast-iron cylinder or pressure bowl C, above, and with a roller or brush (D)—the "furnisher"—below, the furnisher (D) being partly immersed in colour contained by a box (E) situated beneath it. A sharp-edged metal blade (F), known as the "cleaning doctor," rests upon and behind the engraved roller, about midway between its points of contact with the bowl (C) and the furnisher (D), and serves to scrape the superfluous colour from the smooth parts of the roller, leaving it only in the lines of the engraving.

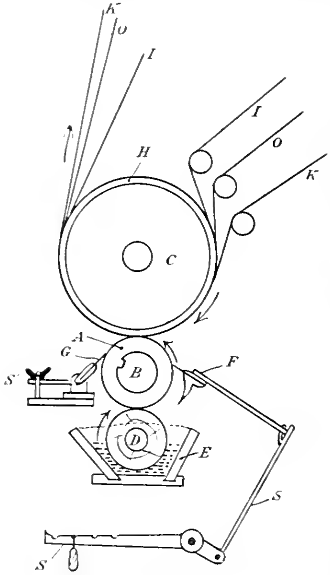

Fig. 24.—Diagrammatic section of a single-colour roller machine.

At the opposite side of the roller a second or "lint" doctor (G) is frequently placed to catch the loose filaments and nap which detach themselves from the cloth and stick upon the moist surface of the roller. In larger machines which print several colours at a time the "lint" doctor further performs the useful function of clearing the surface of the roller from the colour that it picks up from those parts of the cloth that have already been printed by other rollers in the pattern. It is easily seen that if these filaments of cotton or the colours from other rollers were allowed to go forward into the colour box, the colour therein would either become unworkable or would be altered in shade, as the case might be. In order to impart to the cylinder (C) the elasticity that is necessary to obtain a full impression of the pattern, it is wrapped with several thicknesses of a special fabric known as "lapping" (H); an endless woollen blanket (I) also circulates round the pressure bowl, giving additional spring to the surface against which the engraved roller works. The "back grey" (O) is simply interposed between the blanket and the cloth to be printed (K), for the purpose of preventing the former from being soiled by the colour which penetrates through the latter.

The whole machine is worked by one large cogwheel (Z) in fig. 25, which gears into a small pinion (Y) on the end of the mandril (B), and is driven from a steam engine, electric motor, or the main driving-shaft of the "machine room." On the other end of the mandril another pinion is fixed gearing into a similar

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one (X) on the spindle of the "furnisher," which, therefore, works in the opposite direction to the roller. When a brush furnisher is used it is frequently made to work in the same direction as the roller by means of a small spur-wheel interposed between the two pinions.

The pressure cylinder (C) is not directly coupled to the drive of the machine, but is turned simply by the friction caused by its pressure upon the revolving printing roller (A). This pressure is usually obtained, in a single-colour machine, from a system of weighted compound levers, at the end of which the cylinder is mounted in adjustable bearings, carried in massive slotted heads, and capable of being raised or lowered, independently of the levers, by means of screws. In this way dead-weight pressure is avoided, and some allowance made for inequalities such as occur when different sorts of cloth are printed at the same time, or when a seam at a piece-end passes through the machine. In some patterns of single-colour machines the reverse arrangement is adopted, and instead of the cylinder being pressed against the printing roller, the printing roller is pressed against the cylinder by means of screws and weighted compound levers, which act through the sliding bearings in which it is mounted (see Plate I.). Where this system is employed it is obvious that the engraved roller and its accessories—the "doctors," furnisher, and colour box—must all move together, and to this end the latter are mounted on or carried by a plate fixed to each of the roller bearings, and, in consequence, moving along with them.

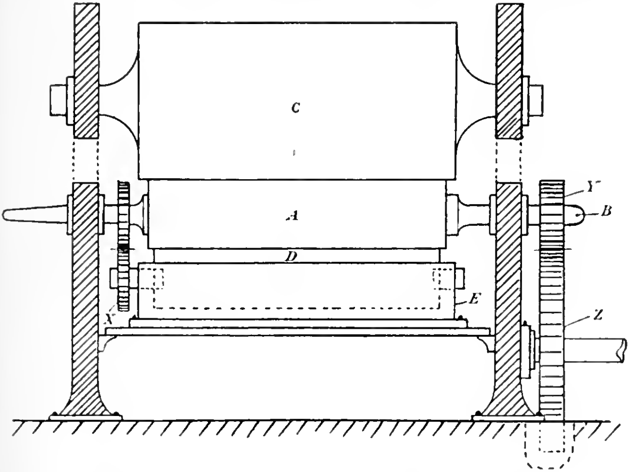


FIG. 25.—Diagrammatic section of a single-colour roller machine. (Doctors not shown.)

In operation the action of the machine is as follows:—The engraved roller (A), during its revolution in the direction of the arrow (fig. 24), first of all receives a copious charge of colour from the "furnisher" (B); the excess is then scraped off its surface by the "doctor" (F), and what colour remains in the lines of the engraved pattern is then transferred to the cloth (K) to be printed, which, along with the blanket (I) and the "back grey" (O), passes continuously through the machine between the cylinder (C) and the roller (A), and is pressed into and absorbs the colour from the engraved lines of the latter. Continuing its revolution, the roller passes under the "lint doctor" (G), which clears it of nap, etc., and the same cycle of operations is then repeated again and again without intermission until the whole batch of cloth is printed. After printing, the goods pass directly over steam-heated drying cylinders or "cans," or through a hot air drying apparatus, or, what amounts to the same thing, between a series of steam-heated iron chests enclosed in a brick or wooden chamber. When thoroughly dry, they are ready to undergo any subsequent operations that may be necessary to the fixation or development of their colours.

The construction of machines that are intended to print several colours simultaneously is, of course, more complex than that of a single-colour machine, but such machines may be considered as combinations of two or more single-colour machines, from which they differ in detail rather than in principle. A separate roller is required for each distinct colour in the design, so that a six-colour machine, therefore, has six rollers, each provided with its own colour box, furnisher, and doctors. These rollers are arranged, as shown in fig. 26, round a central pressure bowl or cylinder common to all, and are driven by a single large cog-wheel—the "crown-wheel"—situated at the side of the machine, and itself driven by any suitable means.

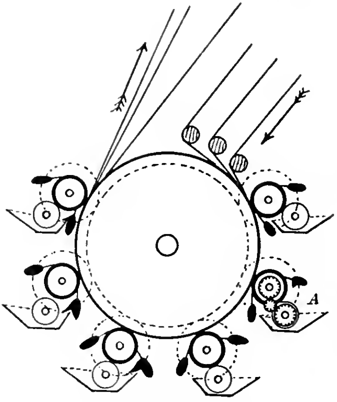


Fig. 26.—Diagrammatic section of a six-colour roller machine.

The dotted circles represent the large "crown"-wheel and the six "box"-wheels by which the rollers are driven. At A is shown the arrangement for driving the back furnishers in the same direction as the rollers.

The lapping, blanket, back greys, and cloth are all disposed and pass through the machine in exactly the same way as for single-colour printing.

Each roller of a multicolour pattern is engraved with a portion of the design corresponding to one particular colour; and for the purpose of enabling the printer to fit these separate designs in exactly their proper places on the cloth (and to keep them in "register" once they are fitted), each roller works in combined spring and lever adjustable bearings, which allow of it being moved whilst the machine is in motion, either (*a*) from side to side horizontally, or (*b*) up and down at either end in a direction tangential to the central cylinder. This latter movement is only applicable within comparatively narrow limits; and although it may sometimes be employed to raise or lower the rollers equally at both ends, its chief use is to preserve their parallelism to each other; for it is obvious that if they were moved too much in this way, their pressure against the cylinder would be appreciably diminished, with the result that an imperfect, or at least uneven, impression would be obtained. If, when all the rollers are perfectly parallel, any one of them happens to print its part of the pattern above or below its proper place *across the full width of the cloth*, it is adjusted, not by being raised or lowered bodily in its bearings, but by having the speed at which it revolves momentarily increased or reduced as the case may require—an effect which is equivalent to raising or lowering the roller without the disadvantage of altering its pressure against the cylinder. This elegant and essential rotary adjustment is accomplished by means of ingeniously contrived differential pinions—known as "box-wheels"—one of which is fixed on the mandrel of each roller, and not only serves to gear it with the main driving-wheel of the machine, but at the same time permits of its speed being regulated, as stated, independently of the driving-wheel, and without interfering in any way with the speed of the other rollers. The following account will convey an idea of its construction and mode of action. It consists of two main parts: (1) the outer shell (*a*, *a*) carrying the cogs (which, of course, go all round, in this case and in the driving-wheel, a few only being shown here) and the two projecting lugs (*g*, *g*); and (2) the inner movable disc (*b*) (shown in section fig. 27A), provided with a hollow axle or sleeve (*c*), slotted endwise as at *f*, *f*, and with the connecting-piece (*d*) through which the adjusting-screw (*e*) passes. The shell (*a*, *a*) is usually about 10 inches in diameter, and 3 inches broad across the cogs; one side of it is hollowed out for the reception of the disc (*b*), which should fit into it as tightly as is consistent with its freedom of movement when turned by the screw (*e*). The sleeve and connecting-piece of the disc (*b*) project through a suitably-shaped opening cut through the centre, and between the two lugs (*g*, *g*) of the outer shell. A large-headed screw (N) passes through and slides freely in the slot (*h*) of the outer shell, and is screwed into the disc (*b*) just sufficiently tightly to hold these two parts of the box-wheel closely together without impeding the movement of the latter. In use the "box-wheel," after being pushed on the mandrel as far as it will go, is firmly secured to it by driving a cotter through the slots (*f*, *f*) of the sleeve, and through a corresponding cotter hole in the mandrel itself. On screwing up the roller into contact with the cylinder, the cogs of the "box-wheel" gear with those of the "crown-wheel," *i.e.* the driving-wheel. When thus in gear the box-wheel *as a whole* can only revolve when the crown-wheel is revolving; but, by means of the screw (*e*), its *inner disc*, and consequently the roller and mandrel, to which this disc is directly keyed, may be turned round quite independently of either its *outer shell* or of the driving-wheel of the machine. The effect of turning the screw (*e*) is to cause it to press against one or other of the two lugs (*g*, *g*), between which it is confined, and in so doing to move round the inner disc by forcing its connecting-piece (*d*) towards the opposite lug. For example, if, whilst the machine is running, and the rollers are revolving in the direction of the arrow in fig. 27, the screw be turned towards the circumference of the box-wheel, it is evident that the corresponding roller will be turned in a direction contrary to its revolution, that its speed will be reduced thereby, and that in consequence its position in relation to the other rollers will be altered, and that its impression will appear lower down on the cloth as it emerges from the machine in front of the printer. If turned in the opposite direction, the speed of the roller is momentarily increased, and its impression is raised accordingly. The increase or decrease in the speed of the roller only lasts during the time that the actual turning movement of the screw (*e*) is in progress: after that, it immediately returns to its original speed, but its altered position is permanent, or at least as permanent as the slight unavoidable irregularities in the working of the machine will allow. In this way the impression made on the cloth, by any roller of a multicolour pattern, may be raised or lowered about two inches, whilst the machine is either in motion or stationary, and without affecting in the slightest degree the relative positions of the other impressions to each other. When the ordinary type of box-wheel, as here described, is employed, it will be seen that the rollers must be placed in the machine within approximately two inches or less of their correct positions: but later improvements render this precaution unnecessary, as the most recent box-wheels allow of their inner discs (to which the rollers are attached) being turned completely round whilst their outer shells are still in gear with the driving- or "crown-wheel" of the machine.

The facilities for horizontal, vertical, and rotary adjustments afforded by the bearings and box-wheels give the machine printer complete control over the movements of his rollers, and enable him to fit together the various component parts of even the most delicate and intricate designs with an ease, accuracy, and despatch impossible of attainment in any other process.

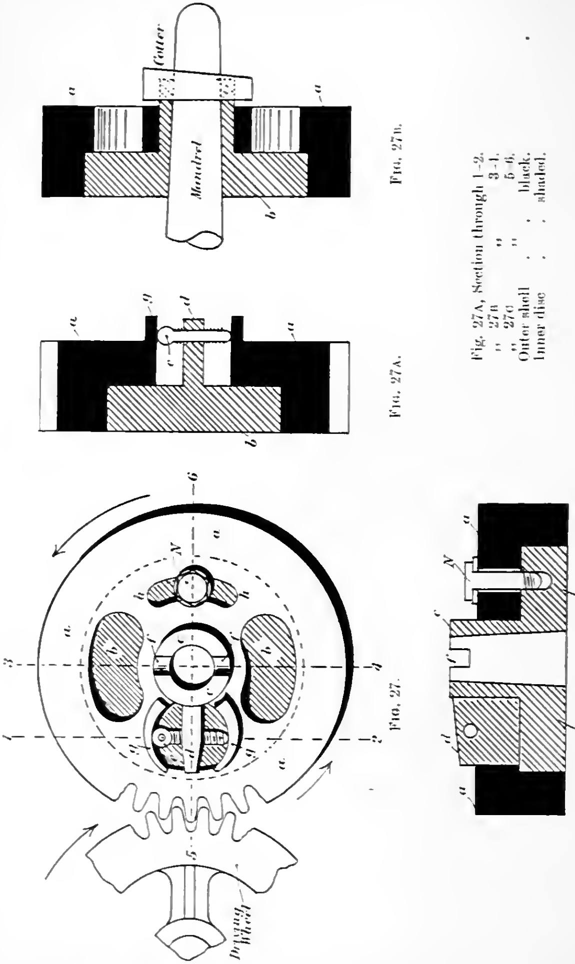


FIG. 27B.

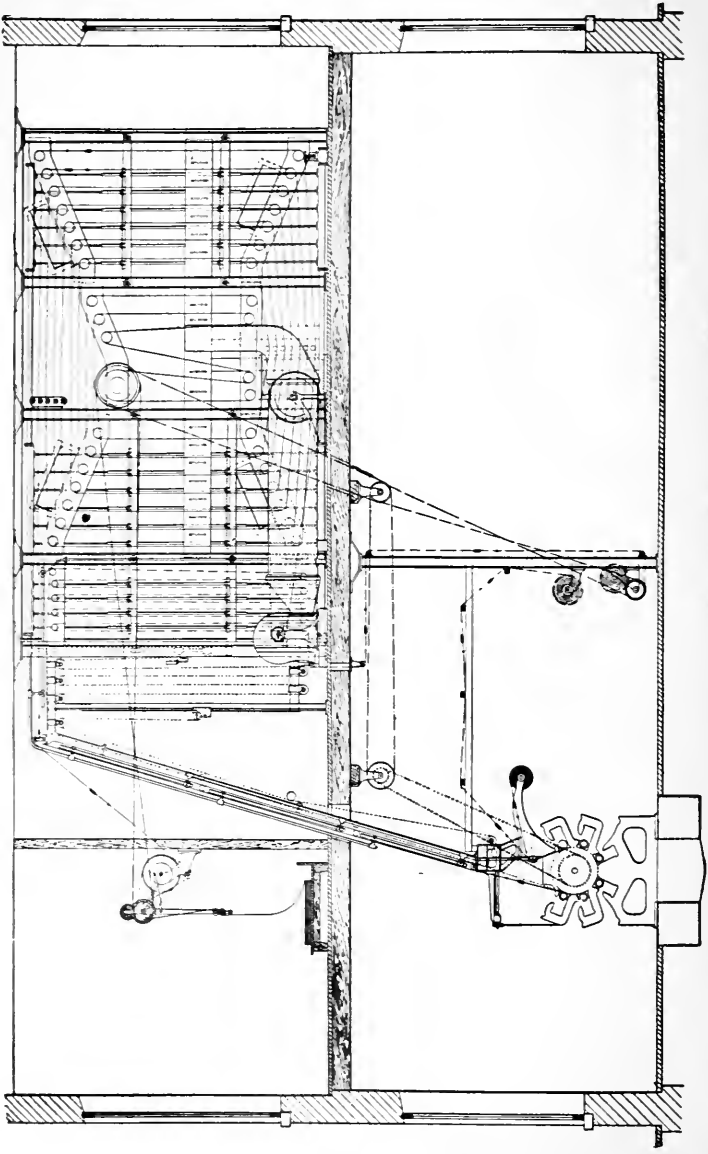
FIG. 27A.

FIG. 27.

FIG. 27C.

Fig. 27A, Section through 1–2.
" 27B " " 3–4.
" 27C " " 5–6.
Outer shell . . black.
Inner disc . . shaded.

FIG. 27.—"Box-wheel" and sections.



Section of Six-colour Printing Machine with Hot-air Drying arrangements.

Fourteen-colour Printing Machine.

The twelve-colour machine described on p. 55 is of similar construction to the above machine.

[*To face p.* 55.

Apart from the extra attention demanded by the increased number of rollers and their accessories, the working of a multicolour printing machine is in all respects similar to that of a single-colour machine. The cloth enters from behind in just the same way, and, in passing between the rollers and the cylinder, receives from each roller in turn a coloured impression of the particular part of the design engraved upon it, so that as it leaves the machine it is found to be fully printed in as many colours as there are rollers.

In Plate II. a sectional sketch of a six-colour machine is shown with Mather and Platt's hot-air drying arrangement; and in Plate III. an elevation of a twelve-colour machine, which shows in a clear manner the disposition of the various rollers and the way in which the traverse motion of the "doctors" is obtained.

The fitting of the rollers in their proper places is but one part of the printer's work; in addition he has to see that the colour boxes are kept well supplied with clean colour, the "back greys" and cloth free from creases, and that the "doctors," lapping, blanket, and drying arrangements are in the condition best suited to the class of work in hand.

"**Doctors.**"—The management of these apparently simple blades of metal makes, perhaps, greater demand upon the skill of the printer than any other branch of his work. As previously mentioned, there are two kinds of doctors—the "cleaning doctor" and the "lint doctor." The use of the former is absolutely essential in every case, but the latter may be dispensed with or not, at the discretion of the printer.

"**Cleaning Doctor**" blades are made of the best quality of medium-tempered steel. They vary in width from 2–3 inches, in thickness from $\frac{1}{32}$ to $\frac{1}{16}$ of an inch, and in length according to the length of the roller, being usually some 2 inches longer. Their top or working edges—*i.e.* those which rest on the roller—are filed to a suitable bevel, and then sharpened by hand with an oil-stone to a razor-like keenness; their bottom edges are firmly clamped between two "sheaths" of brass (or one of brass and one of iron), tightly screwed together, and furnished at each end with (*a*) a supporting pivot, which rests in a bracket attached to the bearing of the roller, and (*b*) a projecting lever, which, by means of weights or screws, serves to press the blade on the roller. The shapes, sizes, and construction of these levers vary according to the place occupied in the machine by their respective rollers—some being simple, some compound—but their general action will be seen by reference to Plate I. and to fig. 24, S, S.

In order to prevent the unequal wearing of their edges, which would occur if they were allowed to rest continuously in one position on the roller, cleaning-doctors are given a slight to-and-fro movement in a direction parallel to the axis of the roller. This movement is effected by the "traverse motion," which consists of a connecting-rod attached at one of its ends to a pin on the doctor sheaths, and at the other to a small crank or eccentric situated at the side of the machine and worked by bevel gearing. In large machines of modern make the connecting-rod is coupled to an oscillating lever, one end of which works in an undulating channel cut in the circumference of a solid iron disc fixed on the axle of the pressure cylinder and revolving with it (see Plate III.). When this latter arrangement is adopted, the disc is frequently made to slide backwards and forwards on its axle—a device which, by constantly varying the "throw" of the "doctor," adds to its efficiency, especially in the printing of broad stripes, where the width of the engraved pattern is greater than the amplitude of the "doctor's" to-and-fro motion.

"**Lint**" or "**Composition Doctors**" only differ from the above in that their blades are made of brass or some similar alloy, and that they have no traverse motion. Formerly, in cases where a colour was affected by the slightest trace of iron, or where it exercised a solvent action on steel, a "lint doctor" was frequently used in place of and as a "cleaning doctor." At the present time it is rarely or never used in this connection, partly on account of its unsuitability for the purpose—its edge being too soft, and requiring to be sharpened up too often—but mainly because the defects which necessitated its being put to such a use have been remedied by modifying the composition of the printing colours.

The sharpening or "getting up" of the "cleaning doctor" edge is possibly the most difficult and most important part of the machine printer's work; for though an apparently simple operation, it demands for its proper performance an amount of skill only to be acquired by long practice, and an unerring judgment as to the kind of edge required for different classes of engraving. No definite rule can be laid down for the production of the "edge" best suited to a given style of work, for its quality depends not only upon the weight and scale of the engraving, but also upon the thickness and hardness of the doctor blade, the angle at which it rests upon the roller, the pressure applied to it, and upon both the viscosity and tenacity of the printing colour which it has to clean off. Moreover, different printers accord different treatment to their doctors, for even the same class of work, each man preferring to adopt that method which his individual experience has proved to yield, in his hands, the best results. Generally speaking, the edge of a well "got up" cleaning doctor is perfectly straight, absolutely smooth throughout its entire length, bevelled to a rather obtuse angle, and as sharp as a razor; any roughness, unevenness, or the slightest snip in the "edge" is sufficient to allow colour to escape under it, with the result that the finished print exhibits serious defects in the form of streaks or cloudy patches of colour. Another point which exerts considerable influence upon the efficient working of the doctor, and also upon the durability of its edge, is the angle at which it rests upon the roller; but this, in common with its sharpening, is a matter which only a practical printer can decide, and, in fact, the whole manipulation of the cleaning doctor is so entirely a question of experience and practice that no amount of description could possibly convey an adequate idea of how it varies according to circumstances.

As regards the "getting up" of the lint doctor little need be said; it merely requires to be sharp enough to catch the lint and the colour that the cloth deposits on the roller. It may be noted, however, that a lint doctor ought to press less sharply on the roller than a cleaning doctor, *i.e.* it should occupy a position approaching the tangential rather than the radial. The reason for this is, that as the roller works *towards* (or against) the edge of the lint doctor, the latter, if set at too sharp an angle, is liable to dip into and tear up the engraving—an accident which entirely spoils the roller for the time being, and in many cases entails the "turning off" of the pattern, and the re-engraving of a quite new roller.

"**Lapping.**"—The lapping used for covering the pressure bowls of printing machines is a special fabric, with a linen warp and worsted weft. It is made in various weights, to fit it for different styles of work, and upon its quality, both as regards materials and weaving, depends its power of resisting the enormous pressure and the grinding action to which it is subjected during the printing operation. For most purposes eight to twelve thicknesses of lapping are wound round the cylinder or pressure bowl, the utmost care being taken to see that every thickness lies perfectly evenly and is absolutely free from creases. If the lapping is in several pieces, the ends of each must be frayed to a fringe about 2 inches in length, and carefully straightened out quite flat so as to avoid leaving a ridge when the other pieces are wound over them. The slightest crease or any inequality whatever in the lapping is sufficient to spoil hundreds of pieces unless it is discovered at once—not always an easy matter, as many colours do not show up until they are dyed or steamed, or otherwise developed after printing. It is of paramount importance, therefore, that the lapping should be properly put on at the outset; and not only so, but that it should be examined from time to time to see that it is in good working condition. The skill of a printer is displayed as much, perhaps, in the management of his "lapping" as in the sharpening and manipulation of his "doctors." If put on too loosely it very soon slips, and if not re-wound at once, breaks across its whole width, and becomes utterly useless for its special purpose. After working for some little time new lapping stretches to such an extent as to require re-winding; and all lapping whatsoever requires changing at varying intervals, according to its condition. The longer it is worked, the harder and less elastic it becomes; and if the style of pattern for which the cylinder was originally "lapped" remains unchanged, the "lapping" itself must be changed, otherwise the quality of the printing will suffer. As a rule, if the lapping is in good condition except in respect of having become too inelastic (from constant use) for heavily engraved patterns, it is not changed at once, but is utilised for the printing of lighter and more delicate designs, the details of which are rendered much better—with a crisper definition, that is—on a fairly hard "lapping" than on one that is "springy" enough for bolder work. In this way a good deal of valuable time is saved and the rate of production kept up; for the changing of lapping is a comparatively slow operation, and whilst it is going on the printer is, of course, producing nothing of saleable value. The quantity of lapping to use for a given style of work and the knowledge as to when it requires changing can only be taught by experience, and on these points the practice of printers varies almost as much as in their treatment of the "doctor."

Generally speaking, however, the finer and more delicate the design to be printed the smaller is the amount of lapping required, and the harder or more compact in texture must it be; whereas for heavy designs, deeply engraved, a larger quantity of a soft, thick, openly woven quality is necessary, especially in cases where the colour is required to penetrate through to the back of the cloth; or, conversely, in other cases, where the great pressure of the printing rollers against the bowl that it is necessary to employ to obtain a good impression of the pattern on a hard lapping would force all the colours (except the last) of a multicolour pattern too deeply into the body of the cloth, and thus detract from their brilliancy, or "face," as it is technically termed. The durability of any quality of lapping is dependent upon many factors, but, so far as it depends upon the skill of the printer, it is a question of the manner in which it is wound upon the pressure bowl. If it is wound on too loosely, the enormous pressure put upon it in printing causes the several thicknesses to slide about over each other continuously, with the result that the constant grinding action thus set up rapidly wears them away, until eventually the lapping "breaks" or is torn asunder, and at once becomes utterly useless. As all good work depends, amongst other things, upon the lapping being of uniform elasticity and density throughout, and of a smooth, even, unbroken surface, it is of the utmost importance to guard against these qualities being destroyed by the passage of hard substances between the lapping and the rollers. Even a small nail or other solid body falling into the machine from the floor above, or during repairs, is sufficient to cause a vast amount of damage to both rollers and lapping—damage which frequently entails several hours of skilled labour to repair.

Blankets.—The ordinary printer's blanket consists of from 30 to 50 yards of a thick, pure woollen fabric, tightly woven, and afterwards shrunk and felted. In common with the "lapping," it must be of uniform texture and of equal thickness and elasticity throughout its whole substance. The function of the blanket is to supplement or increase the effect of the elastic pressure afforded by the lapping, and to this end it is arranged to circulate continuously round the pressure cylinder of the machine between the lapping and the cloth to be printed. In putting it on the machine, therefore, its ends are sewn together so as to convert it into an endless travelling band or web, and sewn in such a way as to leave no ridge at the seam. For this purpose the two ends are first cut perfectly square, then placed in contact with and flush with each other, and sewn together with fine, strong silk thread, the stitch used being generally a sort of "herring-bone stitch," which crosses and recrosses the seam at short intervals, and makes a joint sufficiently strong to resist the working tension of the blanket. When properly sewn in this way a blanket seam ought to leave no evidence on the printed cloth of its passage through the machine; if, however, it is in any way rough or uneven, these defects are at once demonstrated by the appearance of a light-coloured mark right across the whole width of the cloth every time the seam passes. In course of time blankets become hard and soiled from the pressure of the rollers and the wet colour that penetrates through the cloth, and must then either be turned or replaced by a new one. With care and by the use of "back greys" a good blanket can be made to serve for the printing of 10,000 to 12,000 pieces of calico, and even then be in a condition to withstand washing, after which it may be used again for certain styles of work that make no great demand upon its power of resisting "wear and tear."

Mackintosh Blankets.—The mackintosh blanket is composed of three or more layers of fine, evenly woven calico of good quality, cemented together with a solution of india-rubber in naphtha. It is the outcome and the most successful of the many attempts made to replace the expensive woollen blanket by one that would be equally efficient and at the same time much cheaper; and although it is not a quite perfect substitute, it is yet so generally useful that in some works it is employed to the total exclusion of the costlier article. Mackintosh blankets are made in two different forms; one that requires sewing in the usual way, and the other a seamless blanket, which comes into the market as a single piece of calico, three or four times the required length of the blanket, and coated on both sides with a special preparation of india-rubber, neither sticky nor hard, but just sufficiently "tacky" to cause the several layers of the blanket to adhere firmly to each other, without any chance of slipping, when pressed together tightly in the printing machine.

To describe in detail the way of putting this seamless blanket on the machine would be useless without a practical demonstration.

One great advantage of mackintosh blankets over woollen ones is that they can be used for the strongly alkaline colours that play so important a part in modern calico printing, and which would rapidly destroy the wool fibre of the older style of blanket. Another advantage, too, is that they can be washed "*in situ*," a convenience which has led to the introduction of special washing appliances fixed behind the printing machine, and acting continuously on the blanket, so that it always enters the machine quite free from "dried-on" colour.

Mackintosh blankets are eminently adapted to the printing of fine patterns and shallow engraving; but although suitable for most other kinds of work, they are better discarded in favour of a woollen blanket when heavily engraved patterns are to be printed, and in all cases where a large quantity of colour is intended to penetrate deeply in the fabric.

Washing-Blankets.—Of late years the use of washing-blankets has increased enormously, partly owing to the many recent improvements in the washing machines themselves, and partly to the fact that cheap and serviceable blankets can now be obtained to withstand the extra strain put upon them. Most of these blankets are composed of a single thickness of stout cotton cloth, waterproofed in various ways, and, curious though it may appear, they last better than a 3–4-ply mackintosh. For some styles it is even possible to do good work on a simple grey that has merely been passed through a solution of wax and dried, but, as a rule, a much stronger fabric is used. At an important works on the Continent a strongly woven but fine canvas of the best quality is waterproofed by being passed through successive baths of soap and alum, then dried and treated in a solution of blood albumen, and finally steamed and calendered. These blankets yield excellent results, and are as durable as any of their kind. In many cases the quality of the blanket is further improved by "mercerising," followed by the foregoing treatment, or by any of the methods in which alum-soap and wax are used, either separately or together.

Numerous types of blanket washing machines are in use, but most, if not all, are based upon some application of the same fundamental principle, *i.e.* that of subjecting the travelling blanket to the scrubbing action of revolving brushes in conjunction with a copious supply of water. In some systems the blanket passes round a revolving drum against which the brushes are pressed; in others the brushes rest against an upright slab or table of slate, over which the blanket is drawn, and in yet others, again, the blanket simply impinges upon the brushes. In all cases "spirt" pipes are used to throw fine jets of water at a fairly high pressure upon the blanket, and the excess of water is afterwards removed by means of a pair of squeezer bowls, between which the blanket passes on its way to the drying apparatus, from whence it re-enters the printing machine.

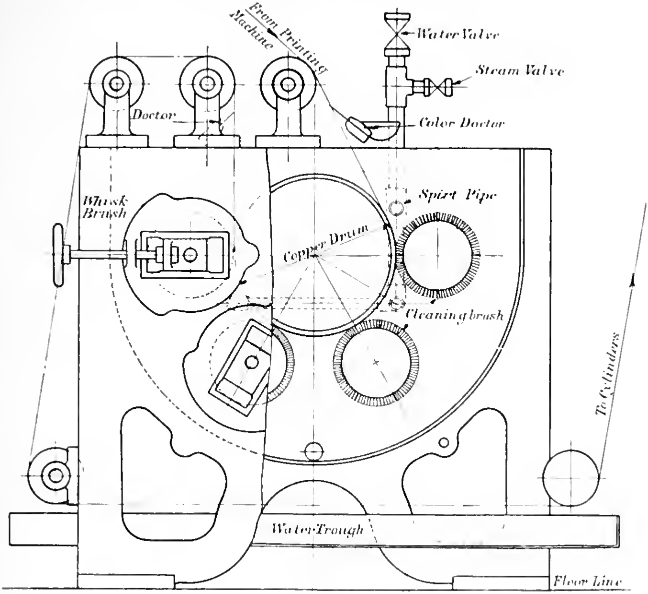


FIG. 28.—Blanket washer (Mather & Platt).

The great advantage of washing-blankets is that, in always presenting a clean, dry surface to the back of the cloth, they render the use of "back greys" unnecessary, for, being unabsorbent, any colour they may pick up is easily removed in the washing machine.

"Back Greys."—Back greys, as previously mentioned, are simply pieces of unbleached calico that are run between the blanket and the cloth to be printed, for the purpose of protecting the former from the colour that percolates through the latter. They are always used for woollen blankets and ordinary mackintosh blankets, but may be dispensed with altogether when washing-blankets are employed, though they are sometimes used along with them for certain styles of pattern. After being used as "back greys," the cloth is sent into the bleach-croft, and, after "souring" to get rid of the metallic salts and thickening agents that it contains, is bleached in the ordinary way, and used for printing just like any other cloth. Calico that is destined for madder work is never used for "back greys," on account of the fact that in most cases the mordants and other bodies it picks up in process cannot be perfectly removed in the usual course of bleaching, and consequently show up when the cloth is dyed. "Bumps" is a name applied to calico that is set apart specially for use as "back greys," and "bump greys" are always employed, as far as possible, in the printing of colours that are either very difficult to bleach out or that affect the cloth in other irremediable ways—such colours, for instance, as Aniline black, Indigo blue, and the alkaline discharges used for tannin mordanted cloth and Turkey-red.

In works where the printing machines are not fitted up with blanket-washers the difficulties of the management are increased considerably by the necessity of providing a *suitable* "back grey" for every piece of cloth printed. A stock of cloth, greatly in excess of what is actually required for the execution of orders, must always be kept on hand, and must, moreover, be bought with due regard to the width of the cloth along with which it is intended to work; for if the "grey" be too narrow it is useless, and if too broad it gets daubed with colour on its edges, and not only wastes colour, but dirties every part of the machine with which it comes in contact—rollers, drying apparatus, etc.—and adds to the difficulties of producing clean work. Apart from the capital involved in stocking a large quantity of cloth, the extra time and labour expended upon the handling of "back greys" augments the "cost of production," and their storage takes up a good deal of valuable space. Taken altogether, the question of "back greys" is one of the most irritating that a works manager has to deal with; and it is not surprising, therefore, that every step taken towards their abolition should meet with the approbation of technical men.

"Back greys" are usually seamed on a fine sewing machine, and for ordinary purposes this is quite sufficient, but where very delicate and full all-over patterns, like zephyrs, minute checks, etc. etc., are to be printed, the ends of the "greys," instead of being sewn, are pasted together, so as to avoid the least chance of a ridge being formed.

Furnishers and Colour Boxes.—The "furnisher" is simply a wooden roller (covered with cotton or wool) which revolves on brass centres in slots cut in the ends of the colour box. Below, it dips into the colour, and above, works in contact with the printing roller, to which it furnishes a constant supply of colour. For most styles of work this plain wooden furnisher is sufficient, but for colours containing much solid matter, such as zinc oxide, sulphur, chalk, and pigments like Chrome yellow, it is replaced by a stiff revolving brush, which, in addition to supplying the printing roller with colour, serves to scrub out any deposit that may stick in the engraving, and thus prevents the production of weak impressions. In order to render this latter operation more effective, the "brush furnisher" is frequently made to revolve against the roller, but this is not essential except in the case of strong pigment colours—especially Guignet's green.

The colour boxes are long, narrow, shallow troughs of wood or copper, supported at each end on small shelves or brackets, carried on a cheek of iron attached to the adjustable bearings of the printing rollers, and moving backwards and forwards with them, so that whenever the pressure of the roller against the cylinder is altered, the relative positions of roller, colour box, and furnisher to each other remain the same. Double-cased colour boxes of various types are used in cases where the colour requires to be kept either very cool or worked hot. For cooling purposes ice is packed between the two casings, while for keeping the colour hot, steam is passed continuously between them.

Rollers.—The rollers used in calico printing are of two kinds—solid and shell. Both types vary in length from 32″ to 80″, and also in diameter, the solid rollers being restricted, for several reasons, to the smaller sizes, viz. those between 5″ and 12″ in diameter. On the other hand, shell rollers may be anything from 5″ to 30″ in diameter, though one firm in England is fitted up to print, and has printed, patterns with a vertical repeat of nearly 120″—equal to rollers 40″ diameter. These large sizes are, however, unusual, and very few firms are able to produce patterns exceeding 36″ in vertical repeat.

The ordinary solid roller is approximately 5″ diameter, and long enough to take a pattern 32″ wide; it consists of a hollow cylinder of copper, the walls of which vary in thickness from ½″ to 1¼″; its surface is ground perfectly smooth, and its circumference must be exactly the same from end to end. Inside, a "tab" or tongue of metal (½″ broad and ¼″ deep) extends throughout the whole length of the roller. This "tab" fits into a corresponding slot cut in the shaft or mandrel, upon which the roller is forced when required for printing, and serves to prevent it from slipping round during this operation. Solid rollers are cast, and afterwards hammered or rolled to increase their density, and to ensure that they will yield a smooth, even surface, free from granulation, when turned, ground, and polished.

"Shell" rollers consist of a cast-iron foundation, upon the surface of which a coating of copper is deposited electrically. This coating varies in thickness according to circumstances, and must be deposited slowly and carefully to avoid granulation or porosity, either of which would render it altogether unsuitable for its special purpose. When a sufficiently thick coating of copper is obtained, the roller is taken out of the depositing vat, well washed, put into a lathe, and ground and polished to size. If its surface is at all granular, it is burnished under a heavily-weighted, polished agate; but nowadays the science of electroplating is so well understood that, in the majority of cases, this final burnishing is unnecessary. The iron foundation or "shell" is in all respects, except that of material, identical with a solid copper roller, and a "shell" roller, therefore, may be used for precisely the same purposes as a copper one; in fact, both types are used in the same pattern in scores of instances.

Solid copper rollers are undoubtedly the best from every point of view, save that of expense; and even there it is only the initial cost that is greater than that of shell rollers. The great advantage of solid copper rollers is that when the pattern engraved upon them is no longer in request it can be "turned off" in the lathe and a new one engraved in its place; and this can be repeated until the roller becomes too thin to use. In addition to this they are much more durable, much less liable to accidents, and much more easily repaired when damaged than are "shell" rollers. They are also eminently adapted to every style and method of engraving; and if any one of a series of solid rollers, each of which ought to be of exactly the same diameter, is out of size, the mistake can be remedied with the greatest of ease in the lathe. On the other hand, "shell" rollers are comparatively cheap; they can be made on the spot; they are lighter to handle; and if well made, they are reliable in use, and can be applied to most of the ordinary styles of printing. But unless the deposit of copper is fairly thick, they cannot be "turned off" and used again for another pattern; neither can they be so easily and readily repaired, for if they are seriously cut or dented it is most difficult to patch or plug them without lifting the copper in the surrounding parts. And again, if they are dropped, receive a heavy blow, are submitted to unequal pressure, or subjected to the great heat that is sometimes engendered by the friction of the mandrel in the bearing, the coating of copper on their surface is very liable to be loosened from the shell, with the result that the roller becomes absolutely useless until it is re-coppered and re-engraved. If this loosening of the copper of a shell roller is not detected at the time of its occurrence, it usually manifests itself in no unmistakable way the next time the roller is put into the printing machine; for, immediately the machine gets well under way and heated up a little, the loosening begins to extend, until finally the "lint doctor" dips into the engraving of the slightly bulging parts and, by tearing the copper bodily away from the shell, spoils at the same moment the "lint doctor," the cleaning doctor, the blanket, and the "lapping." On the whole, however, shell rollers are exceedingly good substitutes for solid copper ones; and, now that their manufacture is thoroughly understood, they may be used with the utmost confidence for most classes of work, and may also be engraved by machine if the copper is moderately thick and the pattern not too heavy. Perhaps the greatest convenience afforded by shell rollers is that they can be made, with perfect safety, to any size desired.

For instance, at the works of Messrs F. Steiner & Co. Ltd., Church, Lancashire, who possess the largest printing machine in the world, one of the authors has dealt with ten-colour patterns, the shell rollers for which were each 80″ in circumference and 80″ wide, and at the same works some of the rollers employed for "sarries" and imitation "batticks," etc., are even larger. In these huge rollers the copper is deposited upon an iron drum, the hubs of which are bored to fit the ordinary mandrels used in the machine. If made in copper alone they would have to be very thick to overcome their tendency to spring in the middle during the printing operation, and would consequently be enormously expensive; and if thin enough to be of reasonable price, they would be very liable to distortion during the course of the various processes and handlings they go through from the time they are first made to being used for printing. Copper deposited on a rigid, hollow iron drum, however, is free from these drawbacks; and although large rollers made in this way are somewhat difficult to manipulate in practice, they yield surprisingly good results when everything is taken into consideration.

Printing rollers are sometimes made of brass, but they offer no advantages over copper rollers, and, if anything, give more trouble, on account of the extra time it takes to burnish out fine scratches, which can be repaired in a few minutes on a copper roller by the printer himself, with a small finger-stone and a steel burnisher. Occasionally, too, copper rollers are nickel-plated to increase their surface hardness, but they are then open to the same objection as brass rollers; and, in addition, the film of nickel is apt to peel off, with disastrous results if it occurs whilst the machine is printing.

Mandrels.—Mandrels are the long steel shafts which serve as temporary axles for the printing rollers when the latter are placed in the printing machine. They are usually about a yard longer than the roller, and project 18″ beyond it at each end. For a distance of 6″ or 8″ on each side of the roller these projecting portions of the mandrel are turned to a perfectly cylindrical neck, so as to work smoothly in the brass steps of the adjustable bearings in which they turn; for the rest they are tapered off, at a convenient angle, to facilitate the slipping on of the rollers and box-wheels, and to reduce their weight. The middle part of the mandrel, between the necks, and upon which the roller is forced, corresponds in diameter to the internal diameter of the roller that is intended for it; it is slotted from end to end for the reception of the "tab" inside the roller, the size of the groove being slightly larger than that of the 'tab"; and it tapers a little, so that the roller may be forced tightly upon it. It ought to have been mentioned before, that the roller itself also tapers *internally* in exactly the same way. The forcing of the rollers on the mandrels is done in a special machine, and requires to be performed with care, as, if the full power of the machine is exerted too suddenly, both roller and mandrel are liable to be strained and rendered quite useless for the time being. Fig. 29 shows a "forcing" machine or "jack" for copper rollers.

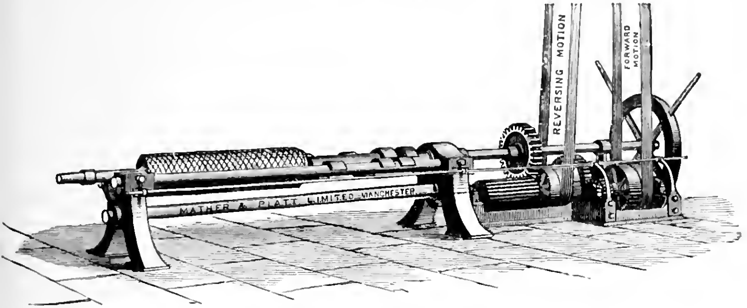


Fig. 29.—Forcing machine for rollers worked by power.

ENGRAVING OF COPPER ROLLERS.

The engraving of printing rollers is a distinct and a highly specialised branch of calico printing, and has been developed, in various directions, to such an extent that at the present time it may be looked upon as a separate industry. So much so is this the case, that many firms devote themselves exclusively to the engraving of copper rollers; and it is not at all uncommon for small calico printing establishments to depend entirely upon such firms for the engraving of all their patterns. Larger concerns, too, send a great many of their most important designs to be engraved by outsiders—sometimes because their own engraving department is too small to cope with all the work they require, sometimes because their staff is not sufficiently expert to execute the best class of engraving, and sometimes in order to relieve themselves of the responsibility for difficult work, and thus ensure themselves against loss; for, of course, if the engraving cannot be made to give a satisfactory rendering of the original design, or the delivery of the rollers is a long time overdue, they have a claim against the engraver. From this it will be seen that a practical calico printer is not necessarily a practical engraver as well; at the same time a knowledge of the different methods of engraving is vastly interesting, and to a certain extent most requisite, so as to enable the calico printer to recognise more fully the scope of his art. To this end, therefore, the following remarks will be confined, the more so as the limits of the present work render impossible anything more than a brief explanation of the three principal methods of engraving. Even these methods embrace so many different processes, and call for the application of machinery of such complexity, precision, and delicacy, that justice could only be done to them in a treatise devoted specially to the subject. Compression is necessary; and consequently, while referring the reader to larger works, such as E. Berthoud's *Traité de la gravure sur rouleaux*, for details respecting the methods of practice and the machines employed in engraving a design on copper rollers, a brief résumé of the following is all that can be given here—Hand engraving, Machine engraving, and Pentagraph engraving.

At the outset it may be well to note that the object of each method of engraving is the same, and that the results of each, although achieved by very different means, present the same general appearances. Lines are obtained by the cutting of a simple furrow or groove in the roller; solid objects, by first engraving the outline, and then filling in the space thus enclosed with parallel lines, engraved close together so as to form a series of angular corrugations, something like the surface of a file. The number of these corrugations or lines to the inch constitutes what is known as the "scale" of the engraving, and the coarser the scale, the deeper must be the engraving, and the more colour will the roller put on the cloth. As several scales can be engraved on different parts of the same roller, it follows that, from a single roller, several tints of one colour can be printed at one operation. In theory it is possible to obtain every gradation of colour tone between pure black and pure white from one engraved roller; but in practice it is found that the uneven surface of woven fabrics is incapable of receiving the impression of more than two or three of the numerous gradations that may be engraved on one roller, and consequently it is but rarely that more than three "shades" or gradations are attempted on a single roller, any additional shades that may be required being ordinarily obtained from a second or even a third roller. A shaded effect may be obtained from a *single* roller, especially if it be engraved in stipple, but such work is usually unsatisfactory on account of its "speckly," "pinny," or "patchy" appearance. To avoid this defect, a second roller is engraved to print a flat tint *over* the whole of the shaded work on the first, the effect of the two wet colours falling together being to cause the shaded portions, which are printed in a dark colour, to "swell" or run into the pale superposed tint, with the result that each tone blends with or melts into its neighbours in a perfectly imperceptible manner. It is not necessary even to print a pale tint of the colour used for the shaded roller; a colourless paste will do quite as well so long as the moisture required to cause the "swelling" is applied to the cloth, or an entirely different colour may be employed, in which case the double gradation of tone and colour is obtained. For instance, if the shaded part of the pattern is printed in red with a yellow superposed, the effect obtained will not only show gradation of tone, but will also display an exactly corresponding gradation of colour, ranging from dark red, through various shades of scarlet and orange, to pure yellow. This facility for the production of various effects from few rollers is one of the most important qualities of roller printing, and one that is largely utilised in every printworks.

As a rule, a combination of "line" and "stipple" is employed for engraving gradated effects on copper rollers; very light line engraving is not suitable for the most delicate tones, and heavy stipple engraving cannot be made to give an even shade over an extended space of solid colour. But using the two styles together, very good effects are easily possible. For example, in expressing the idea of a flower in light and shade, the darker parts of it and those in shadow would be engraved in line, to print as solid patches of colour; from these, lines of diminishing thickness would be made to radiate, according to the shape of the petals, and finally dots (or stipple) of various sizes and depths, and at constantly increasing distances from each other, would be added between and beyond the radiating lines, to complete the scheme of gradation. Rollers engraved in this way, when printed in conjunction with superposed colours, yield wonderfully delicate effects of shading, but it is questionable whether the amount of work they represent is justified by the effect obtained; artistically speaking, flat effects based on frankly conventional lines, with gradation suggested rather than realised, and unmarred by fussy detail, generally give more satisfaction to those best able to appreciate the highest class of decorative work; but, at the same time, "stippling" is quite an easy and natural process in metal engraving, and if used with restraint, it is difficult to see what objection there is to its employment.

Fig. 30 illustrates the usual treatment of a roller engraved to give effects of shading; the dots are exaggerated somewhat for the sake of clearness.

Another method of producing effects of light and shade is to engrave the entire design in various shapes and sizes of delicate masses and different qualities of graduated line, the whole surrounded by a fine regular outline, and then printed in a dark, rich colour. This style is usually employed for single-colour effects, but its range may be extended by allowing a second roller to print a pale flat tint over the greater part of the pattern, the unprinted portions of the cloth then showing in white as high lights.

FIG. 30.—Example of stipple engraving.

Numerous other effects of line and stipple, solid mass and superposition of colour, are also in general use; in the possible combinations of the various qualities of copper roller engraving almost any effect capable of being printed can be obtained, and nowadays it is not so much a question as to how a certain effect is to be got as it is of the *cheapest* way of getting it.

Hand Engraving.—The principal implements used in hand engraving consist of gravers or burins, small punches and light hammers. The gravers are made of fine quality steel bar, square or rhomboidal in section, slightly tapering from handle to point, curved a little, so as to enable them to be worked almost parallel with the roller, and mounted in a short wooden handle with a rounded end. Their points are obtained by grinding their ends off at an angle, so that their cutting edges are formed by the edges at the outside of the curve (see fig. 31).

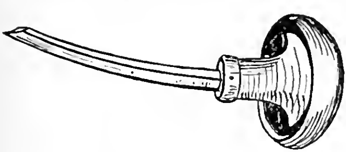


FIG. 31.—Burin or graver.

In use, the graver is held between the thumb and forefinger, and the handle in the palm of the hand. The point is guided by the thumb and driven forward by the pressure of the palm, the tool being held at an angle very slightly inclined to the roller. The pattern to be engraved is transferred to the roller by any suitable means—generally from a tracing in lampblack and oil, or in some colour containing a soluble sulphide, which, when laid upon the surface of a moist roller, leaves its impression in black lines of copper sulphide. After the pattern is engraved, the roller must be polished with "Water of Ayr" stone and water, to remove the burr raised by the action of the graver; and after that it must be burnished, if required to print very intense colours, since the fine scratches left on its smooth surface after "stoning" tend to leave their impression on the cloth (tech. "scum").

Roller-engraving by hand is a slow process. It is only used for the most delicate and important work, and for large designs of which only one repeat can be put on the roller, and which are therefore too big to be engraved by any other method.

"STIPPLING" is a form of engraving that can only be done by hand. In principle it is simple enough, being merely the punching of small dots on the surface of the roller, but in practice it is most difficult to do well, as it requires the utmost delicacy of hand in its final stages. The slightest inequality or suddenness in gradation tells at once in the printing machine; and if the defect is caused by the stipple being too deep or strong, it means that it must be burnished or polished down and re-engraved—an operation which affects the neighbouring portions of the engraving, and thus makes it necessary to re-touch a good deal of the work that was previously satisfactory. "Stippling" is performed by means of fine, sharply-pointed steel punches, which are held in position on the roller with the left hand, and then lightly tapped with a small steel hammer held in the right hand. The handle of the hammer is from 8 to 9 inches in length, and made of a "springy" wood, which ensures the rebounding of the head from the top of the punch, and so adds to the delicacy of the engraver's touch. The difficulty of stipple engraving will be better understood when it is remembered that every dot engraved raises a minute burr, higher in proportion as the dot is deeper, and that consequently the engraver has to make due allowance, at every stage of his work, for the final "polishing off" of the surface roughness caused by the thousands of "burrs" thus produced, which if allowed to remain would lift the "doctor" blade every time they passed under it in printing, and give rise to faulty work.

Machine Engraving.—In machine engraving the pattern, instead of being cut clean out of the surface of the roller with a sharp instrument, is stamped or indented thereon by means of a previously prepared "mill" with the design raised upon it in *relief*. The making of this "mill" involves many consecutive operations, and a number of details to which the most careful attention must be paid to ensure success.

In outline the process of machine engraving is as follows:—At the outset, if the pattern has not been designed for a definite size of roller, it must be altered in scale to repeat *exactly* a given number of times around the circumference of the roller upon which it is to be engraved. One repeat of it is then transferred to, and engraved by hand upon, a small roller of softened steel, known as the "die." Formerly the transfer was made from a tracing in printer's ink or a similar composition, but at the present time it is frequently carried out in the following manner, which has the advantage of giving a non-smearable transfer.

The polished and perfectly clean plain die is immersed in a solution of copper sulphate until its surface is evenly coated with a deposit of metallic copper; it is then washed, dried, and has wrapped round it a tracing of the pattern executed in a colour containing a sulphide; the tracing must be wrapped so that the repeats join up exactly, and in order to prevent it slipping it is made on a polished or varnished paper, which, when slightly damped by being breathed upon, adheres firmly to the die; the whole is now wrapped tightly in several folds of stout paper and tied round with string, and allowed to stand an hour or two, after which, when the coverings are removed, the pattern is found to be transferred to the die in lines of copper sulphide. The engraving of the die completed, the next process is that of "hardening." For this purpose the die is first painted with a thick coating of a chalky composition, to prevent its surface from oxidising, and then packed in an iron case containing bone-ash, and sometimes a little charcoal, and heated to a cherry-red heat in a special furnace, after which it is plunged into cold water, and finally "tempered" to the requisite hardness. It ought to have been noted that, before "hardening," the surface of the die outside the limits of the pattern is punched all round with fairly deep indentations, the object of which is to raise a coarse burr at each side of it—a burr which prevents lateral movement during the subsequent operation of "clamming." To make the mill, the die, engraved and tempered as above, is now placed in a specially constructed rotary press, the "clamming machine," and screwed by hand into close contact with another small roller similar to itself, but of *softened* steel, the mill. The machine is then set in motion, and the first effect of its action is to cause the burrs on the indented edge of the hardened die to sink into the softer metal of the mill, and gradually, as the pressure is increased, to force this latter into the indentations themselves, thus raising corresponding projections on the mill, some of which, being always in mesh, or gear, so to speak, with the "die," effectually prevent the two from slipping backwards and forwards laterally during their rotation. The die and mill are then kept revolving in frictional contact with each other, and under constantly and regularly increased pressure, until the soft mill has taken an impression in *relief* of every line and stippled dot engraved on the die. During this operation the mill and die must be daubed freely with lubricating grease, and it is, moreover, especially important to apply just the right amount of pressure, as otherwise the work will be defective. If the pressure is too light, the pattern will be incompletely transferred to the mill; if it is too heavy, the mill is liable to be crushed out of shape, the relief to be damaged, and the die either strained or broken. After "clamming" the mill is placed in a lathe and has its rough edges turned off and tapered to below the level of the background of the relief, so as to prevent any part of it except that carrying the pattern from coming into contact with the copper roller during the process of engraving. It is now hardened in exactly the same way as the die, and, after cleaning, it is ready for use. The dimensions of dies and mills vary according to the style and scale of the patterns to be engraved. As a general rule, however, the circumference and the width of the working surface of a die correspond to the vertical and side "repeats" of the design; but in the case of very small "all-over" cover patterns, which really repeat at very short distances, several "repeats" are necessarily put on a single die. The dies usually employed vary between ½" to 6" in length, and 3" to 9" in circumference. As regards the size of mills, they may be any multiple of the die in circumference so long as they will repeat a whole number of times round the copper roller; in length or width they must, of course, correspond with the die.

The machine used for engraving the full-sized roller from a small mill is too complicated to describe in detail here, and for particulars of its construction and working the reader must consult one of the treatises dealing specially with the subject of engraving. Briefly described, however, it consists of two strong cast-iron ends, connected together with long wrought-iron stays and each provided with a bearing in which a shaft or axle revolves. This shaft, upon which the roller to be engraved is fixed, may be turned either by hand or power, according as to whether its movement is to be continuous or intermittent. At the back of the machine, and a little below the level of the shaft, a slide or "rest" extends from end to end of the machine, and along this rest a strong pillar-like support for a hinged lever is arranged to travel to and fro when actuated by means of a screw fixed between the double bar of which the "rest" consists. The long lever, hinged at one end to the top of the travelling or adjustable support, extends forward to the front of the machine at some distance above the shaft (and roller), and is furnished at a point immediately over the axis of the latter with an adjustable block bearing for the reception of the mill, which thus rests exactly on the top of the roller when the machine is in use. In addition to these essential parts, a modern engraving machine is provided with various other fittings and devices, designed with a view to giving the engraver perfect control over every movement, and to enable him to adapt it to different sizes of rollers and to special styles of engraving.

The actual engraving is performed as follows:—The roller is first securely fixed on the shaft, and then the mill is brought to bear upon it at one end, the utmost care being taken to see that the two are perfectly parallel, and that their respective axes are in perfect vertical alignment with each other. Any deviation from these conditions results (*a*) in misfitting of the "repeats," and (*b*) in more or less loss of crisp definition, especially in strongly engraved patterns. The machine is now set in motion, and as the roller is in frictional contact with the mill, the two revolve simultaneously, and the latter indents its pattern into the surface of the former. At the commencement of the engraving the pressure of the mill upon the roller is comparatively slight, but, after the first circuit of the roller is completed in shallow intaglio, it is gradually increased from time to time by adding weights to the free end of the lever, until the pattern is engraved as deeply as may be. When a part of the roller equal in width to the length of the mill is fully engraved all round, the mill is lifted, and, together with the pressure lever, is moved laterally to its next position by means of the travelling lever-support. The next position is, of course, that in which the side repeats join up exactly to complete the pattern. The operations are then repeated again and again until the whole length of the roller is fully engraved. It is then taken out of the machine, and "stoned" and polished as usual.

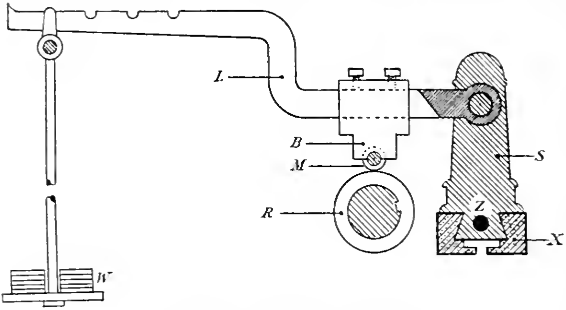


FIG. 32.—Diagrammatic sketch of engraving machine.

In fig. 32 (which pretends to no more than to illustrate, in simple diagrammatic form, the principle of machine engraving) the disposition of the essential parts of an engraving machine are shown. R is the roller, M the mill, B the adjustable bearing for the mill, L the pressure lever, X the slide rail or rest, S the sliding support carrying the lever, W the weights for applying the necessary pressure to the mill, and Z the screw or "worm" for altering the lateral position of the mill.

The introduction of machine engraving not only cheapened and accelerated the process of engraving, but at once rendered available many styles of design that were previously either impossible or too expensive to engrave by hand. Such, for instance, are small "cover" patterns and fine fancy stripes which repeat hundreds of times on an ordinary sized roller, and which would occupy a skilled engraver many weeks to execute by hand. If executed by machine, however, one single "repeat" or a solitary stripe of such patterns, engraved on a die, would be all the hand-work required for the engraving of a full-sized printing roller, and the work would not only be done more expeditiously and cheaply, but would be much more regular than if engraved by hand.

As the dies of a pattern are always preserved it is obvious that, in addition to increased speed of production and economy of skilled labour, machine engraving also affords special facilities for the rapid re-engraving or strengthening of a roller that is worn down, or for the replacing of a broken or worn-out mill—both advantages, the practical value of which cannot be over-estimated.

When a multicolour pattern is to be engraved by machine, it is of course necessary to engrave a separate die for every distinct colour. The dies must be of exactly the same dimensions; but the corresponding mills made from them may vary, so long as their circumferences are a multiple of those of the dies and a divisor of those of the rollers. The rollers, of course, are all of the same diameter and length. Formerly each succeeding roller of a multicolour pattern was made slightly larger than the one preceding it in the machine, so as to allow for the stretching of the cloth as it passed through the machine; but this arrangement had the drawback of requiring the rollers to be always worked in the same order, and was consequently abandoned, as more bother than otherwise; for it is often necessary, when many combinations of colour are printed to one design, to reverse the order in which some of the rollers are worked, for the purpose of preserving, as much as possible, the purity of the paler and more easily soiled tints, it being a principle in printing that the more delicate colours must be applied to the cloth before the darker (or "dirty") colours. The cause of the soiling of delicate colours in machine printing was touched upon in the opening discussion on the relative merits of block printing and roller or "machine" printing, and nothing more need be said about it here, except to mention that it is a well-ascertained fact, known to all practical men, that a film or "scum" of dark colour on the *surface* of a light colour is much more easily removed in washing than if it occurred under the light colour, that is to say, if the light colour were printed on cloth already stained by passing under a dark roller. In the latter event the pale shade is irretrievably spoilt, it being practically impossible to remove the underlying dark tint without removing the light one along with it. For this reason rollers are nowadays always made of the same size for a given pattern, so as to allow of their being changed about as required.

The only exception to this rule is the "blotch" or background roller, which is still frequently made a little larger than the others, in order to fill up any vacant spaces due to stretching, and which cannot well be worked anywhere but last, on account of the mass of colour it puts on the cloth. If it is worked in a pale tint it is often preceded by a plain roller, interposed between it and the others. This plain roller works in a colour box containing starch paste, or gum, and serves to remove most of the superfluous or "top" colour from the cloth before it reaches the "blotch." It is commonly known as the "starch" or "gum" roller; and its use is not confined to any one place in the machine, it being interposed wherever its action will be beneficial.

Pentagraph Engraving.—Pentagraph engraving is based upon a principle entirely different from that of either hand engraving or of machine engraving: the pattern is neither cut out with a graver nor indented by a mill, but is *etched* upon the roller by means of nitric acid. For this purpose the roller is evenly coated with a thin film of a hard-drying bituminous varnish, and then the pattern is transferred to it with a diamond point which cuts through the varnish, at the same time laying bare the copper wherever it touches. On placing the roller in the etching bath, the nitric acid only dissolves out or "etches" the exposed parts, the film of varnish protecting all those portions that are intended to remain white in the subsequent printing. But the distinguishing feature of pentagraph engraving is not in the application of the well-known process of etching to the engraving of printing rollers, but in the method of transferring to the *rounded* surface of the roller at one operation any required number of the "repeats" of a design, one *single* "repeat" of which is engraved, on an enlarged scale, upon a *flat* zinc plate. Two types of machine are used for this purpose—the curved-table and the flat-table machines—but both are so intricate in construction that it would be hopeless to attempt to describe their mode of action in detail without an elaborate set of working drawings or an actual machine to refer to. It is therefore impossible to do more than to touch briefly upon the process of pentagraph engraving, and to refer those who may desire fuller information to the special literature of the subject.

The first pentagraph machine employed consisted of a simple modification of the rhomboidal arrangement of levers well known to draughtsmen as the "pantagraph." It never gained any measure of commercial success, however, and was soon discarded, not that it was altogether too limited in scope, but because the style of design then in vogue was better engraved by other means. In 1854 Rigby made the first curved-table pentagraph used in Europe. It was constructed on the lines of the American invention of Whipple, who had replaced the system of levers by an ingenious contrivance based on the fact that if a large wheel and a small wheel are fixed to the same shaft and revolve together, a point on the circumference of the large wheel will cover a greater distance than a corresponding point on the circumference of the small wheel. The distance travelled by a given point on each wheel is, of course, 3·1416 times the length of its diameter, and consequently a 5-inch wheel would cover 15 inches (in round numbers) while a 1-inch wheel would only cover 3 inches; that is, the ratio varies in direct proportion to the respective diameters of the two wheels. The rotary movement of the wheels transformed into linear movement and communicated by suitable means to diamond tracing-points at once afforded a means of reducing the width of the lateral repeats of a design as much as desired, and a modification of the same principle, in which the roller itself plays the part of the smaller wheel, provided for an equal reduction of the vertical "repeats." This improved machine of Whipple and Rigby being easily applicable to a wide range of styles, was at once adopted by the leading engravers, and, with a few additions and refinements, is still extensively used.

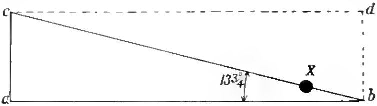


Fig. 33.—Principle of the flat-table pentagraph.

The more convenient and less cumbrous *flat-table pentagraph* was invented by Shields in 1857, and embodied an ingenious and entirely novel method of reducing or varying the dimensions of the pattern transferred to the varnished roller. Its principle is somewhat difficult to describe in words, but it may, perhaps, be best explained by saying that it is based upon the observation that a body starting out from and moving in a direction oblique to a given straight line, travels along the hypotenuse of a right-angled triangle, one side of which is formed by the given straight line, and the other by dropping a perpendicular, from the final point of rest of the body, on to the given straight line. The ratio between the lengths of these two sides of the triangle varies according to the inclination of the hypotenuse, and, consequently, by altering this latter it is possible (within limits) to make one side any fraction desired of the other. A glance at fig. 33 will make this point clear.

Let *a b* be the given straight line. Then a body X travelling obliquely from *b* to *c* will cover, laterally, a distance equal to *a b*, and at the same time will obviously rise a distance equal to *c a* (or *d b*); and if *c b* be inclined at angle of about 13¾°, the line *c a* will be four times less than the line *a b*. In practice, this principle is worked the other way about: that is to say, the body X moves perfectly horizontally along a fixed cross-bar below, and in a groove cut in an inclined and movable lever above, the result being that the inclined lever travels backwards and forwards according as the body X is moved to the right or to the left: and the distance the lever travels always bears a definite relation to its angle of inclination and to the amplitude of the movement given to X.

In a flat-table pentagraph machine two such sliding levers are employed,—one to provide for the horizontal lines of the design, and the other for the vertical lines,—and as their motion is compounded through the medium of a sliding arm which actuates them, either independently or both together, it is possible to reproduce on a smaller scale any kind of line whatsoever, be it vertical, horizontal, oblique, or curved. For this purpose the sliding arm is furnished with a tracing point for going over the design, and the inclined movable levers are connected with diamond points which bear on the varnished roller and cut a reduced replica of the design thereon through the film of varnish, thus laying bare the copper in readiness for the etching bath.

Figs. 34 and 35 represent a section and plan of a flat-table pentagraph machine. They are stripped of detail, and must be taken as purposely exaggerated, to illustrate more clearly the working of the machine.

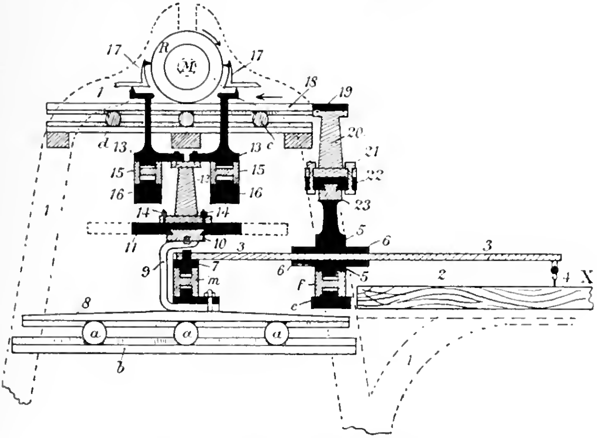


FIG. 34.—Section of the flat-table pentagraph.

The parts are numbered and lettered as follows:—(1) is the framework of the machine, to which the various fixed rails and bars are attached; (2) the table upon which the design to be transferred to the roller R is laid; (3) the tracer-rod, carrying the tracer 4 at one end of it, and at the other attached to the bar 7 which runs on the flanged rollers *m* across the carriage 8, which in turn runs on similar rollers *a*, *a*, *a* on the fixed bars *b*, *b* at each side of the machine. The tracer-rod 3 passes freely through the bar 5 and between the guides 6, which always maintain it at right angles to the bar 5. From the carriage 8 an arm 9 extends upwards, carrying the stud 10 which works freely, but without side-play, in a groove cut from end to end in the lever 11. This lever is attached by an arm 12 to the cross bars 13, 13, running on the rollers 15, 15, along the fixed rails 16, 16; and it may be adjusted at any desired angle, in reference to the tracer-rod, by means of the slotted boss and set screws 14, 14. When thus inclined its groove forms an inclined plane, against which the stud 10 acts when the carriage 8 is pushed backwards and forwards by the tracer-rod 3, the result of this motion being that the lever 11, and with it the two cross-bars 13, 13, are moved transversely a fraction of the distance travelled by the carriage 8. The diamond etching tools are supported on tool-carriers rigidly fixed to the bars 13, 13, and consequently move along with them, scratching a line through the varnish on the roller R at the same time. The bar 5, running on the rollers *f* on the fixed rail *e*, is provided with a stud 23, which works in a groove cut longitudinally in a second inclined lever 22, exactly like the lever 11, in that it can be fixed at any suitable angle by means of the boss and screws 21. This lever 22 is connected by the arm 20 to the cross-bar 19 of the carriage 18, which runs on the fixed rails *d*, being supported thereon by the rollers *c*. The varnished copper roller R is mounted on the mandrel M, which turns in sliding bearings fitted into the two slots at the top of each side of the framework; and as the ends of the roller R rest in frictional contact with the side bars of the carriage 18, the roller revolves every time the carriage moves, and is scratched circumferentially by the diamond points which rest against it.

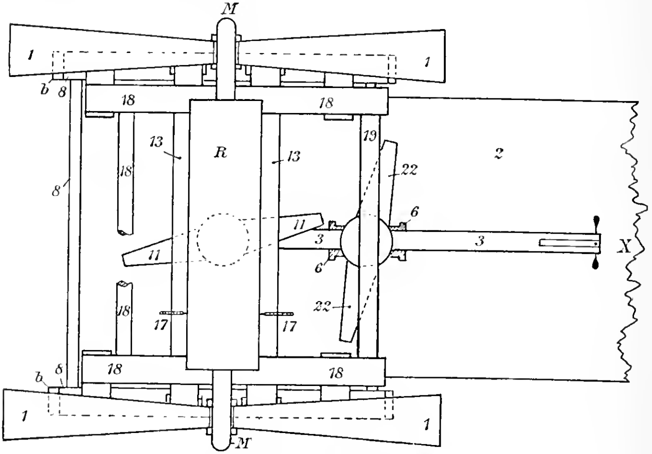


FIG. 35.—Plan of the flat-table pentagraph.

In using the pentagraph machine, the design must be first enlarged and engraved upon a zinc plate. This may be done either by photographing it directly upon a prepared zinc plate, or by placing it in a camera-obscura which throws an enlarged image of it upon a piece of paper placed on a flat table in a dark room. The enlargement is traced, transferred to the zinc plate, and engraved thereon by hand, care being taken to cut the lines smoothly so that the tracing-point will meet with no obstruction to its passage along them. The plate is then placed in position on the table 2 (figs. 34 and 35), and after affixing on the bars 13, 13 a number of diamond cutting tools corresponding to the number of "side-repeats" desired, the operator, seated at X, goes over every line of the pattern on the plate with the tracer 4, thus transferring to the roller R a series of reduced facsimiles of the same. The tracer is hinged on the rod 3 for convenience, and whenever it is lifted off the plate the diamond etching points are also moved out of contact with the roller by means of a foot-lever, not shown in the diagram. The position of the levers 11 and 22 being as in figs. 34 and 35, it is evident that every time the operator pushes the rod 3 away from him the lever 11 will be pushed to his right, and the diamond points will therefore cut a line through the varnish on the roller from left to right, in the direction of its length and parallel to its axis; if he pulls the rod 3 towards him, the reverse effect is, of course, produced. On the other hand, if he moves the rod 3 horizontally to the right, the lever 22 will be pushed away from him, and with it the carriage 18, thus causing the roller R to revolve, or rather partly revolve, in the direction of the arrow (fig. 34), and against the diamond tools 17; if the rod is moved to the left, a line is cut on the roller in the opposite direction. When the pointer is moved obliquely or round a curve, the lateral movements of the diamond tools and the rotary movements of the copper roller are compounded, and the line cut on the roller is an exact reproduction in miniature of the line followed by the tracer on the zinc plate. In this way any kind of line or form whatsoever can be transferred from the flat surface of the table 2 to the rounded surface of the roller R, and that without any distortion. From the foregoing it will be seen that horizontal and vertical lines on the zinc plate change their positions on the roller, becoming respectively circumferential and lateral, thus reversing the "run" of the design by making the "side repeats" vertical, and the "vertical repeats" horizontal. Fortunately this is easily remedied by simply turning the engraved zinc plate halfway round on the table before commencing to transfer the pattern to the roller—the "repeats" then coming in their proper places. When a pattern is required to repeat more than once round a roller, it is usual to arrange the requisite number of diamond points around its circumference, but the same effect can also be obtained by using only one line of points (tools), the position of the roller being altered from time to time according to circumstances.

For multicolour patterns the whole design is engraved on a single zinc plate and is then coloured up like the original; this is for the guidance of the pentagrapher, and not only enables him to pick out and trace just those parts of the pattern that are required to be engraved on each separate roller, but also ensures that each roller will fit exactly to all the others over which the pattern is distributed, according to the number of colours it contains. Suppose, for example, a design was drawn up in red, pink, yellow, and dark and light greens. An enlarged copy of it would be engraved on a zinc plate and coloured in these colours; the pentagrapher would then place a varnished roller in the machine and transfer to it, say, all the red parts, by simply following with his tracer the outlines of the red objects on the plate; then, without altering the adjustment of the machine, he would replace the finished red roller by one intended for printing the pink portions of the pattern, and, after transferring these latter would proceed to deal, in precisely the same way, with the three remaining rollers for the yellow and two greens. The five distinct colour elements of the complete design engraved on the zinc plate are thus abstracted and transferred to separate rollers, to be afterwards re-combined on the cloth during the subsequent printing process. All the five rollers being made from one single plate (Fr. *planche mère*) under exactly the same conditions, the certainty of their impressions fitting their allotted spaces in printing is much greater than if it were necessary to engrave a separate plate for each colour in the pattern; and it is this certainty, coupled with the speed of production, that renders the process of pentagraph engraving so valuable an adjunct in textile printing.

After leaving the pentagraph machine, the rollers are etched in a bath of nitric acid. The acid is contained in a shallow trough of stone, and the rollers are revolved therein until the pattern is etched out to the requisite depth. The strength of the acid and the length of immersion are largely questions of practical experience, but it may be noted that if the action of the acid is too energetic the etched lines, instead of being smooth and even throughout, will be "pitted." To avoid the liability to "pitting," many additions to the nitric acid bath have been suggested—amongst them 12 per cent. to 20 per cent. of acetic acid—but it is questionable whether or no they are of any real value. Rollers etched in a mixture of nitric and acetic acids, used by one of the largest firms in England, are certainly remarkable for their clean, even lines, but whether this result is due to the beneficial action of the acetic acid or to the dexterity of the etcher is still a moot point. When sufficiently etched, the rollers are well washed in water, the varnish is cleaned off with benzine or turpentine, and, after any defects have been re-touched by hand, they are ready for printing. If a roller requires re-etching, it is varnished again and given a short treatment in the acid; in fact, if the engraving is very deep, it is essential to do the etching in stages, re-varnishing between each, as otherwise the effect of "under-etching" would be produced, that is, the acid would eat its way under the varnish and give a line widening out as it got deeper. Such a line would give an impression in printing with ragged or "rotten" edges, and would be quite useless for most purposes.

Varnishing.—The varnishing of rollers is performed as follows:—A plain brass roller and the copper roller to be engraved are placed in a machine and revolved rapidly side by side; the thickish varnish—a mixture of Burgundy pitch, tallow, and Venice turpentine—is then poured on the brass roller and spread evenly over it by means of an inking roller (of glue and treacle melted together and cast in a mould), mounted on a frame and held in the hands of the operator. When the varnish has become "tacky," the "treacle" roller is placed in contact with the copper roller and transfers a thin film of varnish to its entire surface, the operation being continued and repeated until the film is thick enough to protect the roller thoroughly from the action of the acid. By this means an already etched roller may be re-varnished without the slightest fear of the varnish filling up, or even getting into, the etched lines.

The process of etching is not confined to pentagraph work; it may also be employed in combination with machine engraving. For this purpose a mill is used to indent the outline of the object; the whole roller is then varnished and ruled, with a diamond point, with a series of parallel lines, at the angle and the distance apart required by the "scale" of the engraving. The outline and those portions of the roller not to be etched are then "painted" or "stopped" out with varnish, and the roller is finally etched, cleaned, polished, and trimmed up as usual.

In many modern pentagraph machines the diamond points may be made to work in opposite directions to each other—a feature which allows of "turnover" patterns being pentagraphed from a single "repeat" of the subject, engraved in one position only on the zinc plate. Other refinements of motion are also possessed by modern machines which render them applicable to a variety of purposes which cannot be mentioned here.

MODIFICATIONS OF THE CYLINDER PRINTING MACHINE.

Any description, however slight, of the various methods of printing textiles would be incomplete without some mention of the modifications and improvements that have been effected in the cylinder machine with a view to adapting it to styles of work that formerly were either impossible to execute, or that required to be filled in afterwards by hand block printing. Of these modified machines the two most important are the "Duplex" machine and the "Sarrie," "intermittent" or "jumper" printing machine. The "duplex" machine prints *both sides* of the cloth in the same pattern at one operation, the printed parts on one side coinciding exactly with those on the other side. The "sarrie" or "jumper" machine allows a certain number of rollers to print a certain predetermined length of cloth, and then to recede out of contact with, or "jump" away from, the pressure cylinder; simultaneously with this latter motion a second set of rollers moves up against the cylinder and prints that portion of the cloth that has escaped the first set. The second set then "jumps" away in turn, and the first set returns to its original position and prints a further length of cloth, and so on without intermission, the two sets of rollers printing their portions of the design alternately until the whole cloth is finished

The "Duplex" Machine.—The "duplex" or "reversible" printing machine is really a combination of two ordinary cylinder printing machines, arranged one behind the other, and each provided with its own blanket and back greys.

The only real connections between them are the motive power which drives them both, and the cloth, which, when printed on one side on the hinder machine, passes directly round the cylinder of the front machine and is printed on the other side. In all other respects the two machines may be considered as distinct, and they are worked as such, except in so far as the pattern on one side of the cloth must hit off exactly that on the other side, that is to say, that a pin pushed through the point of a leaf on one side must come out at the corresponding point of the same leaf on the other side. In order to facilitate this correspondence of the two patterns the "crown" wheel of the back machine is frequently made in the form of a huge "box-wheel," so that if all the rollers of the back pattern are in perfect fit with each other, but *not* with the front pattern, they can all be moved an equal distance up or down by simply turning the adjusting screw of the "crown-box-wheel," and that, too, without upsetting their "fit." Fig. 36 illustrates the disposition of the parts of a four-colour "duplex" machine.

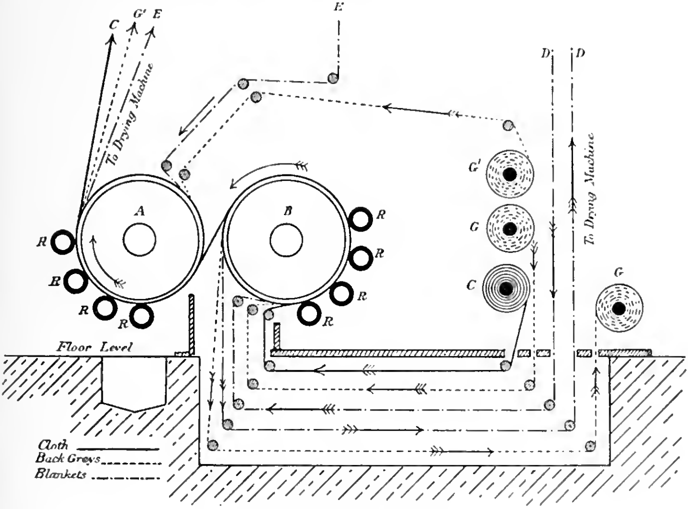


FIG. 36.—Duplex machine (section).

A is the front cylinder; B, the back cylinder; C, the roll or "set" of cloth to be printed; D, D, the blanket of the back cylinder; E, E, the blanket of the front cylinder; G, the "back grey" for back cylinder; G′, the "back grey" for front cylinder; and R, R, R, R, the engraved printing rollers. The boxes and doctors for each of these printing rollers are not shown, but they are arranged in precisely the same manner as in ordinary single-side printing machines. The cloth enters the machine from below, passing, along with the blanket D and the back grey G, under the feet of the printer; in circulating round the cylinder B it becomes printed by the first four rollers R, R, R, R, and then passes on to the cylinder A, as shown in fig. 36, the printed side being next to the back grey G′; the second set of four rollers R, R, R, R then print the other side thus exposed, and the cloth passes forward in the usual way to the drying apparatus, to be afterwards treated as an ordinary print in the subsequent processes. The direction taken by the cloth, the blankets, and the back greys is clearly indicated by the arrows in the diagram. The blankets are of the usual endless type, and circulate continuously through the drying machine and round their respective cylinders. The two cylinders A and B are geared together and driven by an engine common to both. The gearing is arranged so that one of them can be used as an ordinary machine when not required for "duplex" work. Goods printed on both sides are generally known as "reversibles."

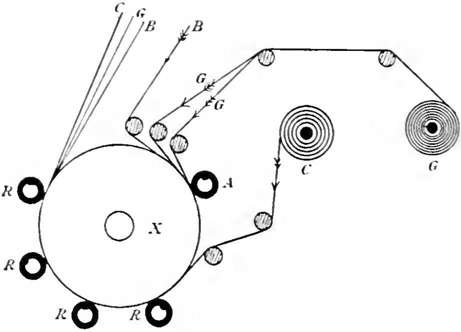


Fig. 37.—M'Nab's method of duplex printing.

Another and older method of printing both sides of the cloth was invented by M'Nab, and is carried out on an ordinary printing machine. In this process the back grey is printed before it meets with the cloth, and consequently, when the two pass together under the rollers that print the cloth, the pressure they are subjected to causes the cloth to take up a goodly portion of the colour printed on the "grey," and thus to receive an impression on the back. Fig. 37 will sufficiently illustrate M'Nab's process without further description.

X is the cylinder; A, the printing roller for the "grey"; R, R, R, R, the rollers for printing the face of the cloth; G, G, a double "grey"; C, the cloth to be printed; B, the blanket. It will be seen from the above diagram that the "grey" is printed first; that the back of the cloth then comes in contact with the printed side of the "grey," and that it must of necessity receive an impression therefrom. The front of the cloth is printed in the usual way. The double "grey" is employed solely for the purpose of keeping the blanket clean, and can be dispensed with in the case of wash-blankets. Practical difficulties render M'Nab's process unsuitable for printing "reversible" effects in more than one colour on the back; but for this purpose it is well adapted, and is still largely used in some works, especially for thick materials like flannelettes, on the back of which it is frequently required to print a fine "all-over" stripe pattern in some colour that will harmonise with the design on the face of the cloth.

In all "duplex" work, provided the cloth be sufficiently thick and the colours properly prepared, it is possible to print the two sides of the cloth either in two different patterns or in two different colour combinations of the same design. This style, however, requires to be carefully executed if success is to be obtained. The colour must be thick, and the pressure of the rollers against the cylinder as slight as is consistent with a good impression; otherwise, when two different designs are printed, either one or both is almost certain to show through the cloth, or if two different colourings of the same pattern are printed, their colours will penetrate through the cloth, and by intermingling will produce, in most instances, a most unpleasant, uneven, and "muddy" effect.

The intermittent or "jumper" printing machine.—The means employed for throwing the printing rollers in and out of action in "jumpers" are both numerous and varied in principle. Some makers make use of lugs or cams fixed on an endless chain, which revolves with the machine, and in contact with rods which act directly on the bearings of the rollers, forcing them back every time a lug passes under them; others, again, employ revolving cams which act, through a system of levers, in just the same way; and yet others force the rollers into contact with the cylinder by means of steam or compressed air acting on a piston the rod of which communicates with the roller bearings, and moves them backwards and forwards at regular intervals.

In practically every type of intermittent machine the length of cloth printed and the length allowed to pass unprinted by certain rollers is determined by cams, which act either directly, or through levers, or by opening steam or compressed-air valves, upon the rollers. Endless-chain machines are no longer made, although there are several still in use. They have been superseded by the revolving cam system, which is not only more reliable in action, but is easier to manipulate, and gives a much crisper definition at the beginning and end of its impression. The steam and compressed-air machines are of comparatively recent introduction, and up to the present they have not succeeded in replacing the latest improvements in the cam machines, though it is quite likely that in course of time they will do so, especially as the wear and tear on their valve-opening cams is much less than on those which have to act more or less directly on the rollers themselves. That the cams should be of exactly the right size is one of the most important factors in good "sarrie" printing, and it is, therefore, a great recommendation to any system if it can be shown to prolong the life of the controlling cams. Moreover, by utilising steam or compressed air for moving the rollers, it is probable that the shocks they occasion in coming into and out of contact with the cylinder could be considerably reduced, if not altogether obviated,—an advantage which would add, in no small measure, to the facilities for keeping the various rollers in "register," and would at the same time lessen the cost of upkeep. On the whole, the cam machine is at the present time the most widely used of its class, and amongst the many excellent makes on the market it is difficult to say which is the best.

Another modification of the cylinder machine used for printing on one side of the cloth only is the "SQUEEGEE" MACHINE of Messrs Sackville and Swallow. The great advantage claimed for this machine is that it dispenses with the necessity for "lapping," blankets and back greys, their place being taken by a cylinder covered with a thick layer of india-rubber, which does duty for all, and which is kept constantly clean by being washed at every revolution of the machine. In other respects the "squeegee" machine is worked in the usual way. Fig. 38 is a section of it, showing all its essential features—the washing arrangement and india-rubber pressure bowl, etc.

The cloth to be printed, C, enters the machine at the point shown and passes round the cylinder D covered with the layer of india-rubber I, and between it and the engraved printing rollers, R, R, R, in the ordinary manner. Any colour that may have penetrated through the cloth on to the surface of the cylinder, D, is removed by means of the washing tackle A, B, S, which consists of a "spirt" pipe, A, delivering a constant stream of warm water; a reciprocating brush, B, which scrubs the adhering colour off the face of the cylinder; and the india-rubber "squeegee," S, which effectually removes the excess of water, leaving the surface of the cylinder perfectly clean, and sufficiently dry to allow the printing to be proceeded with without any fear of the colours "running" into each other. The "squeegee" machine is said to yield excellent results in the hands of its inventors in whose works it is installed, but so far it has failed to recommend itself to the majority of calico printers, who find the older machine better adapted to the various styles of work with which they have to deal. So long as the india-rubber covering of its cylinder is in good condition, it is possible that the "squeegee" machine may be worked much more economically for three- and four-colour patterns than the ordinary machine, the working expenses of which are augmented by the necessity for increased drying accommodation, by the cost of blankets, lapping and "greys," and by the extra time and labour that are required in their manipulation. On the other hand, india-rubber covered bowls of all descriptions are liable to rapid deterioration under pressure, and, from what has already been said respecting the conditions of calico printing, it is easy to see that once the bowl of the "squeegee" machine is damaged or becomes uneven from constant use, it immediately becomes quite useless for its purpose, and must either be repaired or replaced. It is well known that repairs or "patchings-up" are rarely satisfactory, and that in the long-run it is always best to re-cover entirely a rubber bowl; so that possibly the cost of maintaining the efficiency of a "squeegee" machine may more than counterbalance the gain derived from its doing away with blankets, back greys and lapping, for rubber-covered bowls of large size are expensive items in any machine. At any rate, the principle of the "squeegee" machine is scarcely applicable to machines printing from six to twelve colours at a time. In the first place, the large amount of space taken up by the washing apparatus would make it necessary to employ cylinders of abnormal size, and these, covered in rubber, would be very costly; secondly, the enormous sum-total of the pressures of the various rollers would, judging by the analogy of ordinary rubber squeezer bowls, very soon cause the rubber to detach itself from its iron bed, and thus render the cylinder utterly useless; and thirdly, the rollers would always have to be wider (or longer) than the cylinder, to prevent the rubber covering from being crushed or squeezed outwards towards the edges, and gradually accumulating there, until it finally interfered with the regularity of the printing. As in many (probably most) cases the printing rollers are shorter than the width of the cylinder, the employment of "squeegee" machines would add considerably to the cost of production in all works where thousands of patterns are in constant use, and thus the extra capital sunk in copper alone would probably absorb the gain in other directions. Add to all this the fact that every additional roller increases the risk of damage to the bowl, and it is easy to understand why the "squeegee" machine has not been more generally adopted.

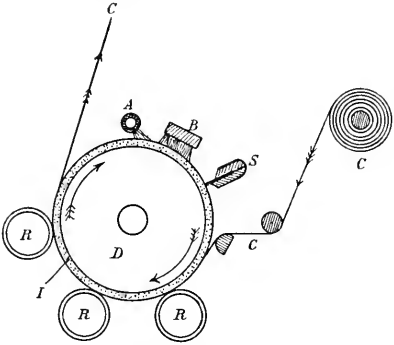


FIG. 38.—Squeegee printing machine.

Many other forms and modifications of the printing processes have been suggested, and even introduced into practice, for special styles; but as they are not of general interest, an account of them must be looked for in the files of the various periodicals that are devoted to the review of current events and improvements in the dyeing and printing industries.

Before leaving the subject of methods of printing textile fabrics, it may be well to mention that all cloth for printing is wound on hollow wooden or iron "shells," through which a loose iron centre or axle is passed when the roll is required for placing in the machine. The ends of this axle rest in slots prepared to receive them, and the cloth is simply unwound by being drawn through the machine between the printing rollers and the pressure bowl. On its way it passes under and over a series of tension rails, and over one or more scrimp rails, which free it from pleats and creases, so that it enters the machine stretched to its full width, and presents a perfectly even surface to the action of the rollers.

Defects incidental to roller printing.—Apart from the actual misfitting of a pattern, which is not an accident, but due to carelessness, the principal defects to which patterns printed by machine are liable are the following:—

1st, Scratches.—These may be caused in many ways, but they are usually due to gritty particles (sand or metal) in the colour, which cut into the surface of the roller deeply enough to show themselves when the goods are fully developed. Scratches are remedied by burnishing.

2nd, "Snappers."—Large, ugly-looking double stripes of colour running up the piece are caused by some foreign substance getting under the doctor-edge and lifting it off the roller, thus permitting a large amount of colour to pass and be transferred to the cloth in the form of a smudgy stripe. "Snappers" may be either long or short, according as the obstruction gets jammed between the roller and doctor, or works itself loose almost immediately; in either case it is advisable to stop the machine, to wash both doctor and roller, and to send the colour to be strained afresh. One of the commonest causes of "snappers" is due to loose threads from the cloth escaping under the "lint doctor," and afterwards being carried up with the colour under the "cleaning doctor," which they lift, with the result already described. Bits of dried colour, pieces of starch that have not been mixed in properly, and other hard bodies are all likely to give rise to "snappers" if they are allowed to remain in the printing colour.

3rd, "Lifts."—These are very like minute "snappers," but they usually occur at regular intervals on the cloth, although they are sometimes veritable "snappers," caused by the passage under the doctor of a minute particle of grit. When they recur at regular distances, corresponding to the circumference of the roller, they will invariably be found to be caused by a particle of steel that has become embedded in the roller, and which, by projecting a little, lifts the "doctor" every time it passes under it, and so allows a small quantity of colour to remain upon the smooth, unengraved surface of the roller—colour which, of course, is transferred to the cloth.

4th, "Streaks."—Streaks consist of fine lines or series of fine lines running along the piece in a direction more or less parallel to its selvedges, and they may result either from a scratch on the roller or from a snip in the doctor-edge. Both scratches and snips are mainly caused by grit in the colour, and not infrequently by the steel filings that have escaped removal when the doctor-edge was sharpened. A "doctor streak" is easily distinguished from a scratch in the roller by its wavy appearance, which is due to the "traverse" motion of the "doctor"; streaks arising from scratches in the roller are always straight, unless it happens that the offending particle of grit sticks on the doctor, and is carried to and fro with it, thus cutting an undulating line on the roller. As a rule, a scratch of this latter description forms a broken line or "streak," whereas a snip in the doctor gives a continuous line throughout.

Streaks can only be remedied by either polishing the roller or re-sharpening the "cleaning doctor."

5TH, "SCUMMING."—Scumming is a term applied to the effect produced by the insufficient cleaning of the unengraved smooth surface of the printing roller—an effect which consists in the whole surface of the cloth being soiled by a film of one or more colours. "Scumming" may arise from any one of the following causes:—(*a*) a rough doctor-edge; (*b*) a badly adjusted doctor, the edge of which does not rest upon the roller sufficiently sharply to scrape off the superfluous colour; (*c*) a badly faced roller; that is, one with a rough surface which retains enough colour, after passing under the doctor, to soil the piece of cloth in those parts which ought to remain unprinted by it; and (*d*) defective colour, which either obstinately resists the cleaning action of the doctor, or abrades the polished surface of the roller, or destroys the smoothness of the doctor-edge by acting upon it chemically or physically. Strong basic colours, colours containing much acid, badly ground pigment colours, and those, too, containing a large amount of solid matter or strong alkali, are all liable to act detrimentally in one or other of the above ways, and their preparation therefore demands the utmost care. In the case of printing pastes made up with energetic oxidising or reducing agents, and with strong alkaline lyes, it is frequently necessary to prepare the cloth with some substance capable of neutralising the action of the thin film of "colour" which always remains on the roller, even when the machine and colour are in the best condition it is possible to attain to in practice. Re-polishing of the roller, re-sharpening of the doctor, or modifying the composition of the colour and re-straining it are all remedies for "scumming" that are applied, according to the circumstances under which it occurs.

6TH, "SCRIMPS."—These and "doubled edges" are simply creases in the cloth which pass through the machine, and, in preventing the colour from reaching the underlying parts of the cloth, show up as white places in the finished goods. As a rule, good "scrimp rails" of corrugated brass are all that are necessary to smooth out and stretch the cloth, but occasionally fine creases that have been "dried in," on the drying-machines after bleaching, resist all attempts at removal in this way, and the only thing to be done in such cases is to wet out the cloth and re-dry it, either over the ordinary drying cans or on a stentering machine.

7TH, UNEVEN PRINTING.—Uneven distribution of colour takes place under many different conditions and manifests itself in various ways, all of which may be accounted for by some defect in either the cloth, the rollers, the colour, or the working of the machine. If light, granular looking, irregularly shaped patches are developed during the operations of steaming or dyeing, their occurrence may be put down in most cases to the presence of lime left in the cloth during the bleaching. Lime stains occur at irregular intervals, and are easily identified.

When one side or edge of the cloth is consistently darker than the other, the unevenness is caused by the pressure of the roller against the cylinder being greater at one end of the roller than at the other; if the dark (or light) band runs up the middle of the piece, it is attributable to inequalities in the lapping, or, in the case of long rollers, to their springing in the centre, where pressure cannot be applied, except by "packing" the lapping, *i.e.* by introducing strips of calico to increase its thickness in the middle. Uneven effects of a similar nature, but not so regular in appearance, are also caused by feeding fresh colour into the colour box at one point only instead of distributing it evenly from end to end; in the case of colours that froth much, or that are apt to decompose, it is most essential to replenish the box as evenly as possible, in order to keep them of the same composition, strength, and tone throughout. Unevenness is also produced by colours that are badly mixed, or which separate out in the course of working.

Of these latter, pigment colours are perhaps the worst: the heavy precipitates of which they are composed are very apt to settle, especially if the printing colour is thin; and it frequently happens that, in mixtures, one constituent settles more rapidly than the others, with the result that not only is the colour weakened, but is altered in shade at the same time. The only way to prevent this settling down is to stir the colour up from time to time, both in the colour box of the machine and in the tub which contains the supply.

If a roller has been polished a good deal in one part to eradicate scratches, etc., it often happens that that particular part gives a weaker impression than the rest of the roller, owing to the engraving having been reduced in depth: or the polishing and burnishing may have been so drastic as to cause a "low place" on the roller, so that the doctor fails to clean it properly, and thus allows a smudge of colour, a sort of local "scum," to be transferred to the cloth. Weak and uneven impressions are also due to the unequal depth of the engraving in different parts of the roller, and defects arising from this cause always occur at perfectly regular intervals, corresponding to the circumference of the roller.

Another factor in causing uneven printing is what is known as "lobbing," that is, the slipping of the roller round its mandrel at every revolution. "Lobbing" only takes place when the roller is put on too loosely, and when its tongue or internal "tab" is too narrow for the groove in the mandrel, into which it ought to fit tightly, or when the mandrel itself is too small for the particular roller put upon it. In such cases the mandrel is frequently wrapped with calico to make it fit the roller better, but this operation is not always effective, as the grinding action set up rapidly reduces the calico to small pieces, even powders it at times, and the "lobbing" re-commences, gradually increasing in extent until the machine has finally to be stopped, the roller taken out, and a fresh mandrel inserted.

Many other accidents are liable to happen to a piece of calico during the process of printing by machine, but the foregoing are the most usual, and to them can be traced most of the mechanical defects of work spoiled in printing. Considering how many risks have to be guarded against, and that these risks increase with the addition of every extra roller, it is really wonderful how many thousands of yards of cloth can be printed without a blemish and with so small a percentage of jobs (spoiled work), for once a piece is badly printed it is very rarely that it can be improved by any subsequent treatment short of re-bleaching and re-printing.

PART III.

PREPARATION OF THE CLOTH FOR PRINTING.

PREPARATION OF THE CLOTH FOR PRINTING.

The operations connected with this important branch of calico-printworks routine consist of—

(*a*) Bleaching.

(*b*) Mercerising (if required).

(*c*) Winding-on, brushing, and shearing.

(*d*) Impregnation of the cloth (when necessary) with substances that are essential to the full development of the colours.

(*e*) Stentering and weft-straightening of cloth that is to be printed with certain styles of pattern.

Most of these operations are susceptible of much variation, and no one of them is carried out in exactly the same way in every works; nor is the order in which they are performed by any means invariable. Every firm adopts that process which yields the best results with its plant and under the conditions obtaining at its works, and consequently it would be impossible to describe in this work even a tithe of the numerous modifications that are employed. All that can be done, therefore, is to cite a few typical examples of the methods of bleaching, and of the preparation of cloth for printing; and as practically all methods in general use on the large scale are based upon the same principles, any variation in the details of their application will usually be found to have been adopted for the purpose of making the best possible use of existing machinery or of new plant.

Such being the case, the following processes must be regarded as a series of operations that have given good results in particular cases, and not as affording definite and unalterable data for the production of equally good results under all conditions.

(*a*) BLEACHING.

The theory of bleaching and the *rationale* of the numerous operations that are involved in its practical application have been treated exhaustively by the authors of *A Manual of Dyeing*, a work which the present volume is intended to supplement. Reference can be made to that work for scientific details respecting the composition and properties of the cotton fibre and the effect of the action of various reagents upon it, and it only remains here to deal with the process of bleaching in its relation to calico printing.

For goods intended to be dyed or printed, the cloth must not only be white (with one or two exceptions), but it must be entirely freed from foreign matters, and also from its natural impurities, which, if allowed to remain, tend to the production of stains, and in any case detract from the purity and brilliancy of the finished goods.

Apart from moisture, cotton contains about 5 per cent. of natural impurities that are more or less insoluble in water, but may be removed by successive treatments with alkalis and acids.

According to Dr Schunck, these impurities consist of fatty and waxy bodies, colouring matter, pectic and margaric acids, and albuminous substances. In addition to these, cotton cloth contains various added impurities, such as the sizing pastes, etc., that are employed to facilitate the weaving. These consist of starch, flour, tallow, paraffin wax, soap, zinc chloride, magnesium chloride, etc., not to speak of the dust, dirt, and mineral oil from the machinery that gets incorporated with the fibre, and is most difficult to get rid of afterwards.

It is the object of bleaching to remove all impurities whatsoever, to leave the cloth in a condition approximating to pure cellulose, and to render it capable of absorbing, evenly and regularly, the various colouring matters and "mordants" that are applied to it. To this end the cloth is boiled in alkaline solutions, followed by a treatment in warm or cold acids, and finally submitted to the action of oxidising agents, which are the only substances that will remove effectually the last traces of the natural colour of the fibre.

The alkalis used are caustic soda, carbonate of soda, and milk of lime, and the boiling of the cloth with their solutions is effected in large boilers or "kiers," arranged either singly or in pairs, through which the liquor circulates continuously.

The acids employed for (*a*) decomposing the soaps formed by the alkalis with the fatty matters of the cloth, and (*b*) neutralising the excess of alkali, are, as a rule, restricted to sulphuric acid and hydrochloric acid, but acetic acid is sometimes used for special purposes, though not often, on account of its expense. The acids are applied in large machines, through which the cloth passes continuously in the rope form. In processes for bleaching cloth in the open width, the acid, and indeed all operations except boiling, are carried out in "becks," through which the cloth runs over a series of rollers fixed therein. Bleaching powder is the oxidising agent in most general use. It is applied in weak solution, and in machines similar to those used for "souring" (the treatment with acid). Between each operation the goods are well washed in a plentiful supply of water, and upon the final wash depends much of the ultimate success of the work.

The ordinary process of bleaching is carried out as follows:—

(1) **Marking and Sewing of Pieces.**—Each piece on entering the works is examined in the "grey-room" (where all unbleached goods are stored) for faulty weaving, dirt, damages, and other defects, and after being passed, is stamped or marked, in gas tar, with distinctive letters and numbers, which not only denote its quality, source of origin, and date of arrival, but also serve as valuable aids in tracing faults and in making comparisons with previous deliveries. A suitable number of pieces are then sewn end to end and run into the "singeing"-room. The sewing is done on machines worked by power; they are of simple construction, as such machines go, and call for no more than mention.

(2) "**Singeing.**"—The object of "singeing" is to burn off, as completely as possible, all the filaments and fine hairs that are to be found on the surface of the calico as received from the weaver. Singeing is effected in three ways: (1) plate singeing; (2) revolving-roller singeing; and (3) gas singeing.

In its most perfect form the plate singeing-machine consists of two copper plates bent to a semicircular section, and arranged to form a portion of two flues leading from a coal- or coke-burning stove. By this means both plates may be heated to a glowing red heat, but, as a rule, one plate is kept considerably cooler than the other—a practice whereby great economy of fuel is secured without reducing the efficiency of the machine. The cloth passes over, and in contact with, the cooler plate first, and is thus prepared for being thoroughly singed on the hotter plate. On leaving the two red-hot plates the cloth is drawn through a steam-box or water-trough to extinguish any adhering sparks or filaments of burning cotton, and it is then ready for bleaching,

Fig. 39 represents a modern plate singeing machine in sectional elevation: fig. 40 a view of the traverse motion by means of which the wear of the plates is equalised, owing to the constant change in the position of the moving cloth thereon.

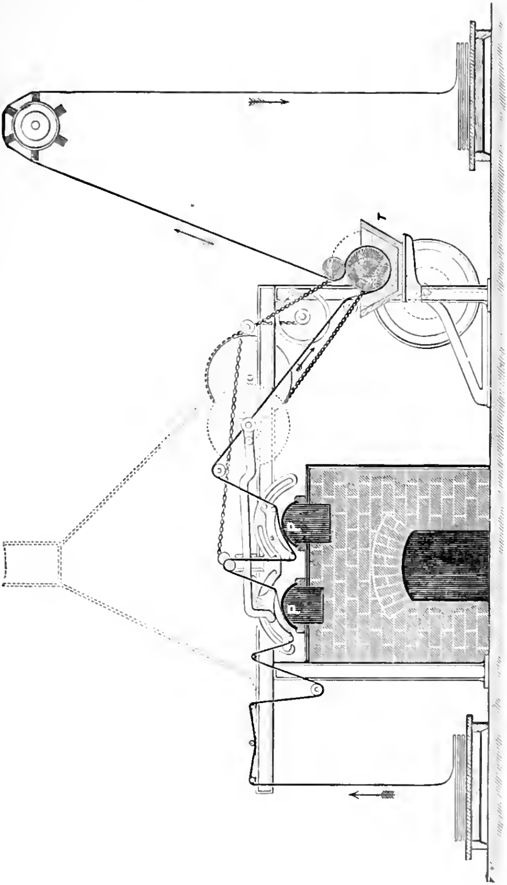


FIG. 39.—Plate singeing stove (Mather & Platt).

The chief disadvantage of plate singeing is that, owing to irregular heating or unequal wear of the plates, the singeing is apt to be uneven or "stripey," a defect which shows up very distinctly in some styles of dyeing, printing, and finishing.

This objection may be almost entirely overcome by singeing the pieces on a *revolving* roller machine. This improved machine really is a modification of plate singeing; but the goods, instead of being drawn over *fixed* red-hot plates, are passed over a hollow copper or cast-iron cylinder, through which the fire is made to pass, and which, in slowly revolving, continually brings into contact with the moving cloth a fresh part of its glowing surface. The cylinder revolves in a direction opposite to that travelled by the goods, so that the nap of the latter is raised, and thus allows more air to pass between the cylinder and the cloth, with the result that more perfect combustion is secured, and the goods singed with greater regularity. By arranging two cylinders to work side by side it is possible to singe both sides of the cloth at one operation, thus effecting a great economy of time.

Fig. 41 is a section of a revolving roller singeing machine.

In *gas singeing*, which is in every way more convenient, more economical, and more effective than either of the preceding systems, the pieces are drawn over one or more powerful gas flames issuing from specially constructed burners, supplied, under pressure, with a suitable mixture of air and coal gas. Exhaust hoods are frequently placed above the cloth, immediately over the flames, for the express purpose of drawing the flame through the body of the fabric, the idea being that its singeing power is thereby increased. Whatever theoretical reasons may be advanced in support of this idea, it is certain that, in practice, gas singeing machines yield better results when the flame is allowed to play freely on the under side of the cloth than when the "exhaust hoods" are in operation, and that, except in the case of very open fabrics, the exhaust hoods do not even draw the flame through the material, as is claimed for them. A long series of practical trials carried out on different types of gas singeing machines amply demonstrated that the only effect of the exhaust hoods was to localise the flame without adding to its intensity, as judged by the quality of the "singeing" it gave. As a matter of fact, the machines fitted with exhaust hoods yielded consistently poor results: the hoods were removed, and the flame allowed to spread out along the under side of the cloth, the result being that the "singeing" was perfectly satisfactory. The only inference to be drawn from this was, that the hoods were not merely useless, but harmful. They doubtless increase the actual temperature of the flame by concentrating its power within narrower limits, but at the same time they reduce its efficiency by restricting its sphere

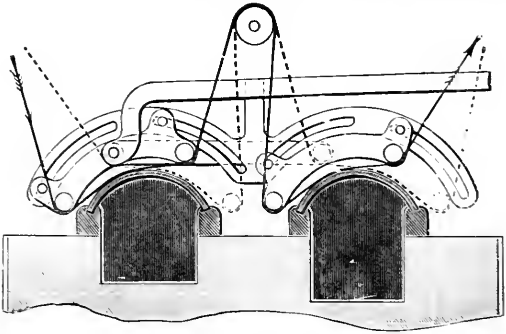


FIG. 40.—Traversing movement of plate singeing machine.

of action, the increase in the temperature of the flame not being commensurate with the decrease in the area of the cloth upon which it acts at a given moment.

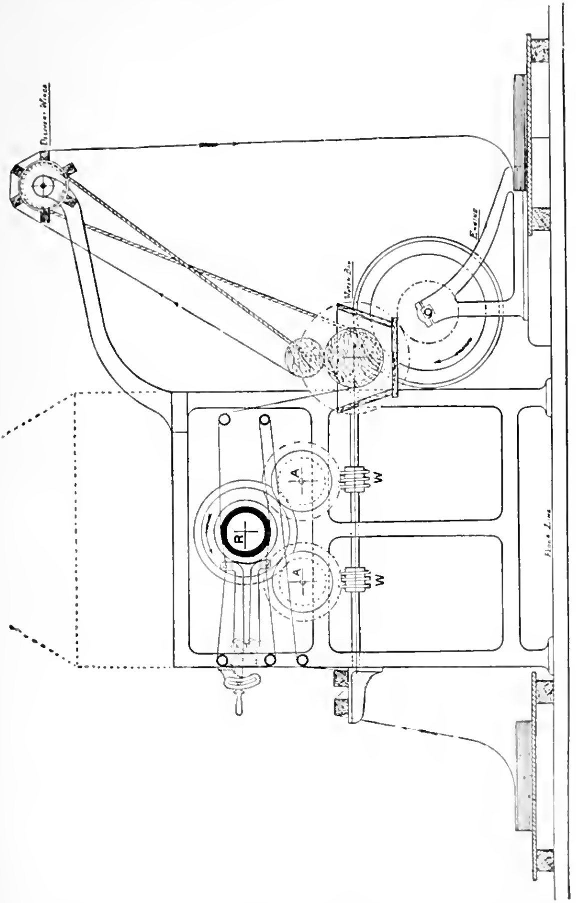


Fig. 41.—Roller singeing machine (Mather & Platt).

Of course, if the speed at which the cloth passes over the flames is reduced, it is possible to secure satisfactory singeing, but at the cost of lower production.

Fig. 42 is a diagrammatic sketch of a three burner gas singeing machine, showing how the cloth may be arranged so as to be singed either three times on the face side, or twice on the face and once on the back, at a single operation.

The passage over two or three steam-heated drying cylinders and a revolving brush working against the cloth to raise up the flattened nap greatly facilitates the "singeing," and permits of greater speeds being run.

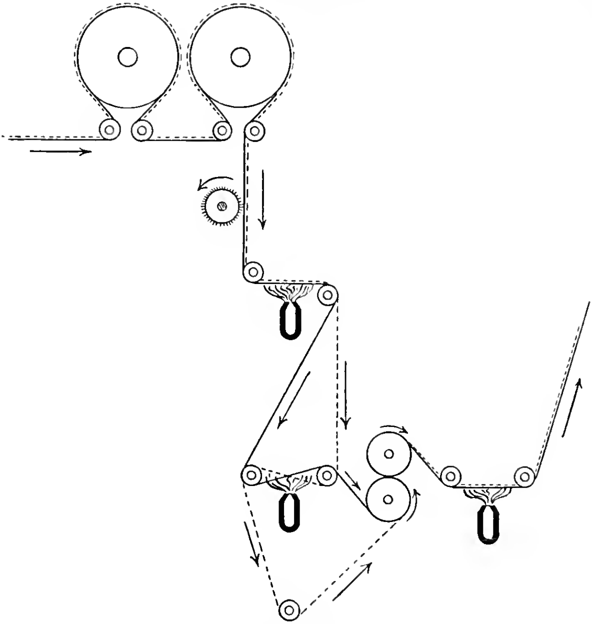


FIG. 42.—Diagrammatic section of a "double width, three-burner, gas singeing machine," showing the arrangements for the different treatment of two separate pieces of cloth at the same time. The cloth travels in the direction indicated by the arrows, and the *solid black line* represents one piece singed three times on one side only, while the *dotted line* represents the other piece being singed *twice* on the face side and once on the back.

(3) **Washing.**—After "singeing," the pieces are either passed through hot water or through sulphuric acid at 3° Tw. and allowed to lie in pile overnight. In the former case—the "grey wash"—the impurities soluble in water are removed, and the starchy substances used in sizing are rendered soluble by the fermentation set up; the goods are also thoroughly wet out, and in the best condition for being acted upon by the alkalis used in the subsequent processes. Nowadays the "grey wash" is usually discarded in favour of a run through weak sulphuric acid, which is found to eliminate the sizing materials much more effectually than water alone. The acid may be used either cold or at a temperature of about 60° C., and the pieces, after being passed through it, are allowed to lie from eight to twelve hours in pile, care being taken to prevent them from drying. They are then well washed in the machine shown in fig. 43, and afterwards saturated in milk of lime in a similar machine.

(4) **The Lime Boil.**—In this operation the pieces saturated in "milk of lime" are subjected, under pressure, to the action of boiling lime water, which circulates continuously through the material. The boiling is effected in large cylindrical boilers or "kiers" of wrought iron and of different types, and the liquor is made to circulate by rotary pumps, steam injectors, or by the mere pressure of the steam itself. Those in most general use are the Injector kier and the coupled high-pressure kier. In the former (figs. 44 and 45) the boiling liquor is maintained in constant circulation by a steam injector (or a pump), which continually draws it from the bottom of the kier, forces it up a rise-pipe to the top, and distributes it there over the cloth, through which it is drawn again to the bottom of the kier, the operations being repeated as long as the kier is working.

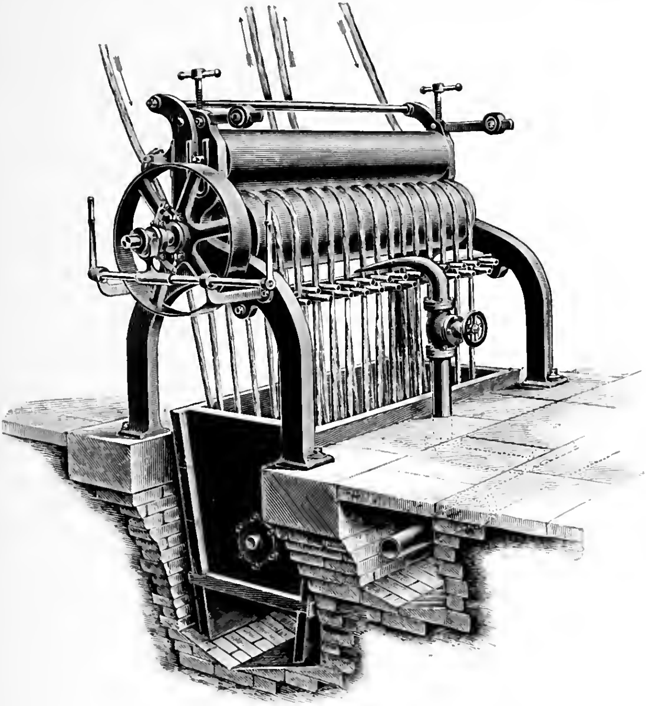


FIG. 43.—Washing (and liming) machine (Mather & Platt).

Coupled high-pressure kiers are used where it is necessary to bleach quickly; the pressure employed reduces the time of boiling. The bottom of each kier is connected by a rise-pipe with the top of its neighbour, and through these pipes the liquor is forced, by steam pressure, from the bottom of one into the top of the other. When all the liquor has passed over, the steam pressure is reversed, and the alternate action takes place, the liquor passing back into the first kier. In this way two kiers full of cloth are treated with one kierful of liquor, so that a good deal of time and some material is saved. Coupled kiers are dangerous to use for the "lime boil," however, on account of the cloth becoming tendered by contact with the hot, dry sides of the empty kier.

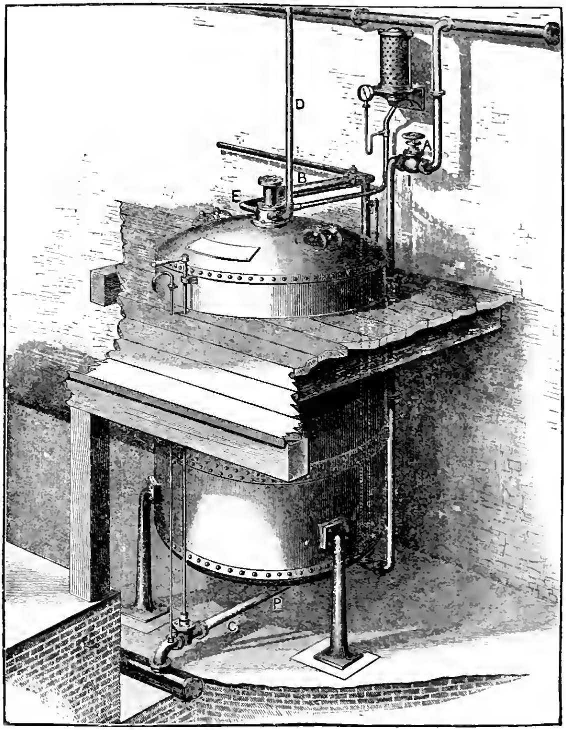


Fig. 44.—Injector kier (Mather & Platt).

Low pressure and open kiers are also used in some works, but they are now almost obsolete.

Whatever form of kier is employed, the cloth must be "plaited down" in it in a certain way, so as to be well packed, but at the same time not too tightly as to impede the flow of the liquor, nor so loosely as to get displaced during the boiling. The "plaiting down" is done by boys who enter the kier by the manhole at the top and who distribute the cloth (which enters at the same place) evenly all over the kier with a stick, tramping down each layer, as it is completed, with the large wooden "clogs" they wear for the purpose. When the kier is full of cloth the manhole is closed and a quantity of lime water, sufficient to cover the cloth entirely, is run in. The amount of slaked lime used is equal to about 5 per cent. of the weight of the cloth. Steam is then turned on, and as soon as all the air is driven out, all outlets are closed and the injector is set to work. The goods are boiled six to eight hours, the lime water is then run off as rapidly as possible, and the kier filled up immediately with cold water. If this is not done, the pieces will be found to be quite rotten wherever they have come into contact with the hot kier sides, and even during the boiling they must be kept fully immersed, as if they emerge above the surface of the liquor they are certain to "tender."

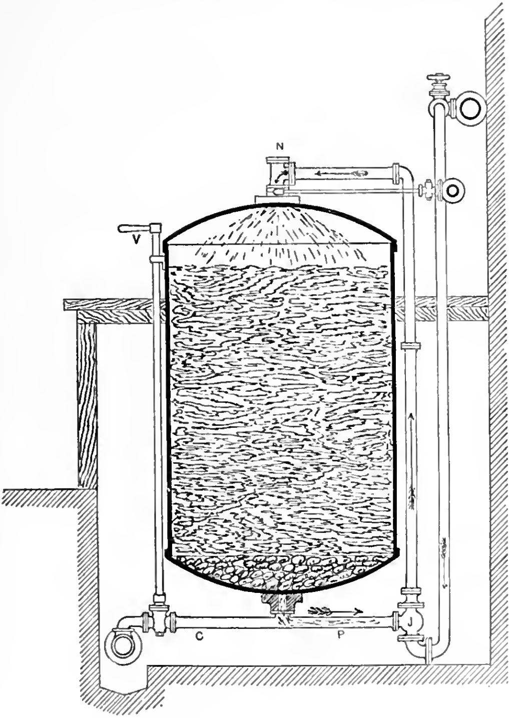


Fig. 45.—Section of injector kier.

During the lime boil the fatty and oily matters contained in the cloth are converted into insoluble lime soaps, the starch, flour, and gums are eliminated, and the remaining impurities so acted upon as to greatly facilitate their removal in the various operations through which the cloth afterwards passes. Curiously enough, the pieces appear much darker after the lime boil than in the "grey" state.

On leaving the kier, the cloth is well washed (in the machine shown in fig. 43) to free it from all uncombined lime and soluble matters, and is then "soured."

(5) **Souring.**—Souring consists in running the goods through sulphuric or, better, hydrochloric, acid at 1° Tw. to 2° Tw. It is conducted in an ordinary washing machine (fig. 43); and although it is usually carried out in the cold, excellent results have been obtained by souring at a temperature of 60° to 70° C. with acid at about half the above strength ($\frac{3}{4}$° to 1° Tw.).

In the "grey sours" (the first souring) iron and other stains are removed, and the lime soaps are decomposed, leaving the free fatty acids on the fibre in such a condition as to be readily converted into soluble soda soaps in the subsequent processes.

After a thorough washing to get rid of the "sours," the goods are subjected to the action of boiling soda-ash or caustic soda. Either may be used alone or a mixture of them employed: some bleachers prefer one method, others another; and, practically speaking, there is nothing to choose between them so long as the boiling is long enough. Caustic soda is certainly more energetic and does its work more quickly than soda-ash, but, for some reason, the latter is still largely used in some works, even to the total exclusion of the stronger alkali. The treatment with alkalis is known as the "lye boil."

(6) **The First "Lye Boil."**—In this operation the goods are treated with either $2\frac{1}{2}$ per cent. of their weight of caustic soda or 5 per cent. of soda-ash, and with from 1 per cent. to 2 per cent. of resin (in the form of a liquid soap made by boiling it up with $1\frac{1}{2}$ times its weight of caustic soda). The boiling, if conducted at a pressure of 35–40 lbs. per square inch, takes from 5–7 hours, but if a lower pressure is employed the time occupied is correspondingly longer. After the first "lye boil" the pieces are well washed, and passed on to the second lye boil.

(7) **The Second "Lye Boil"** simply consists of treating the goods, under the same conditions of temperature and pressure, to a four hours' boil in a 2 per cent. (on the weight of cloth) solution of soda-ash, after which they are well washed again through one or two machines running tandem. The second lye boil is known in some parts as the "scald-off."

The function of the "lye boils" is to convert all fatty matter left on the fibre from the lime boil and "grey sours" into soluble soaps, and they also effect the complete solution of any other impurities that may be present in the "grey" cotton. If the goods have been insufficiently washed after the "grey sours" they are apt to become "tendered" during the first "lye boil" with resin. How this comes about is not well understood, but it is a well-ascertained fact that it is due, in some way, to the combined action of the resin and the acid left in the cloth. What rôle the resin soap actually plays during the first "lye boil" has never been satisfactorily explained, but it certainly has the effect of removing certain bodies that tend, in after processes, to produce "bad whites" in dyed and printed goods. Many attempts have been made to dispense with it, but it still retains a place in the list of the calico printer's drugs; and although beautifully white cloth can be obtained without its aid, such cloth almost invariably develops mysterious stains in dyeing or "steaming," or, worse still, after being kept for some time in the warehouse.

After the two "lye boils," followed by a "souring" and a thoroughly good wash, the cloth may be considered, for all practical purposes, to be entirely free from all impurities, with the exception of some little natural colouring matter that still remains. This can only be removed by "chemicking," or by a treatment with other oxidising agents.

(8) **Chemicking.**—In this operation the cloth is run through a clear solution of bleaching powder contained in a washing machine; it is then squeezed and

allowed to lie in pile overnight in order to give the "bleach" time to act. The carbonic acid of the atmosphere helps to liberate the chlorine[1] from the bleaching powder. The strength of the solution of bleaching powder used varies between ½° and 2° Tw., according to circumstances; but it is always better to chemic twice with a weak solution than once with one that is too strong. The oxidising action of bleaching powder is very powerful, and requires to be carefully watched. For this reason the solution must be absolutely free from undissolved particles of bleaching powder, the smallest of which is quite sufficient to eat a hole in the cloth. After the "chemicking," the cloth is washed, then soured in sulphuric or hydrochloric acid 1° to 2° Tw., washed again, and finally passed through a "squeezer" (fig. 46) and dried up over steam-heated cylinders, after which it is ready for printing.

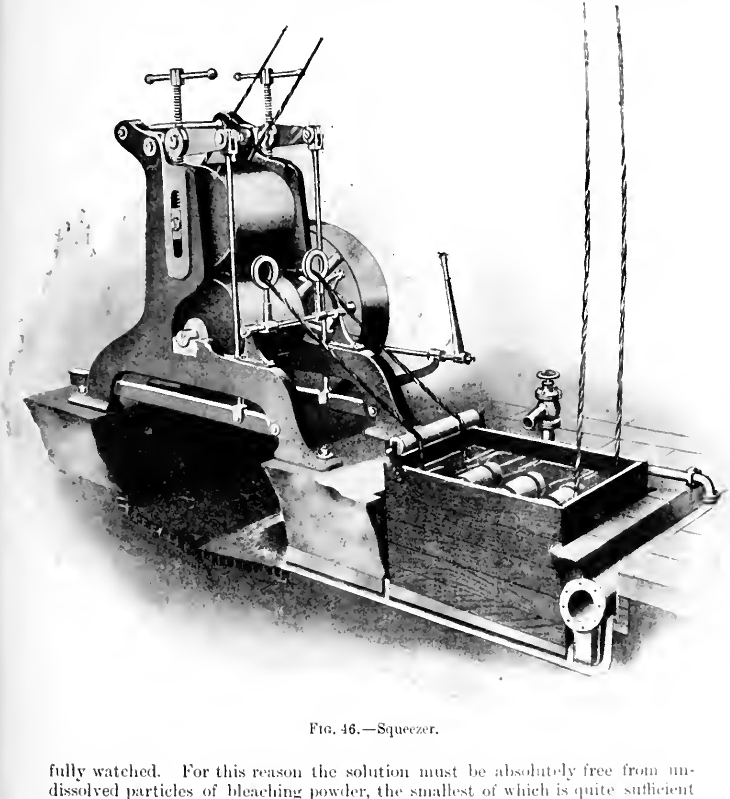


Fig. 46.—Squeezer.

Many modifications of the foregoing process are employed in different works and for different purposes. Some firms use only caustic soda for the "lye

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[1] R. L. Taylor, *Jour. Soc. Dyers and Colourists*, April 1911.

boils"; others only soda-ash; and others again a mixture of the two Occasionally, too, both lime and resin are dispensed with altogether, the cloth being merely treated with boiling alkalis (soda), acid, and bleaching powder. The latter procedure answers well enough for certain styles of printed goods and for white finishing, but in all cases where the goods are intended for "madder" dyeing it is advisable to use both lime and resin in the bleaching, not so much because they produce a better white, but because they discharge from the cloth, more cheaply and better than anything else hitherto suggested, those substances that attract colouring matter in the dye bath, and which are most difficult to "clear" from the unprinted parts of the cloth, which ought to remain a sparkling white when the goods are finished. A "white," equal to the best, can easily be obtained by treating the "grey" cloth with bleaching powder alone, but cloth so treated is absolutely useless for printing purposes; it simply retains the bulk of its original impurities in a modified form, and these impurities give rise to unsightly and ineradicable stains and patches when the cloth, after printing, is exposed to the action of hot steam or boiling dye liquors.

As an addition to the "lye boils," bisulphite of soda was recommended by H. Koechlin, and used by him at the works of Koechlin, Baumgartner & Co. at Loerrach in Alsace. The following process, based upon this suggestion, is given by E. Lauber, and is said to yield excellent results. For one ton of cloth:—

(1) Singe.
(2) Pass through sulphuric acid at 3° Tw.; allow to lie four or five hours or overnight, and then—
(3) Wash.
(4) Boil eight to ten hours at 25 lbs. pressure in—
    50 lbs. caustic soda,
    20 ,, soda-ash,
    8 ,, olive-oil soap,
    1 gal. bisulphite of soda 72° Tw.
(5) Wash well.
(6) Chemick with bleaching powder solution at about 1° Tw.
(7) Wash.
(8) Sour with sulphuric acid at 2°–3° Tw.
(9) Thoroughly wash.

For lighter goods, correspondingly smaller quantities are taken

When the grey cloth contains a good deal of mineral oil the addition of aniline has been found beneficial; spotting with a saponifiable oil, such as olive oil, also helps to remove mineral oil stains during the lye boils, and other substances are likewise employed for the same purpose—phenol, Turkey-red oil, and various soaps.[1]

In the Mather-Thompson process the goods, after boiling in alkalis, are passed successively through a solution of bleaching powder and an atmosphere of carbonic-acid gas. This process is very little used, if at all, and cannot be said to possess any striking advantage over the older processes when they are properly carried out.

With the introduction of Mather & Platt's patent steamer kier, a section of which is shown in fig. 47, the process of bleaching was much shortened, as the operations of boiling and washing (and even chemicking, if need be) can be performed in the kier itself, though this is not usually done. The kier consists of a wrought-iron horizontal boiler, closed at one end, and provided at the other with a heavy wedge-shaped circular door, capable of being raised or lowered by means of a counterpoise or hydraulic arrangements.

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[1] No practicable and absolutely sure method of completely eliminating mineral-oil stains has, as yet, been discovered. See *Jour. Soc. Dyers and Colourists*, March 1911.

The goods are packed in sheet-iron waggons with perforated bottoms, and furnished with a perforated column in the centre, so that the boiling liquor can penetrate thoroughly and evenly throughout the whole mass of cloth. The waggons are run into the kier on rails laid therein for the purpose; the door is then lowered into position and bolted securely, and steam turned on. When all the air in the kier is driven out a solution of caustic soda is introduced, and caused to circulate by means of a centrifugal pump which draws the liquor from beneath the perforated bottoms of the waggons and showers it again *over* the cloth through sprinklers fixed inside the top of the kier immediately over the centre of the waggons. In this way the cloth is kept thoroughly saturated with boiling liquor, and all risk of "tendering" is avoided. As a rule, two waggons fit into one kier; and the temperature of the circulating liquor is maintained by means of a steam-heated coil of copper pipes situated under the waggons and between the rails upon which they rest.

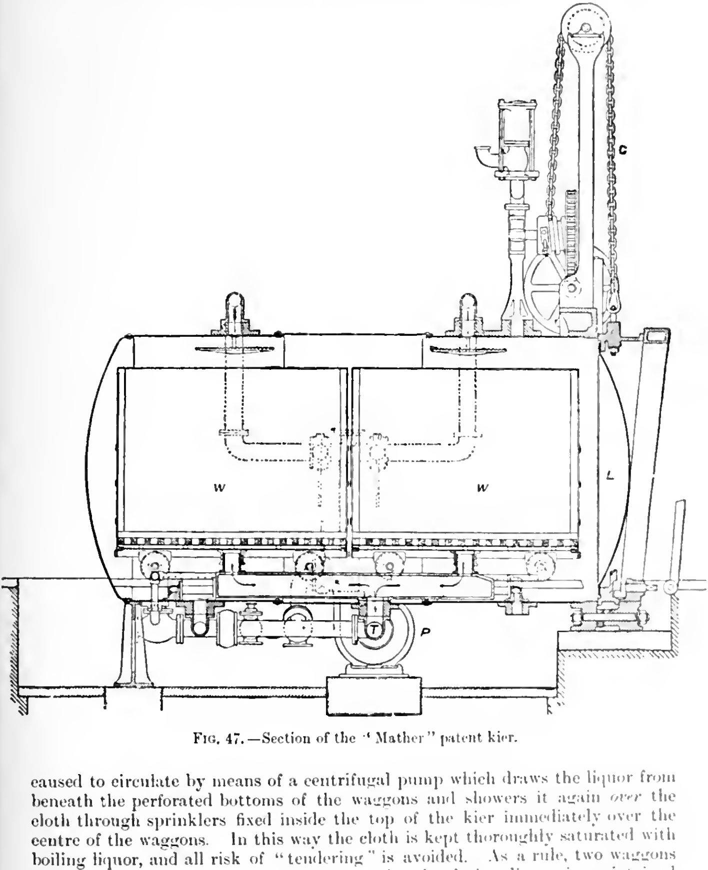

FIG. 47.—Section of the "Mather" patent kier.

Under proper conditions the steamer kier is capable of yielding a good ordinary bleach with only one boil. As a rule, however, two lye boils are preferable, especially for printing-cloths. The following is an example of a single-boil bleach:—

(1) Singe.
(2) Wet out or pass through H_2SO_4 2° Tw.
(3) Wash.
(4) Boil four to six hours at 15 lbs. pressure with a sufficiency of caustic-soda solution at 2° to 4° Tw., according to the kind of cotton under treatment.
(5) Wash well.
(6) Chemick at $\frac{1}{2}$° to $\frac{3}{4}$° Tw. and allow to lie several hours.
(7) Wash.
(8) Sour in sulphuric or hydrochloric acid (H_2SO_4 2° Tw.—HCl 3° Tw.).
(9) Wash well and dry.

At the present time the "steamer kier" is largely used, not merely because it reduces the time of bleaching, but also because it is very convenient, in that it can be emptied and re-filled with great rapidity, and can be used in conjunction with practically every existing process of bleaching. In the form employed for "lye boils" it is unsuitable for "liming," but with very slight modification it can be adapted to this purpose without any fear of destroying the cloth.

Of late years many new methods of bleaching have been proposed, in which advantage has been taken of the oxidising action of the peroxides of hydrogen and sodium, and of potassium permanganate, but, so far, none of them have replaced bleaching powder to any extent, except perhaps for special purposes with which this volume is not concerned. Sodium hypochlorite is the only oxidising agent, apart from bleaching powder, that is of any great use for bleaching in a printworks. Its great advantage is that it obviates the risk of calcium sulphate being left in the fibre if by any chance the pieces are insufficiently washed before they are "soured" in sulphuric acid. Notwithstanding this, it is rarely used for bleaching proper, its chief employment being for the final "chloring" of printed goods, and for mixing with the soap solutions used for clearing purposes in some styles.

Most of the new systems of bleaching depend for their value upon some improvement in machinery, very few of them being based upon anything that can be considered as involving a radical departure from the old-established chemical treatment.

Of these new systems the open-width bleaching arrangements of Tagliani & Rigamonti, Bentz & Edmeston, and Jackson & Hunt are the best known and perhaps the most efficient, though the last named does not give a very high production. The advantage of open-width bleaching is that the surface of the cloth is disturbed as little as possible, and that the warp and weft threads suffer a minimum of distortion. When sateens and other goods with a fine close surface are bleached in the rope form, as in ordinary bleaching, their threads get twisted and their surfaces affected by the tension and pressure they are subjected to in passing through the various operations and machines. In passing between squeezing rollers the cloth gets crushed; and although the creases so formed are quite unnoticeable in the "white" state, they show up in all dyed goods, and many printed goods, that are afterwards finished on the Schreiner calender. As the cloth is denser where the creases or "scrimps" occur, it takes the dyestuff unevenly, and results in "streakiness," to the utter ruin of the market value of the work.

A system of bleaching in use at one of the most important works on the Continent consists in performing all the operations of bleaching, except that of boiling, in the open width, and it yields eminently satisfactory results. The boiling is conducted in the rope form, in a "steamer" kier, but whilst in this state the cloth undergoes no squeezing whatsoever, and consequently all risk of abrasion to its surface and the formation of creases is avoided. On leaving the singeing machine the cloth is passed in the open width through boiling water, and then directly through a cistern containing sulphuric acid 3° Tw. at a temperature of 60° C. After standing a few hours it is washed and saturated in a series of becks furnished with top and bottom guide rollers, and india-rubber bowls at the exit end of each beck. The first beck is filled with water and the following ones with caustic soda 3°–4° Tw. The cloth passes through continuously in the full open width; as it emerges from the last beck it passes through a "pot eye" (a ring of porcelain), and, assuming the rope form, is "plaited down" directly in the waggons of the steamer kier. The "lye boils" are conducted in the usual way, and the cloth, on leaving the kier, and after draining a short time, is again opened out by passing over a Birch patent "scutcher." It then passes in the open width through two becks of hot water into a smaller beck filled with "chemick" ¾°–1¼° Tw. at a temperature of 60° C. From here it runs on to a travelling band or "creeper" of mackintosh, arranged to travel at a speed of 10 feet per minute; from the "creeper" it passes at once through a beck of water, and then into a second beck containing hydrochloric acid at 2° Tw., followed by a thorough wash in a series of deep becks or cisterns, through which a constant flow of clean water is maintained. After leaving the kier the pieces pass continuously through the operations of washing, chemicking, washing, souring, and final washing, and the speed at which these several operations are carried out is equal to a production of 80 to 90 yards per minute, according to the sort of cloth under treatment.

This combination of open-width and ordinary "rope" bleaching is suitable for all classes of goods, from the most delicate "fancies" to the heaviest of shoddy flannelettes, and has been in use for some time, with conspicuous success, for all descriptions of cloth between these extremes. It is especially useful for low-grade flannelettes which, in the rope form, are excessively liable to have their selvedges torn (or "cracked," as it is termed) in passing between the bowls and squeezers of washing machines, etc.

Bleaching for Turkey-Reds and Indigo Discharges is often described as a "half bleach," because the cloth is only subjected to the action of boiling soda, and is not treated with bleaching powder afterwards.

Experience has demonstrated that a good, full, rich shade of Turkey-red cannot be produced on fully bleached cloth, and consequently for this style of work the goods are not bleached in the ordinary sense of the word, but are merely freed of their fatty and waxy impurities. Apart from the omission of bleaching powder, the operations are exactly as already described. The cloth is singed, "grey" washed, boiled, soured, and boiled and soured again, after which it is well washed and dried.

Although it is not usual in England to use "half bleach" cloth for Indigoes that are afterwards to be printed in discharge colours, it is none the less very applicable to this purpose. The slight buffy tinge of the ground has no effect in dulling the pigment colours that are printed over it, and it is removed entirely in the white parts of the printed pattern by the oxidising action of the chromic acid liberated from the bichromate of soda or potash that is used for discharging the Indigo-dyed ground. Moreover, the Indigo dyes up a fuller shade, and more evenly, on half bleached than on fully bleached cloth, so that it is not only more economical as regards time, labour, and material, but yields a better result. These are important considerations, well worthy of a wider recognition than they have hitherto received.

In all methods of bleaching, the greatest care must be observed at every stage to avoid the formation of oxycellulose, iron, and other stains, and "tendering" during the lime boil, etc. The kiers must be kept well white-washed; the water must be clean; the cloth kept below the surface of the boiling liquors, or thoroughly saturated with them; the acids must not be allowed to dry on the cloth; the solutions of "chemick" must be filtered or settled until they are perfectly clear; they must not be allowed to come into contact with red-lead, or even flow through lead pipes; and the cloth, after chemicking, must be kept away from clean iron. The most fruitful cause of oxycellulose is the drying of pieces impregnated with bleaching powder solution; it is also caused by their contact with bright iron, and by any lead that they may happen to contain. The slightest trace of lead is sometimes sufficient to cause serious damage; it is converted into the peroxide,[1] which is a powerful oxidising agent, by the chemick. If dirty water is used for the "lye boils" the top layers of the cloth in the kier act as a filter for it, and become so imbued with dirt that it is difficult to clean them in any subsequent operations. Both caustic soda and lime act detrimentally on the cloth in an atmosphere of high-pressure steam, and their solutions must therefore always be present in sufficient quantity to cover the cloth entirely during the boiling. Strong solutions of bleaching powder and undissolved particles of it convert the cotton into oxycellulose, which, if it does not render the cotton weak, at least gives rise to irregular work by attracting dyestuff unevenly.

Iron stains occur in goods that have been in contact with the bare kier sides, nails in stillages, and the iron parts of machinery. They can generally be removed by treating the cloth in a warm solution of oxalic acid. The effect of mineral acids dried on the fibre is too well known to require more than mention.

The defects incidental to bleaching, and their causes and cure, might be gone into at much greater length, but sufficient has now been said to show how important bleaching is to the ultimate success of a calico print, and how defects that are quite unnoticeable in the bleach-house are liable to manifest themselves in most exasperating ways in subsequent processes, and after a good deal of valuable work has been put upon the cloth.

Before leaving the subject of bleaching it may be well to note that "back greys" used in the printing machine are always "singed" before they are sent to the printer. After he has done with them they are "soured," and allowed to lie *wet* in pile, to decompose the thickening and dissolve out the "mordants" and colouring matter that have been transferred to them from the rollers and cloth. They are then well washed and bleached in the ordinary way.

(*b*) MERCERISING.

As generally understood at the present day, "mercerising" is held to denote that treatment of woven cotton goods which imparts to them a permanent silky lustre. Strictly speaking, however, it consists in acting upon cotton with strong alkalis or other reagents which contract it, the lustre being obtained or not according to the conditions under which the fibre is treated.

In 1844 John Mercer, of the Oakenshaw Printworks, Lancashire, made the interesting and important discovery that when cotton cloth was immersed for a short time in a strong solution of caustic soda it contracted to a considerable extent, and was so altered, both physically and chemically, that it not only possessed a much greater strength than before treatment, but also a greatly increased affinity for dyestuffs and mordants. This discovery he patented, but it never came into general use on account of the enormous shrinkage of the cloth. The process was almost forgotten when Thomas and Prevost noticed that if cotton hanks were mercerised *under tension*, to prevent their shrinkage, they

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[1] W. H. Pennington, *Jour. Soc. Dyers and Colourists*, 1909, p. 46.

attained a silky lustre in addition to the other properties resulting from the action of caustic soda, and that this lustre was practically unaffected by the various operations of dyeing. Other workers were not slow to investigate further the great possibilities of Thomas and Prevost's process, and it was not long before its successful application to piece-goods became an accomplished fact.

Strong caustic soda causes the fibre to swell up, to shrink, and to become transluccent and elastic—in short, to become entirely changed, so that when examined under the microscope it is found to have lost completely its ordinary appearance. The fibres are no longer flat and twisted like ribbons, but round, straight, and transparent; their walls have thickened and their central opening is closed up; and they display no surface markings whatever. In this state the cotton, after washing, shows no lustre, but if it has been treated and washed under tension it exhibits a fine lustre similar to that of silk. The property of elasticity imparted by the caustic soda is, practically speaking, of the utmost importance, as it enables piece-goods to be "lustred" or "mercerised" in two different ways, according to the conveniences at disposal. They may be either impregnated with soda and stretched and washed in a continuous way, or they may be "batched" after being run through caustic soda and stretched out to width and washed afterwards, care being taken neither to allow them to lie too long nor to get dry before washing. Both processes are used in printworks, the first named being the most usual, and, all things considered, the most convenient.

If the goods are to be mercerised before bleaching, they are first singed and "grey" washed or "soured" in the ordinary manner. They are then well washed again, and either squeezed in the rope form or through a water mangle in the open width, to extract the excess of water. The latter is the better method, as it prevents the formation of crease marks. Then, without drying, they are passed through a padding machine, provided with a box containing caustic soda at 50° to 60° Tw. and with two or three iron bowls, between which the cloth passes, and which serve to express all excess of liquor from it. The goods may now be either "batched" and allowed to stand awhile, or they may be passed directly on to the "stenter" or stretching machine, upon which they are both prevented from shrinking and, at the same time, washed by means of "spirt" pipes which deliver a constant supply of wash water. As a rule, the first few spirt pipes are arranged to shower dilute caustic soda on the cloth so as to maintain the greater part of the washings from the cloth at a strength suitable for using in the kiers. The rest of the wash water is employed for dissolving more caustic soda, or is concentrated in multiple-effect evaporators and utilised over again. In the case of goods mercerised, in the "grey" state it is not necessary to wash all the caustic soda out; all that is required is to reduce its strength below the point at which it contracts the fibre—say 10° to 15° Tw. When bleached and dried pieces are mercerised, the strength of the caustic soda may be reduced a little, but the best results cannot be secured under 50° Tw., and it is therefore always advisable to work with the stronger solution. Bleached goods, after mercerising, must be "soured," and then thoroughly well washed in spiral washing machines, unless, of course, they are specially intended for some process in which the presence of free alkali is not detrimental.

The type of mercerising machine most commonly used consists of a padding mangle, a "stenter," and a series of washing becks provided with top and bottom rollers, over and under which the cloth runs. The "stenter" consists essentially of two travelling chains, the links of which consist of clips which grip the selvedges of the cloth. The distance apart of these two endless chains can be regulated, and the degree of their divergence can be adjusted at will, according as the cloth is to be stretched out rapidly or gradually. The links are con structed so that the greater the pull of the cloth the tighter is it held; and they are also furnished with a device which not only straightens out creases at the edges of the cloth, but also prevents the clip from gripping any part of it but the selvedge. Both chains run at the same speed, and for a certain distance they diverge; after that they run parallel, or nearly so. On entering the machine the cloth impregnated with caustic soda is therefore stretched until it reaches its full width at the point where the chains commence to run parallel with each other; at this point, and whilst still held at the full stretch, it is subjected to the action of the first "spirt" pipe, and during its passage through the remaining length of the machine it is continuously washed by a series of perforated "spirt" pipes, arranged to play upon it from both above and beneath. The washings are retained by cisterns situated under the machine, and planned so that the first and stronger washings are kept separate from the later and weaker ones, which are generally utilised by being pumped into the first few "spirt" pipes. On leaving the stenter the cloth runs directly into the hot-water washing becks, and finally, after passing between the bowls of a mangle, into the kiers or into spiral washing machines, according as to whether it has been mercerised in the "grey" or the "white" (bleached) state.

Many other systems of mercerising are in vogue, but the above-mentioned is the most popular, and possibly the best for general work. Plate IV. shows the machine sent out by Messrs Mather & Platt.

The most lustrous effect is to be looked for when the mercerisation is performed in the cold; and it can be always taken that the lower the temperature, the better the result. This, however, refers more especially to comparatively weak solutions of caustic soda; for the mercerising action of concentrated solutions is so energetic that a considerable elevation of temperature makes but little difference to the lustre produced. The effects obtained by working with caustic soda at 65° Tw. between temperatures so widely separated as 0° C. and 75° C. can scarcely be distinguished from each other, whereas, on the other hand, caustic soda at from 20° to 30° Tw. will only mercerise in the cold. All the same, temperature does influence the result, and it is always advisable to work in the cold if possible.

Although mercerising has long since passed the experimental stage, considerable difference of opinion still exists as to whether it is better to mercerise before or after bleaching. In some quarters it is held that cloth mercerised before bleaching is less lustrous than that mercerised in the "white"; and in many instances this is perfectly true. But it constitutes no argument in favour of bleaching before mercerising; for it is found that "grey cloth" mercerised *first* and afterwards bleached by boiling in soda-lyes, followed by the usual chemicking, is quite as lustrous and silky in appearance as similar cloth that has been bleached *before* mercerising. The loss of lustre in mercerised "grey cloth" is due to the action of the *lime boil*, and can be avoided if this operation is omitted—a fact which has been proved conclusively by a long series of comparative trials on the large scale.

On grounds of economy and convenience, the stage at which the mercerisation should take place is indisputable. It should undoubtedly precede bleaching, and in most up-to-date works it does. The only feasible objection that can be made to this order of working is, that calico in its crude unbleached state is liable to absorb the caustic soda unevenly, and thus give rise to various defects in the way of stains, streaks, and irregularities of shade. In practice, however, it is found that "grey cloth" properly "soured" and washed after "singeing" is no more liable to contract these defects than is white cloth, and that, in point of fact, being thoroughly "wet out," it allows the caustic soda to penetrate more rapidly and completely into the body of the fabric. Moreover, when cloth mercerised in the "grey" is once bleached, it is finished and ready for printing,

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etc., whereas cloth mercerised *after bleaching* requires additional "souring" and washing and drying at least, not to speak of still further treatment that is necessary in most cases to eradicate the stains produced by contact with the clips and other parts of the machinery. Mercerised cloth is very apt, in the white state and when wet, to contract stains from anything with which it happens to come in contact—iron or wooden rollers, stillages and waggons, etc.,—and these stains are generally so "fast" as to resist all efforts to remove them by washing and soaping alone. It then becomes necessary to re-chemick and sour the pieces—all of which adds to the cost of production. For this reason it is better to mercerise in the "grey," when all accidental stains are removed during the ordinary course of bleaching, and the cloth enters the "white room" in a finished condition. Quite apart from this consideration, a notable economy is effected in time and material; the amount of caustic soda retained by the cloth is allowed for, and utilised in the "lye-boils"; the operations of washing, souring, and drying are reduced in number; fewer chemicals are used; and less labour is required, the cloth going through fewer processes. In addition, "mercerising" becomes part of the bleaching process, for the strong caustic soda employed, and the effective hot-water wash used, must perforce exercise some influence upon the natural impurities of the fibre.

Open-width bleaching is the system *par excellence* to adopt for all classes of mercerised goods; not that it gives a better white, but because it prevents the distortion of the warp and weft threads and the formation of crease marks. Good results can be, and are regularly, obtained in ordinary high-pressure, low-pressure, and "steamer" kiers, but they are more or less uncertain, owing to the fact that goods in the rope form are liable to be irregularly acted upon by the soda during the boiling. The outer folds of the rope are more thoroughly scoured by the soda than the inner, and then, again, the cloth at the bottom of the kier is pressed into a compact mass by the weight above it, and this obstructs the regular percolation of the circulating liquor, so that the lower layers of cloth are subjected to a less searching scouring action than the upper, with the result that the cloth is irregularly treated, and thus develops stains and patches in subsequent operations. Streaks running in the direction of the warp are of everyday occurrence in sateen, twill, and broché cloth that has been bleached in the rope form, but they rarely appear in that bleached in the open width. Such defects are due, in the main, to the folds of cloth being crushed into each other in passing between the squeezer bowls of washing, souring, and chemicking machines, which abrade the cloth and displace its threads; they may also be caused by the weight of cloth in the kiers. Whatever their origin, they are serious disadvantages in any cloth that relies for the greater part of its value upon its lustre. In plain goods the distortion of the threads is scarcely noticeable, but in mercerised sateens and the like, especially if they are finished on the Schreiner calender, every such defect manifests itself distinctly, and detracts considerably from the value of the goods. Open-width bleaching, therefore, is to be preferred for mercerised goods whenever possible, although, with care, satisfactory results can be obtained from ordinary kiers.

Within recent years Edmeston and Reuss have patented a process of combined mercerising and "lye boiling," the cloth running directly from the mercerising machine into the well-known "Bentz" continuous kier. It is an attractive process, and, in *experienced* hands, might be expected to yield good results at a minimum cost for labour and material. In common with all long, continuous processes, however, it has the disadvantage that if the cloth happens to break, or any part of the machinery to get out of order, the whole arrangement comes to a standstill, and a considerable amount of time is required to adjust matters and get the machine running again. As a rule, the simpler and shorter a process is, the more likely is it to work with regularity.

(c) SHEARING, BRUSHING, AND "WINDING-ON."

Before the bleached calico can be placed in the printing machine it requires to be wound into a compact "batch" or roll on a hollow wooden or iron roller, through the central opening of which an iron spindle is passed for the purpose of supporting it in the machine. In addition to winding-on, the cloth usually requires shearing to remove the nap from its surface, and then a thorough brushing to clear it from all adhering loose threads and cotton down or fluff, which would, of course, lead to "snappers" in printing if allowed to remain. The brushing, shearing, and winding-on are all performed on one machine (fig. 48), which is provided with helical cutters, revolving at a high speed, revolving brushes, and a batching arrangement.

In certain classes of work it is necessary to damp the cloth and dry it over a "stentering" machine, fitted with a weft-straightening arrangement and a "batching" apparatus. Amongst the styles that require the cloth to be treated in this way the following may be regarded as the most important:—Fancy woven goods in which the woven pattern and the printed pattern must be quite straight (example: transverse printed stripes on vertical woven stripes, or *vice versâ*, forming a check); large printed spots on geometrical woven designs; bands of pattern printed between woven stripes; check patterns printed on any kind of cloth; and also such things as madder-dyed handkerchiefs, which have to be "filled in" afterwards by hand block printing. If any of these styles are printed on crooked cloth to start with, the printed design will be pulled out of shape when the cloth is subsequently straightened in the finishing processes. Either the printed pattern must be sacrificed or the cloth pattern must be left crooked; it is impossible to have both right if the cloth is not properly prepared at the outset. Printed on fancy woven fabrics that are not straightened after bleaching, large spots and designs based on the circle become distorted when the cloth is afterwards straightened; squares take the form of irregular diamonds; straight lines become undulating; checks, instead of being regular, float about in all sorts of directions; and, in short, the whole work is bad. It is an important point, therefore, to consider carefully the style of design for which the cloth is intended, and act accordingly.

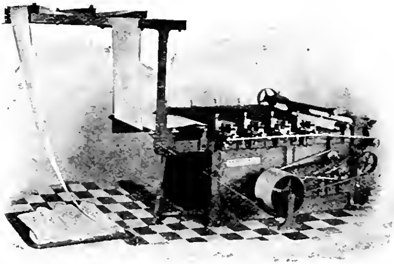

FIG. 48.—Shearing machine. (Mather & Platt.)

Drying to width over a stretching machine or stenter is also essential in the cases of patterns that are engraved for a certain width of cloth and with a border at each side. Any trusting to luck to provide the proper width in these cases usually results in one or other of the borders running over the edge of the selvedge, and being printed on the "back grey" or blanket.

(*d*) PREPARATION OF THE CLOTH WITH "PREPARES."

"Preparing" is a technical term used to denote the impregnation of the cloth with various chemical preparations that are essential to the "brightening" of the printed colours, or to their formation and full development on the fibre. The composition of these various "prepares" will be dealt with farther on in connection with the particular styles with which they are associated; but as their application to the cloth takes place before printing, it falls within the scope of the present chapter.

The "preparing" of cloth is usually conducted in a padding mangle by the process known as "slop padding." The padding mangle or "foulard" (see fig. 49) consists of two squeezing bowls—the upper one (A) of iron covered with india-rubber, and the lower one (B) of brass—arranged over a box or beck (C), fitted with guide rollers of wood provided with brass journals and working in brass bearings. The box ought to be of wood, and capable of containing from 15 to 30 gallons of liquor, according to the work in hand. The guide rollers R, R are arranged so as to allow of the cloth passing five or six times through the liquor before going through the squeezer bowls.

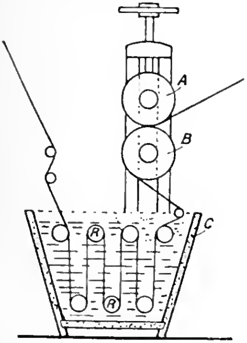

Fig. 49.—Padding mangle.

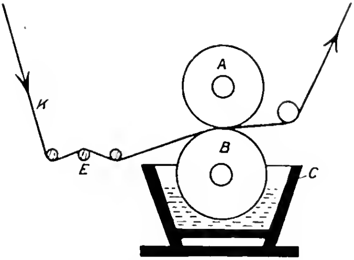

Fig. 50.—Another type of padding mangle.

On emerging from the padding mangle, the goods run directly either on to a cylinder drying machine or through a hot-air drying apparatus, after which they are "wound on" in the usual way, and are then ready for printing.

In many cases the squeezer bowls are made of wood, the bottom one being wrapped with several folds of calico; and for special styles and fancy woven fabrics the goods are treated either wholly or in part on "stentering" machines, for reasons already given.

A special form of padding mangle is used for cloth which has been printed in certain "reserve" or "resist" colours, and which has afterwards to be either "prepared" or dyed-up in the padding mangle. In such cases, if the printed cloth were passed through the liquor contained in the box of an ordinary padding mangle, the printed portions would be dissolved off, and either spoil the padding liquor or run into the surrounding parts of the cloth. To avoid this, the bottom squeezer bowl is arranged to dip into the padding liquor, and the cloth is passed straight through the "nip" (that is, between the bowls), and then dried before the solvent action of the liquor can take effect. The bottom bowl is wrapped with calico, and carries the liquor up to the cloth in much the same way that a furnisher does to an engraved roller in a printing machine.

Fig. 50 illustrates the principle of this method of working.

Fig. 50, A, india-rubber bowl; B, brass bowl; C, padding box; E, tension rails, corrugated to open the cloth out; K, the cloth.

Padding straight through the "nip," or slop padding, is not, strictly speaking, a preparation of the cloth for printing, but as "preparing" is used for purposes other than printing, it may as well be mentioned here as elsewhere; goods dyed before printing will be dealt with under Discharge Styles.

PART IV.

PREPARATION OF COLOURS FOR PRINTING.

PREPARATION OF COLOURS FOR PRINTING.

The preparation of the colours for calico printing, and of such of their constituents as are made in the works, is at the present time more of a science than an art, and demands for its proper carrying out a large amount of chemical knowledge. It is useless nowadays for a "colour mixer" to attempt to keep abreast of the times unless he possesses a sufficient knowledge of the chemistry of his business to enable him to get his effects without referring to his grandfather's "receipt book," and without spending a vast amount of time in making trials, trusting to a lucky "fluke" to yield him the effect he is groping for. Although many old colours, that were applied successfully to calico in the early days of the industry, were the outcome of scientific research on the part of chemists, the greater number of old-time colour mixers worked on the principle of trying "a bit of this and a bit of that"; and if success occasionally crowned their unaided efforts, it was usually a long time in coming, and when it did arrive it was due rather to chance than to any systematic method of working. With the introduction of coal-tar colours the importance of the "rule of thumb" colour mixer and of his mysterious secrets began to dwindle, and has continued to do so, until now he is expected (if he still exists) to do little more than to supervise routine work. The chemist has taken his place in all that relates to the introduction of new styles, and in many cases, more especially on the Continent, the colour mixer himself is a trained chemist. In the old days practical experience counted before everything—and indeed it is no less valuable to-day, for there are still many "tips" and "knacks" that no amount of university training can impart; but nowadays a printworks run on unscientific lines has absolutely no chance of equalling the best work of its up-to-date competitors who employ a staff of specially trained chemists. Experience is necessary, but it must be supplemented by a thorough knowledge of the principles upon which modern calico printing is based. Many substances, such as Paranitraniline red or Aniline black, would never have been brought within the range of practicability save by the investigations of chemists; they afford little or no indication of their tinctorial powers; and if, in many cases, these powers were hit upon accidentally, they were at least discovered during the course of scientific work that would never have suggested itself to the mind of, or been undertaken by, the purely "practical man."

Quite apart from all questions of discovery, the mere application of many modern colouring matters demands the supervision of a chemist; and indeed all the operations relating to calico printing ought to be under scientific control. The conditions under which a colour is prepared, the proportions of its ingredients, the order in which they are added, and other points, all affect the result. Again, on the other hand, the result may be perfectly satisfactory, but obtained at too great a cost. In all these cases the services of a chemist are essential, if only on grounds of economy, not to speak of the improved quality of the work turned out.

The actual composition of the various colour pastes used in calico printing will be dealt with in another part of this volume under the heading of "Styles of Printing," the object of the present chapter being merely to treat, in a general way, of the more important means, methods, and materials employed for the purpose of thickening solutions, etc., of colouring matters and mordants. The substances used for this purpose may be divided into two distinct classes: (1) those which are used solely as thickening agents, and are afterwards removed, as completely as possible, from the cloth; and (2) those which are thickening agents and fixing agents combined, and are allowed to remain on the cloth, forming, as they do, an integral part of the finished colour. The function of a thickening belonging to the first class is simply to act (*a*) as a vehicle for carrying the colour to the cloth, and (*b*) as a preventive against its spreading, by capillary attraction, beyond the limits of its allotted space in the design. It ought, therefore, to possess no affinity for the colour or the mordant with which it is mixed, otherwise, on washing it out of the cloth, a good deal of the colour would be removed along with it.

The following are the thickening materials in most general use:—

1st Class: Starch, flour, gum tragacanth or "dragon," gum Senegal, gum arabic, dextrin and other artificial British gums—with or without the addition of china clay, etc.

2nd Class: Albumen, casein, lactarine, and glue.

Other materials, such as linseed mucilage and Iceland moss, etc., are also sometimes employed for special purposes, but they are not essential to any style of work, and can be replaced in all cases by one or other of the many natural and artificial gums.

Starch is a substance very widely diffused throughout the vegetable kingdom. It is found in almost every plant, and occurs in the form of minute granules in the seeds of various cereals, in the bulbs and tubers of many plants, and also in the bark and pith of many trees. It is an important article of manufacture, and, on the large scale, it is obtained chiefly from wheat, maize, potatoes, and rice. Wheat, maize, and rice are ground up with cold water and a little caustic soda, which dissolves out the gluten and facilitates the separation of the starch. The milky liquor is well stirred up, and then run through coarse sieves (to separate any fibrous matter that may be present) and allowed to settle. The clear water is then drawn off, and the deposited starch well washed several times with cold water, again allowed to settle, and finally dried in shallow trays or boxes at a gentle heat. When perfectly dry the cakes break up into thousands of the small irregular masses so characteristic of starch, and the starch is either sold in this form or is ground to powder. Potatoes contain practically no gluten, and the starch is simply washed out of them with cold water. The potatoes are pulped, placed on sieves, and washed in a stream of water. The milky liquid is then allowed to settle, the deposited starch washed by decantation, and then dried as above.

Starch $(C_6H_{10}O_5)_n$ is a carbohydrate, insoluble in cold water and alcohol. With boiling water the granules swell up and burst, forming a smooth, homogeneous, gelatinous mass, in which form it is used for stiffening printed goods and for laundry purposes; but the "starch paste" obtained in this way is not really a solution of starch. When, however, starch is heated under pressure with water at a temperature of 150° C. it goes into solution, and the solution, on cooling, deposits what is known as "soluble starch," a product largely employed for "finishing" all kinds of cotton fabrics. Soluble starch dissolves sparingly in cold water, but is completely soluble at 70° C. and upwards. Other methods of making this modified form of starch are practised, but they are not of interest to the colour mixer on account of the impossibility of thickening printing colours with soluble starch. When boiled with very dilute sulphuric or hydrochloric acids, starch is converted into dextrin and loses a good deal of its thickening power; indeed most ordinary acids, except acetic and formic acids, have the effect of thinning starch paste, and consequently it is unsuitable for use in strongly acid "resists" and "reserves," which consist for the most part of citric, tartaric, and oxalic acids in combination with bisulphate of soda. It *is* used for these "colours," but British gum is usually preferred.

With caustic soda, starch paste forms a stiff, white, transparent jelly, known as "apparatine." This finds a limited employment in "finishing" operations; but, so far, it has not been used to any extent for printing colours, although, when neutralised with hydrochloric acid, it has been tried as a substitute for gum tragacanth.

Diastase converts starch into maltose and dextrin without injury to the fabrics upon which it is printed, and without affecting the colours, and is used occasionally to assist in removing starch thickenings from cloth that is required to be specially soft in feel.

All starch pastes give a characteristic dark blue coloration with iodine, but the colour is so intense that if the various starches do give slightly different tones of blue it is impossible to distinguish them sufficiently well to use this reaction as a test for any particular starch. For this the microscope must be used: each starch has a differently-shaped granule, and these can be easily distinguished from each other under a moderate power.

The most important starches to the calico-printer are the following:—

(1) Wheat Starch.—Wheat starch is the most largely used of all the thickening agents employed in textile printing. It is cheap, is not easily acted upon by colours and mordants, is useful for a greater variety of purposes than any other thickening, and gives a good, sound, workable paste, which keeps well, and may be either used alone or mixed in any proportion with other suitable thickenings as required.

As a general rule, it may be taken that the greater the weight of thickening material contained by a given colour, the lighter will be the shade it ultimately yields; and, conversely, the greater the weight or quantity of water, the deeper will be the shade. Starch paste containing 12½ per cent. of wheat starch forms a more or less aqueous thickening, which, despite its fairly thick consistency, allows the colour to penetrate well into the body of the cloth, and thus yields shades that are fuller and more opaque in quality than those yielded by any of the gums (except tragacanth), which only thicken from one to three times their own weight of water.

Starch paste prepared with water alone is somewhat too "sticky" to work well in machine printing; it adheres tenaciously to the rollers, and if at all thick it frequently escapes past the "cleaning doctor," unless great weight is put upon the latter—a practice which tends to wear down its edge rapidly, and is, moreover, unnecessary with properly prepared colour. It also sets into a stiff mass when cold and after standing awhile, and requires warming up again before it can be used. In order to avoid these disadvantages, it is rendered softer or more emollient by being boiled with a small quantity of some vegetable oil, which brings about the desired end without reducing the consistency of the paste, and makes it possible to work very thick colours without difficulty. The oils used are generally either olive, rape-seed, cotton-seed, or castor, and the quantity added varies between 25 and 50 per cent. of the weight of starch used, according to the thickness of the colour and the purpose for which it is intended.

In making starch paste, the starch is first of all stirred up with cold water into a smooth, creamy paste; the oil is then added, and the whole boiled until the thickened mass begins to thin again. At this point the boiling is stopped and the paste cooled down. To obtain the best results, the paste should be stirred continuously during the whole of the time that the boiling and cooling are in progress. When dyewood extracts and solutions of dyestuffs are thickened directly with starch, the same procedure is adopted; the starch is beaten up with water, and the dyestuffs are added, either hot or cold. The mixture is then boiled and cooled, and before removal from the pan, the necessary mordants are added and well stirred in. Acetic and other organic acids are largely employed for dissolving dyestuffs, but their presence makes no difference to the method of working. The thickness of starch pastes varies according to the style of work in hand and the strength or depth of the engraving of the rollers. For most work a paste containing from 12 to 15 per cent. of starch is quite thick enough; but for coarse engraving, from which a sharply-defined impression is desired, and for all crisp, delicate designs, not too lightly engraved, the quantity of starch may rise to 20 per cent.; on the other hand, for "padding," that is, printing a flat colour over the whole surface of the cloth, the weight of starch in the paste rarely exceeds 6 or 8 per cent., as otherwise the printing is apt to appear thin or bare.

A good wheat starch ought not to contain more than 15 per cent. of moisture, nor leave more than 0·5 per cent. of ash after incineration. In other respects its suitability for calico printing can only be determined by a practical trial. A sample of the starch is taken and made into a paste; its whiteness and thickness are then noted and compared with a sample of the standard starch in use, boiled up at the same time under exactly the same conditions. A pale Alizarin pink and a pale Methylene blue are then made up from both starches, and printed, steamed, and washed together; the shades they give are compared, when the brighter colours denote the better starch. A portion of each of the two pastes is now allowed to stand a few days, and then tested with litmus for acidity, and further examined to see whether it has retained its original consistency, or whether it has broken up into a rough, curdy-looking mass of lumps of paste, floating about in a watery medium. The whiter and thicker the paste obtained from a given weight of starch, the brighter the colours it yields; and the longer the paste will keep without turning sour and without breaking up into lumps, the better is the starch for all purposes connected with the thickening of printing colours.

Wheat starch is almost always used for thickening dark shades of all classes of colouring matters; it is not better than gum tragacanth, but is much cheaper and quite as good for all styles in which the cloth is not required to be particularly soft after finishing. It certainly does impart a somewhat harsh feel to the cloth when printed in large, heavy masses, such as occur in cretonne designs; but in practice this defect is more or less overcome by mixing the starch thickening with various proportions of gum tragacanth thickening, which, although it may be quite as thick as starch paste, contains a very large percentage (95 per cent.) of water, and consequently does not stiffen the cloth to anything like the same extent that starch does. Fine patterns in fast colours are almost invariably printed with wheat-starch thickenings, unless the colours used are pigments, Indigo and other alkaline colours, or mordants for "madder" dyeing.

MAIZE STARCH finds but limited application in textile printing. Its chief use is for thickening aluminate of soda (alkaline mordant), and occasionally it is mixed with British gum for Indigo and Sulphide printing colours.

RICE STARCH forms an unstable paste, and is not used for anything but "finishing" or stiffening printed goods, for which purpose it is prepared as required.

POTATO STARCH is also restricted to "finishing" operations, and is of no use whatever for thickening printing colours which have to be kept for any length of time.

FLOUR.—In addition to the starch it contains, wheat flour also contains a nitrogenous body—gluten—the presence of which renders it unsuitable for use with many modern dyestuffs and their mordants. It finds its most important application in thickening the acetates of alumina and iron, which are still largely used for the production of Madder reds, chocolates, and purples, a style that was formerly in much greater demand than at present, but is still produced in large quantities whenever the best and fastest work is required. For this purpose wheat flour is eminently adapted; it is a powerful thickener, forming a soft, full paste, which allows the mordants to penetrate well into the cloth, and yields, on dyeing, dark, rich colours that are remarkable for their evenness and bloom. With the "ice colours" (diazotised Paranitraniline, etc.), wheat flour gives darker shades than most other thickenings, and possesses the further advantage of producing the most stable printing pastes, although no "ice colours" will remain in good condition for many hours, except in the coldest weather. Flour is frequently mixed with starch or gum tragacanth, according to the quality of paste required for a given style; it is very rarely used alone nowadays. The testing of wheat flour is carried out in exactly the same way as the testing of starch, and its technical value depends upon practically the same properties. The colour-printing trials are, of course, made with the colours for which it is best adapted, but in other respects the same good qualities are to be sought in flour as in starch, namely, whiteness, thickness, and stability.

GUM TRAGACANTH.—Gum tragacanth or "gum dragon" is a natural gum obtained from a genus of leguminous plants, of which the most important is the *Astragalus gummifer*. Tragacanth comes into the market in the form of dry, "horny" scales or leaves, which vary in colour from white to deep yellow, and are more or less translucent according to their source of origin. The best and most expensive quality of gum tragacanth is white, very translucent, and free from sand, woody fibre, and dirt; it ought to dissolve completely in water, and form a thick, smooth paste with at least twenty times its weight of water. When boiled, the mucilage becomes thinner, but smoother; and if boiled under pressure, the solution becomes very thin. In common with all natural gums, tragacanth varies in its behaviour towards tannic acid, metallic salts, and alkalis, the best sort for calico printing being that which does not become gelatinous with the above substances. Most qualities will mix fairly well with dilute alkalis, but, curiously enough, the best quality is converted into a "ropy" mass by strong solutions of caustic soda, whereas the cheaper and poorer quality, yellow in colour, and containing a comparatively high percentage of foreign matter, can in many cases be mixed perfectly with soda sufficiently strong to discharge tannin mordant. It varies considerably, however, in this respect, no two seasons' deliveries being quite alike in their behaviour towards alkalis.

Gum tragacanth is chiefly used, either alone or in combination with a little starch, for printing dark, heavy "blotches," and for this purpose it is unexcelled, as it is easily removed from the cloth in washing, and leaves it almost, if not quite, as soft as it was before printing. It is also extensively employed for pale blotches or grounds for delaine printing, and for all first-class work in which softness of feel is a desideratum. It is mixed with albumen in the making of pigment printing colours, and enters into a good many of the dye liquors and "prepares" that are padded on the mangle. In the latter case it tends to equalise the absorption of the liquors by the cloth and ensures level padding. The tragacanth thickening or mucilage used for ordinary "blotch" printing contains from 6 to 8 ozs. of gum per gallon (say 4 to 5 per cent.); stronger mucilages are made (7½ to 10 per cent.), but they are employed solely for adjusting the thickness of colours that are too thin, and for mixing with solutions of dyestuffs, etc., in order to bring them up to the proper consistency for printing.

In making tragacanth thickening, the requisite quantity of gum is soaked in water until it has swollen up into a thick paste; it is placed in a jacketed, steam-heated pan, fitted with mechanical agitators, and boiled and stirred until perfectly homogeneous, after which it is cooled and strained ready for use.

GUM SENEGAL AND GUM ARABIC.—Both these gums (including gum gedda, etc.) are exudations from various species of *Acacia*, and come from various parts of the world. They occur in commerce in the form of rounded or irregularly-shaped pieces, varying in size from that of a pea to that of a chestnut, and in colour from a very pale yellow to a deep brownish-red. They are nearly odourless, and of an insipid or slightly sweet taste. They are complex in composition and constitution, but they are composed in the main of one or all of the three bodies, arabin, cerasin, and bassorin, together with a little lime, potash, and magnesia.

The best qualities of gum Senegal are obtained from *Acacia Senegal*, a tree which forms dense forests in Nubia, Senegambia, and Kordofan. The various sorts of gums that come from India, Australia, and the Cape are of inferior quality; they all contain a comparatively high percentage of bassorin, which is insoluble in water, merely swelling up into a sticky, gelatinous mass, which reacts unfavourably with the various components of most printing colours.

In choosing a gum of the Senegal class for printing purposes preference ought to be given to that sample which is most easily soluble in water, gives the clearest and lightest solution, keeps the longest, and is not coagulated on standing a week or two when mixed with various metallic mordants or tannic acid. A good gum will dissolve completely in its own weight of water, but many gums require at least double that quantity for their proper solution. Some samples are so soluble that, in the powdered form, they can be added directly to the printing colour, and will dissolve very rapidly therein if well stirred up for a short time. Most qualities, however, require boiling water for their complete solution, and in the case of Indian, Australian, and Cape gums, the boiling must be conducted under pressure, and even then complete solution is not always obtained without the addition of acetic or other acids.

In making a natural gum thickening, the gum is first stirred up with cold water for some time; the floating bits of chip, woody fibre, etc., are then skimmed off, and the whole is heated for several hours in a jacketed pan provided with agitators, which keep the gum from setting into a solid mass at the bottom of the pan. When the solution is complete, the hot thickening is ladled out of the pan into deep casks and allowed to stand several days for the purpose of allowing the sandy matter to deposit; the gum is then strained and is ready for use. All gums contain sand and fine grit, and the longer they can be kept in the casks before use the more likely are they to give satisfaction in printing; the finest grit is almost imperceptible, and takes a long time to deposit.

Besides testing a gum for its solubility, thickening power, clearness, and behaviour towards mordants, a practical printing trial must always be made. Many gums, although they fulfil all other requirements, cannot be made to give either a clean impression with sharply cut edges or a sufficiently bright colour, and in such cases the gum is absolutely useless for most classes of work. This is especially the case with gums which have been dissolved under pressure and contain a large proportion of insoluble matter. On cooling, the insoluble portion frequently settles out again in an extremely finely-divided state; and although the thickening may appear to be perfectly homogeneous, it consists in reality of minute particles of gelatinous matter which are held in suspension by the thinner solution, and prevent the even absorption of the thickening by the cloth, thus giving rise to "fuzzy" prints.

Gum Senegal, gum arabic, gum gedda, and other thickenings of the same family, are best used by themselves. When mixed with starch, flour, or gum tragacanth they break up the thickening, deprive it of "body," destroy its nature, and convert it into a slimy mixture, very apt to separate into its constituents during the printing process, and rarely or never giving satisfactory results, even if it happens to retain its original consistency. The addition of a small quantity of gum Senegal solution to starch and flour pastes is a common "colour shop" makeshift for softening and thinning colours that are too stiff; but it is a practice that is deprecated by most experienced colour mixers, and is only adopted to avoid the trouble of making up a fresh lot of thinner colour with a smaller quantity of the proper thickening.

Colours printed with gum Senegal and similar thickenings give beautifully even and transparent shades, but they come out much paler than when starch or gum tragacanth is used, and for this reason gum Senegal is only employed for the printing of light colours, and especially for those which form the ground or "blotch" of the pattern. The natural gum thickenings generally used for printing contain from 30 to 50 per cent. of solid gum, and consequently do not allow the colouring matter to penetrate very deeply into the fibres of the cloth. The result of this is that goods printed with "gum colours" lose a good deal of their colour in the washing and soaping operations that follow printing; and it is evident, therefore, that if very strong dark colours be printed with gum thickenings, the large amount of colour dissolved out during the washing of the pieces would seriously affect the brilliancy and purity of any other colours that might be associated with them, for the colours and mordants used in textile printing are extremely susceptible to the soiling action of any highly-coloured wash-waters through which they may have to pass.

Gum Senegal and its class mix well with both strong alkaline solutions and with strong organic acids, a property which enables them to be used for all kinds of discharges, and resists, and for Indigo printing. But in practice they are usually replaced in these styles by the cheaper and more rapidly prepared British gum thickenings, which act quite as effectively in most instances.

DEXTRIN AND BRITISH GUM.—The terms *dextrin* and British gum are somewhat loosely applied to various descriptions of torrefied or roasted starch. What one maker calls "dextrin" another calls "dark British gum," and, in like manner, "yellow dextrin" is known also as "light British gum." The terms are also applied to the products derived from different kinds of starches, so that, taken altogether, they represent no definite compound, although, strictly speaking, dextrin is a definite degradation product of starch, obtained by heating it with dilute mineral acids, or by roasting it at a temperature of 160° C. until it becomes completely soluble in water.

From a practical calico printer's point of view, the difference between dextrin and British gum is largely a question of colour and thickening power. A dark-coloured product, easily and completely soluble in water, is generally described as dextrin, whereas a light-yellow or fawn-coloured product, containing a variable quantity of insoluble matter, is usually known as "British gum." On the other hand, both are known as either "dextrins" or "British gums," and, in point of fact, they may both be made from the same starch, the great differences in colour and solubility being entirely due to the duration of the roasting process. In the case of the "dextrin" or "dark British gum" this is continued until the whole of the starch is completely converted into a perfectly soluble and chemically true dextrin, while in the case of the "yellow dextrin" or "light British gum" the roasting is stopped before the whole of the starch is so converted. It is this unconverted, unaltered starch that forms the insoluble portion of all "light British gums," so that when they are boiled up into pastes they really consist of a mixture of starch paste and dextrin solution. On the large scale, a small quantity of nitric acid is frequently mixed with the starch before it is roasted, and this affects its ultimate colour to some extent, but in the main this and the solubility depend upon the duration of the roasting. A highly torrefied starch gives a thin dark-brown solution; a lightly torrefied starch, a thick light-yellow paste, which requires boiling before it can be used as a thickening for printing-colours. The more starch a "British gum" contains, the more will its mucilage approximate to the qualities of starch paste and the less "gummy" will the thickening be; but all brands of "British gums" and dextrins can be mixed together in any proportion, and thus it is possible to vary the consistency and quality of the thickening in almost any way desired.

British gums are made from both wheat and maize starches. For most purposes it is immaterial which starch is employed, but if a *yellow British gum* is to be used for thickening strongly alkaline colours like Indigo, a maize starch gum ought to be selected, as maize starch itself forms a much better thickening with strong alkalies than wheat starch. If dextrin or dark British gum is used in conjunction with strong alkalies, any brand may be taken so long as it contains no more than a trace of unconverted starch. Many recipes, made up with British gum and strong alkali, which work perfectly in one works cannot be worked at all in another. The explanation of this is that the British gum in the former case was made from maize starch, whilst in the other it was a wheat-starch product.

With very few exceptions, British gums of good quality can be used for exactly the same purposes as gum Senegal, etc., the only drawbacks being that they give a somewhat yellower tone to pale shades, and leave the cloth a little harder in feel. On the whole, however, they are very valuable substitutes for the more expensive gums, and, if chosen and used with care, are capable of yielding perfectly satisfactory results.

British gum thickenings contain from 20 to 50 per cent. of dry gum according to the quantity of free starch they contain; they are simply boiled in water and cooled without any further additions.

Albumen.—Albumen is obtained from the whites of eggs and from the serum of blood. Both these substances are evaporated to dryness at a gentle heat and under reduced pressure, and they come into the market in the form of thin, small scales: egg albumen, quite transparent and of a pale yellow colour, and blood albumen, semi-opaque and from light to dark brown in colour. Albumen is soluble in water, and can be coagulated either by heat alone or by warm mineral acids—two properties which enable it to be used as a mechanical fixing agent for pigment colours and certain insoluble lakes. Egg albumen coagulates at a temperature of 75° C.; blood albumen between 73° and 80° C. Blood albumen is cheaper than that obtained from eggs, but its dark colour prevents it from being used for delicate tints, for which egg albumen must always be employed. Various processes have been tried for bleaching blood albumen, but so far without any conspicuous success; it can be improved in colour to some extent by the action of turpentine, and it is always advisable, for other reasons, to add a little of this to the solution.

Albumen is best dissolved in tepid water 20°–25° C., the usual strength of the solution being anything from 35 to 50 per cent. At the latter strength it gives (after straining) a good gum-like thickening, which mixes in all proportions with gum tragacanth. Pigment printing colours and colours for indigo discharge styles usually contain 12–15 per cent. of albumen, which is quite sufficient to fix them. Formaldehyde forms an insoluble compound with albumen, but this reaction is more interesting than useful, and is rarely applied practically in textile printing.

In dissolving albumen, 200 lbs. are mixed with 30 gallons of water and well stirred up for a few minutes; the whole is then allowed to stand twenty-four to thirty-six hours (being again stirred up every few hours), when, if the albumen is of good quality, the solution ought to be complete.

The addition of ammonia or borax facilitates solution, and in warm weather it is usual to add a little phenol or other disinfectant to retard the decomposition to which albumen solutions are liable.

Apart from its use as a mechanical fixing agent for pigments and lakes, albumen finds but little application in a modern printworks. It is employed occasionally for waterproofing the "wash-blankets" of printing machines, but this use is by no means general, and probably the albumen could be replaced with advantage by other substances.

Casein and Lactarine.—Casein is the essential constituent of cheese, and closely resembles albumen in many properties. It is obtained by acting on skimmed milk with "rennet" or an acid, either of which throw down a curdy mass—casein—which, after repeated washings in tepid water, is dried at a gentle heat, and put on the market in the form of a yellowish-white powder. It is insoluble in alcohol, and in hot or cold water, but dissolves easily in warm, slightly alkaline solutions, and if a sufficient quantity is taken it gives a thick, smooth paste, very suitable for machine printing. Casein is used in exactly the same way as albumen for the fixation of pigment colours, but it is not so good for the purpose, as the colours do not resist washing to anything like the same extent as do those fixed with albumen, and if the soap used contains free alkali they can be removed almost entirely from the cloth. Formaldehyde acts very energetically on casein, forming an insoluble compound which fixes pigment colours much more permanently than when the casein is simply "steamed." In order to make use of this reaction the pigments are ground up with a casein paste and printed in the usual way; the goods are then either padded in a solution of formaldehyde, dried, and steamed a short time, or are passed through a chamber containing hot steam and formaldehyde vapour. In either case the casein is coagulated, and encloses the pigments in a sort of insoluble envelope, similar to that produced by the "steaming" of albumen. The colours so fixed resist washing almost, if not quite, as well as "albumen colours," and are equally bright and "toppy," that is, they stand out well.

Notwithstanding this, casein has never replaced albumen to any considerable extent, probably because the latter is much simpler in its application, and, taken altogether, produces better and more reliable results.

The alkali generally employed in dissolving casein is borax, which answers the purpose perfectly, and has no effect on the shade of the pigments with which it is mixed.

Lactarine is to all intents and purposes identical with casein, and is applied in the same way. Some samples contain borax, and therefore only require warm water for their solution.

Glue.—Glue (an animal substance obtained by boiling bones, etc., in water) comes into the market in the form of hard, transparent, dark brown cakes. It swells up in cold water into a soft gelatinous mass, which dissolves completely on gently heating. Formerly it was employed for the printing of metallic powders, being mixed with starch and printed as a hot paste, upon which the powder was dusted before the glue set; but at the present time its use as an addition to thickenings is limited to a few "resist pastes," from which it might very well be left out. It is chiefly used now as an addition to the dye bath, for the purpose of preserving the purity of the "whites" in the madder and other dyed styles.

China Clay, pipe clay.—China clay or kaolin is not a thickening agent as such; but as it enters largely into the composition of "resist" and "discharge" colours, it can be most conveniently mentioned here. Its function in printing pastes is to prevent the acids, etc., from spreading or running, and it also acts as a mechanical resist, and thus aids in the production of the effect desired. It ought to be white when ground up with water, and free from all gritty particles.

China clay is added to gum or starch thickenings in paste form (50 per cent. paste), and is boiled up with them in order to incorporate it thoroughly with the other ingredients. Acid "resists" and various "discharges" contain from 10 to 20 per cent. of china clay, according to the quantity of water used and the kind of acid employed. Citric acid and citrates are extremely liable to spread during the steaming process, and they require more china clay than most other substances used for similar purposes.

China clay is also largely employed for "back filling" printed goods, and in other operations connected with the finishing of woven goods.

THE MAKING OF PRINTING COLOURS.

Generalities.—The "colour shop," as the colour making department is usually designated, should be a large, well-lighted room, situated on the ground floor of the works, and, for convenience, as close as possible to both the "drug room" and the "machine room." It ought to have a flagged or a concrete floor, and should be well ventilated above to allow the steam and acid vapours disengaged during the boiling of colours to escape freely into the outer air; it should also be well drained to carry off all waste waters and liquors, and, above all, should be provided with a copious supply of pure, clean water. In many establishments the whole of the condensed water produced in the many drying machines of the various departments is collected and utilised in the colour shop for the preparation of mordants and colours. There is nothing better for this purpose than condensed water; it is clean, soft, and pure, and, in addition to giving the best colours, it represents a considerable saving in steam. The high-pressure steam used for driving the machinery is run through reducing valves into a low-pressure range of pipes instead of escaping into the air, and thence into the drying machines, from which a large proportion of it issues, as condensed water, at a comparatively high temperature. The utensils used in "colour making" or "colour mixing" are neither numerous nor complicated. They consist of boiling pans of various capacities, of storage casks, tubs for transporting the colour to the machine room, scales, measures, stirring sticks, and different qualities of straining cloths, together with cisterns and becks for washing such of the articles as are portable. In most colour shops, too, there are grinding mills for pigment colours, Indigo, and other insoluble substances and, where large quantities of Aniline black and Madder colours are used, mechanical straining machines through which 15 to 20 gallons of colour can be passed at once.

The boiling and cooling of the colours is effected in double-cased pans of copper, steam or cold water being made to circulate between the two casings, according as the colour is to be boiled or cooled. The larger pans are provided with two mechanical agitators which keep the colour in constant motion, and thus ensure a smooth paste and the perfect mixing of its ingredients. The agitators turn on their own axes and at the same time travel continually round and round the interior of the pan, so that every particle of colour, except that which cakes on the sides of the pan, is thoroughly stirred up. They are worked on the well-known "sun and planet" system, and are actuated by bevel gearing and a vertical shaft (see fig. 51). The latest colour pans are made to swing, for convenience of emptying and cleaning, and they can be tilted to any desired angle by means of a toothed wheel which gears into a screw worked by hand. The toothed wheel is fixed on one of the two hollow trunnions upon which the pan swivels. One end of each of these trunnions communicates with the space between the double casing of the pan, and the other fits into a stuffing box carried by a short hollow pillar. Each pan is thus supported on two hollow pillars (one at each side), one of which is connected to the steam supply and the other to the water supply, and, through their respective trunnions, both communicate with the space between the casings, so that either steam or water can be introduced as required (see fig. 51).

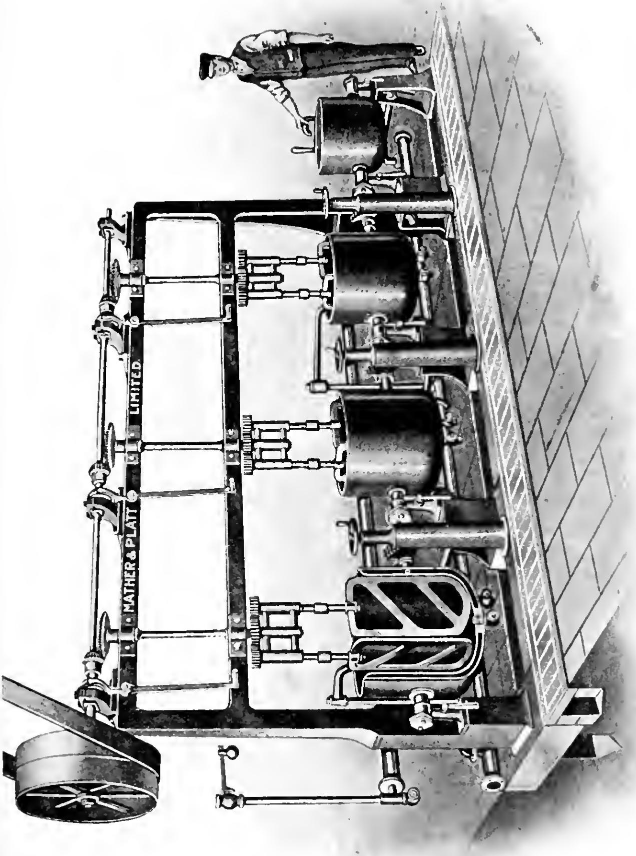

FIG. 51.—Colour pans. (Mather & Platt.)

Printing colours are made up in two different ways. The first method is to boil the thickening agent and colouring matter or mordant together; the second, to mix either hot or cold solutions, etc., of colouring matters or mordants with a previously prepared thickening. In many cases it is quite immaterial which method is employed, but some colours always require boiling, others are better boiled, and yet others again can only be prepared with ready-made thickenings, and often only in the cold. Wherever possible, and when only small quantities of colour are required, it is preferable to make use of the second method; it is more convenient, and the colours can be prepared more quickly. On the other hand, when *large* quantities of a colour that *can* be boiled are required it is always better to boil it, because large quantities can be much more thoroughly mixed in a pan with mechanical agitators than by "raking" or stirring up in a cask by hand (especially if the colour be at all thick), and further, because the whole batch of colour being of exactly the same thickness and shade throughout, will give perfectly uniform results in printing, whereas if it were mixed in small separate lots it would be likely to vary somewhat in both consistency and depth of shade.

Direct-dyeing colours and basic aniline colours can be prepared by either method; but when they are very strong or deep they are better boiled, for the simple reason that the quantity of water (and acid) required for their solution, and for that of their mordants, would be so great as to thin down the thickening paste to a point unsuitable for printing.

Dyewood extracts can also be mixed by either method, but they generally work better when boiled up with the thickening; and Logwood is always much better boiled than when mixed in the cold with starch or any other paste. Alizarin, too, gives brighter shades when boiled with its thickening, but it and also the extracts of Quercitron bark and Persian berries are, as often as not, mixed with cold ready-prepared thickenings, and the results obtained in this way quite justify its adoption. Many so-called "Alizarin colours" are in paste form, finely ground, and can be readily dissolved in cold starch paste or gum; and Alizarin blue S. is so extremely soluble that it can be added, as a dry powder, directly to its thickening, in which it dissolves at once. Auramine and several other colours decompose on boiling, and must therefore be added to their thickenings at a lower temperature; pigments and diazotized bodies can only be compounded in the cold, the first because their thickening (albumen) is coagulated by heat, and the second because diazo compounds are excessively unstable at the ordinary temperature, and must be cooled by ice or other means.

These are a few examples of the general methods employed for combining colouring matters and thickening agents; but as each of the above colours merely represents a class, each member of which possesses its own peculiar properties, it will be easily seen that before any particular colour can be properly thickened its special characteristics must be thoroughly studied, so that it can be prepared in the best, most convenient, and cheapest way. There is a good deal of latitude in colour mixing; each colour mixer adopts the method that yields him the best result, and no two work on quite the same lines; each adapts, and must adapt, his methods to the conveniences at his disposal, and to the demands made upon his department. A colour mixer ill provided with pans cannot hope to keep pace with the printing machines if his system of working depends upon the keeping in stock of a large number of boiled colours. He must make up as many of his colours as possible in the cold, and to this end he utilises his pans for the preparation of large quantities of those thickening pastes that are most generally useful, confining his "boiled colours" to the few that cannot well be prepared in any other way. On the other hand, in a well-fitted colour shop many colours are boiled that could be satisfactorily made up in the cold, and for this reason—that in boiled colours no uncertainty exists as to the complete solution, and even distribution of the various constituents, whereas in "mixed" colours made up from cold pastes it frequently happens that the colour is both imperfectly mixed and "specky," that is, it contains particles of undissolved colouring matter which show up in the finished print as minute points of dark colour. On the whole, however, the tendency nowadays is to boil as few colours as possible, and, except in small works devoted to the production of one or two special styles, a constantly increasing number of colours are made up from previously prepared thickenings. This tendency is the direct outcome of the introduction of artificial, synthetically prepared dyestuffs. In former times the number of colouring matters at the disposal of the calico printer was comparatively small, and large quantities of a few colours only were consumed, the bulk of the work being produced in what is known as the "dyed way." At the present time the reverse is the case, small quantities of an enormous number of colours, diverse both in shade and properties, being in daily demand. The result is that the sum-total of the colour consumed in a modern printworks is distributed over so vastly increased a range of colours that it is virtually impossible to work on the old lines of boiling large quantities of stock colours. The boiling of a colour occupies (with the cooling) the better part of two hours at least, from which it is evident that, if the majority of modern printing colours had to be boiled, an enormous number of pans would be required, not to speak of the extra floor space that would be needed for storage purposes, or of the time lost by the machine printer in waiting for his colours. Moreover, all printing colours are better, in most respects, when freshly prepared. When kept for any considerable length of time they all deteriorate in one way or another: either they lose their tinctorial strength, or their thickenings decompose or otherwise become unworkable. Starch and flour pastes become sour and thin; albumen decomposes; British gums set into a solid mass; natural gums are apt to be coagulated by the substances mixed with them; and the constituents of colours which contain all the elements that are necessary to the formation of an insoluble colour lake are liable to combine more or less, and thus form in the colour paste itself the lake that ought to be formed on the fibre. For these reasons it is inadvisable to prepare an unnecessarily large stock of any colour, which, although in constant demand, is only worked off in comparatively small quantities at a time. The only colours that are made in large quantities and always kept in stock are those which keep exceptionally well, and which enter largely into the majority of the various colour combinations of most of the patterns printed. These colours are known as "standards"; and in works where a large amount of cretonne and other heavy styles of printing are carried on—styles which are executed, for the most part, in the same range of colours—a good supply of such standards is necessarily kept on hand, since they are not only used alone, but also in combination with other colours to form compound shades, such as olives, browns, greys, etc.

Fortunately, the greater number of artificial dyestuffs now sent out by the best aniline colour firms are eminently adapted for mixing with previously prepared pastes.

They are very soluble and of great tinctorial strength, a combination of properties which makes it easily possible to prepare full, deep-printing colours in this way without making the thickening paste too "sloppy" to work properly in the machine. The amount of colour solution required to produce a dark colour is so small, as compared with the quantity of paste used for thickening it, that the printing quality of the mixture remains unimpaired, and in most cases would yield results indistinguishable from those yielded by a "boiled" colour of the same strength and consistency.

All thickened pastes that are printed on woven fabrics are technically known as "colours," whether they contain any colouring matter or not. Some "colours" contain only a thickening agent and a "mordant"; others, a thickening agent and a colour; others, again, contain all three; and yet others are nothing but thickened mixtures and solutions of various substances that are used for the purpose of producing "discharges" or of preventing the permanent fixation of any colour upon those parts of the cloth upon which they are printed.

The preparation of printing colours by the two methods already mentioned can be most conveniently explained by describing the making up of a "steam" colour, that is, a colour developed and fixed on the cloth by a passage through hot steam. Steam colours consist essentially of four parts:—

(1) The solvent.

(2) The colouring matter.

(3) The thickening material.

(4) The mordant or fixing agent, which forms an insoluble lake with the colouring matter.

These four component parts may be either simple or compound, that is, they may, and frequently do, consist of one, two, three, or more members of their class, according to circumstances, and to the effect that their combination is required to produce. The more complex colours will be dealt with in detail in another section of this volume: for the present purpose it is sufficient to take a simple example which will illustrate the general methods of making up a printing colour.

Suppose, for instance, that it is required to prepare a printing colour containing 2 per cent. of Methylene blue which is to be thickened with starch and fixed with tannic acid. In this case the solvent used is generally a mixture of water and acetic acid, together with a small percentage of tartaric acid. If the colour is to be boiled, the *modus operandi* is as follows:—2 lbs. of Methylene blue and 1 lb. of tartaric acid are placed in a small pan and dissolved in 1 gallon of water and ⅛ gallon of acetic acid: whilst this is going on, 12½ lbs. of starch are stirred up in a ten-gallon pan with 8⅛ gallons of water: the colour solution is then added to the creamy starch and water in the larger pan, and after further adding ¼ gallon of rape or olive oil the whole is boiled until the thickened paste just begins to thin down again: at this point the steam is turned off and water turned into the space between the casings of the pan for the purpose of cooling the hot paste: when the paste is cold, 5 lbs. of tannic acid, previously dissolved in ½ gallon of either water or acetic acid, is added to it, and after it is thoroughly incorporated the colour is ready. The above quantities make 10 gallons of colour, which correspond in strength to a 2 per cent. solution of Methylene blue.

The preparation of the same colour from ready-made paste calls for little description. Seven gallons of thick starch-paste are first measured into a tub: 2 gallons of a 10 per cent. solution of Methylene blue, in acetic and tartaric acids, are then poured into it through a fine silk or sateen sieve, a little at a time, each portion being well mixed with the paste before the next is added; when all the colour solution is added, 1 gallon of a 50 per cent. solution of tannic acid is stirred in, and the whole is then ready for use as a printing colour.

Pigment colours and other insoluble substances are usually ground up in a mill with their respective thickenings, any additions being made afterwards: or they are added to their pastes in the form of finely-ground mixtures (with water, etc.) of a "creamy" or "buttery" consistency. Both methods are used, but the former is the more reliable, and is always employed in works furnished with the necessary grinding mills.

With very few exceptions, all printing colours are prepared by one or other of the above general methods; modifications are, of course, introduced in many cases in order to comply with the conditions under which certain colours and mordants must be compounded, but these are questions of detail rather than of principle, and wherever they arise in the following pages they will be noted in connection with the particular styles with which they are associated.

Some colouring matters are capable of forming several different lakes with different metallic salts, and others combine very rapidly with their mordants. In both these instances the colour paste is made up without the mordants, which are added afterwards as required. It is not absolutely necessary to proceed in this way, but it is both the most convenient and most economical system to work upon, because it enables the colour mixer to obtain several effects from one standard paste. For example, Persian berry extract forms with certain tin mordants a strong and brilliant orange lake; with other tin salts it gives a bright yellow; with aluminium and tin it gives another tone of bright yellow; and with chromium mordants it yields a strong yellowish-brown; all of which shades can be produced from one "standard" of thickened Persian berry extract by simply adding the different mordants as required.

Alizarine blue is another colour that yields different shades according to the mordant used. Copper acetate gives reddish-blue, very fast to light; chromium acetate, a quiet, somewhat less reddish shade, also fairly fast to light; nickel acetate, a much purer blue, fast to soaping, but not very fast to light; zinc sulphate, a still purer and brighter blue, similar in other respects to the last; and manganese salts, a bright, quiet shade of blue, much greener than any of the preceding. All these different mordants act very rapidly on the Alizarin blue, so much so in fact that fully made-up colours will not keep good for more than two days at the outside. Alizarin itself is perhaps the most typical of this, *the adjective*, class of colouring matters, since it gives entirely different colours with aluminium, iron, chromium, and tin mordants; but, with the exception of the reds and pinks that are made from it, it is made up in one of the two ordinary ways. The reds and pinks are unstable, and are usually prepared fresh each day.

Formerly it was the custom to manufacture most of the various dyewood extracts, mordants, and other liquors used for colour making in the printworks itself. At the present time, however, the making of colouring matters and extracts is a separate industry, which has been developed to such an extent and brought to such a pitch of perfection that its products can be bought in the market at a much cheaper rate than they could possibly be made at in any printworks. One or two vegetable extracts and a few simply made colouring matters are still manufactured occasionally in some printworks where the necessary plant exists, but, generally speaking, the whole of the raw material of calico printing that requires special plant, and a specially trained staff of chemists for its manufacture, is now bought ready-made, and in a condition fit for immediate use. Artificial dyestuffs, in particular, could not possibly be made at a profit, and in any quantity in a printworks; for their manufacture on a commercial scale they demand not only a specialised knowledge of the subject, but the constant supervision of experienced expert chemists, who are thoroughly conversant with every detail of the various stages through which the raw material passes. Artificial dyestuffs, then, must be bought as such, but this does not apply, except in a few cases, to the mordants and other preparations which are used for fixing them on the cloth, or for enhancing their brilliancy and effect.

These are always made on the spot in all printworks of any standing: their composition is then known, and they can be modified at will and without any trouble. Besides, they are cheaper, because they entail no charge for the carriage of mere water, which constitutes the greater part of their weight. "Mordants" possessing all sorts of extraordinary advantages can be and are bought by the score, but they are best left severely alone. Their composition is usually disguised under a fancy name; and even if it be given, it will be found frequently to represent only partially what the "stuff" contains. Many of these mordants are quite good and answer their purpose perfectly, but none of them, unless they be patented articles, are any better than those made by a capable printworks chemist, and, in addition to being more expensive than the latter, they cannot be modified until their composition has been ascertained by a more or less lengthy analysis; in a word, such mordants, etc., are unnecessary additions to the cost of production, and ought to be avoided, on all counts, if at all possible. Such products as tannic acid cannot be made in the colour shop, but most of the other mordants and preparations in common use can and ought to be made there, partly because they are cheaper to make than to buy, partly because they are more regular in composition, and partly because the colour mixer then knows exactly with what he is working, and can thus alter his colours at once, and in the best way, for any special purpose.

Working instructions for the making up of the more important mordants, etc., will be given in the section on "Mordants."

Straining of Colours.—No matter how carefully colours have been made, they always contain either lumps and hard pieces of thickening, or foreign insoluble substances, which give rise to imperfect printing if allowed to remain. A certain amount of thickening invariably cakes on the sides of the colour pan during the boiling process, and portions of it are unavoidably detached and fall into the colour when it is emptied out, making it "lumpy"; and, again, when colours are kept in stock, a skin of dried thickening forms on their surface, and although this can be skimmed off to a great extent, portions of it are liable, nevertheless, to become incorporated with the smoother paste beneath. Another cause of "lumpy" colour is due to the drying of the thickening on the sides of partially empty storage casks: the dried paste forms hard, brittle scales, which drop off into the colour below. The foreign insoluble bodies usually present in freshly prepared printing colours consist, for the most part, of grit, chips of wood, woody fibre, leaves, sand, and particles of metal,—small quantities of all of which are apt to get into thickening materials and colouring matters during the process of manufacture. Natural gums are especially liable to contain sand and woody fibre, as might be expected from the way in which they are collected; and substances that come into the market in the form of finely ground powders are also exceedingly liable to contain all sorts of grit and dust, which no amount of care can entirely prevent from settling upon them whilst they are kept in stock. Particles of metal are also mixed with them during the operation of grinding. In the case of gums and substances that are used in solution, the greater part of the gritty impurities can be eliminated by allowing them time to deposit; but with thick pastes like starch and some of the dyewood extracts this cannot be done, and the only way to get rid of solid impurities is to strain them out. Some low qualities of starch and British gum contain a peculiar organic body which is disseminated in an insoluble form throughout the entire thickening and cannot be removed in any way. The finer parts of it pass through the straining cloth, and, in printing, they fill up the engraving with a sticky glue-like paste; the coarser parts stick in the meshes of the straining cloth and gradually fill them up with a gelatinous mass, which effectively prevents the passage of the colour, and renders straining impossible. Such thickenings are absolutely useless, and ought to be returned to the vendor at once.

Colours are usually strained by hand directly into the tub that is to be sent into the machine room. A piece of calico is spread over the tub and the colour poured into it; the ends and edges of the calico are then gathered up in the left hand of the operator so as to enclose the colour in a sort of bag; this bag is now twisted with the left and squeezed with the right hand until its contents have passed through, leaving behind only such portions as are too large to escape through the meshes of the calico. If the colour is very rough to start with, or contains a good deal of grit, it is strained through one cloth into another, as many cloths being used as are thought necessary, and each one being finer in texture than the one preceding it. The advantage of using a series of graduated "strainers" is obvious: any large, soft lumps of thickening are broken up in passing through the coarser cloths, the bulkier pieces of hard starch, undissolved gum, or dried scales of colour are removed at the outset, and the paste gradually becomes smoother and smoother, until it will finally pass through the last and finest cloth almost unchanged.

Very lumpy colour, or colour composed of several standard colours roughly beaten together in the "mixing tub," cannot be properly strained through one cloth, however fine. The lumps squirt through the interstices in little worm-like masses, which cannot be beaten into a smooth paste, and mixtures of different colours, especially if they be of different thicknesses, are always better when strained twice at least, since the act of straining goes a long way towards mixing them into a homogeneous paste.

Various kinds of mechanical strainers have been put on the market from time to time, with the object of replacing, or at least reducing the amount of, hand straining. So far, they have failed to do this to any very great extent, not because they are not efficient so far as straining *per se* is concerned, but because they can only be used with advantage when large quantities of one colour are required by several printing machines at the same time. In an ordinary modern printworks, doing a great variety of styles, these occasions are of rare occurrence (once or twice a year maybe), so that, unless the straining machines are used for the needless straining of standard pastes and colours, which always have to be strained again before use, they stand idle for the greater part of the time. On the other hand, they are exceedingly useful to those firms who turn out large quantities of "madder work"—a style in which but few printing colours are used, and those regularly and in enormous quantities. Madder colours are always boiled; and they are frequently consumed at so great a rate that there is no time to cool them before printing, if the printing machines are to be kept constantly running. In such cases a straining machine, capable of straining fifteen or twenty gallons of almost boiling colour in a couple of minutes, is of inestimable value, and can scarcely be dispensed with. There is no constructional reason why straining machines should not be used for small lots of colour; but, considered from a practical point of view, they are altogether useless for this purpose, for the simple reason that they require thorough cleansing every time a fresh colour is put through them. More time would thus be occupied in washing them out than in straining colour. Apart from loss of time, machine-strained colours are only suited to comparatively coarse work, so that in any case straining by hand must be resorted to for delicate engraving, and for all designs of the highest class. The better a colour is strained the better will it work, and the more perfect will be the final result.

Defects in Printing Colours.—Apart from accidents, defects in colours may be attributed to (1) bad straining, (2) faulty or careless mixing, (3) to the colour being too thin or too thick, (4) frothing, and (5) "sticking-in."

(1) BAD OR INSUFFICIENT STRAINING is answerable for that kind of bad work which consists of "streaks" and "snappers," both of which have been mentioned already in dealing with roller printing. However carefully a thickening is made it is liable to contain solid substances, which, if allowed to remain in the colour, become jammed between the doctor and the roller, and by lifting the former out of contact with the latter at the particular point where the obstruction happens to be, allow a certain amount of colour to escape the cleaning action of the "doctor," and thus cause a long, unsightly smear, varying in width according to the size of the obstruction in question. Such defects are known as "snappers" or "snaps" from the sharp sound made by the "doctor" in returning to its original position on the roller when the hard particle escapes from under it. In addition to lifting the doctor blade, these solid particles of grit either snip the

doctor edge or scratch the plain surface of the roller, thus producing "streaks"—fine lines—which ought not to appear at all. Loose filaments of cotton and lint, left in the colour from a previous printing also give rise to "streaks" and "snappers" in the same way, that is, by sticking between "doctor" and roller. Fortunately they neither injure the roller nor spoil the doctor edge, but they usually give much broader smears; and if they happen to stick on an engraved part of the roller, they prevent it from taking up colour, and consequently that portion of the pattern fails to appear on the cloth. The only remedy for these defects is to re-strain the colour, and make perfectly certain that it is quite free of all foreign matters before it is returned to the printer. Any particles of finely divided copper that may be found on straining have found their way into the colour in the machine room, and their presence is to be put down to the roller grinding against some hard substance with which it ought *not* to be in contact.

(2) Faulty "Colour mixing."—It frequently happens that printed colours, instead of being perfectly flat and even in tone, present a mottled appearance, due to the presence of numerous and minute "specks" of dark colour. These "specks" may be caused in newly-made colour by imperfect solution of the colouring matter; by the insufficient sieving of pastes, like Alizarin, etc., before they are added to the thickening; by not grinding insoluble lakes and pigment colours finely enough; and by irrationally mixing together colours or mordants which mutually precipitate each other. A particularly flagrant instance of the last cause of "specky" colour occurred in a large and old-established printworks near Manchester, where the foreman colour mixer attempted to modify the shade of a "steam" Alizarin colour with lampblack ground up in albumen. The formation of "specks" in colour that has been used previously with satisfaction is due to the precipitation of the colouring matter by the mordant: it occurs chiefly in old, basic aniline colour pastes, Alizarin colours, and in various mixtures of these with each other and with natural dyestuffs. There is no way of remedying "specky" colour; and the only way of preventing it is to see that it is prepared properly in the first instance, and to avoid using colours that have been in stock a long time—at least, such as are liable to decomposition.

Very often colours made up of mixed thickenings cause a great deal of trouble in working. They may appear to be all right at first, but little by little the thickening separates into its constituents, which, being of different consistencies, are absorbed unequally by the cloth, thus causing bad work in the way of cloudy, uneven colour. Sometimes this separation of the thickening is caused by the chemical action of the various substances contained in the colour, and cannot always be foreseen; but generally it is the result of carelessness (or ignorance) on the part of the colour mixer, in mixing together such things as starch and gum Senegal, or flour and gum arabic, both of which combinations are excessively unstable when mixed in the cold, and are always unreliable even when boiled together. Flour, starch, and gum tragacanth work well together; also starch and the British gums; but the latter ought not to be mixed with tragacanth unless they are very starchy, and even then they are apt to separate out again. The natural gums—Senegal, gedda, arabic, and the more insoluble sorts—ought to be used alone, as they very rarely work well with any thickening outside their own class.

It is scarcely necessary to point out that compound shades made by mixing two or more standard colours together, and colours reduced in strength by the addition of extra thickening paste, must be always well stirred up in order to ensure their perfect incorporation. Any neglect of this elementary precaution results in uneven printing, and is inexcusable in an experienced colour shop hand. With strong pigment colours it is often quite impossible to maintain the homogeneity of the colour, especially if it has to be used thin. Heavy bodies like vermilion and the lead chromates cannot be prevented from settling to the bottom of the tub, or, if in the printing machine, to the bottom of the colour box. All that can be done to lessen this great disadvantage is to use only the most finely ground pigments, to make the printing colour as thick as is consistent with the work in hand, and to stir it up well at frequent intervals, both in the tub and in the colour box of the machine.

(3) THIN AND THICK COLOUR.—The consistency of a colour exerts considerable influence on the quality of the impression produced by the engraved roller or block upon the cloth. Within certain limits the printer is the best judge of the thickness of colour required for certain styles of work and different scales of engraving, and wherever possible he ought to be supplied with the sort of colour he thinks he can work with best. But it is no part of the printer's duty to dictate the kind of thickening material to be used in any given case, although, if he be an experienced workman, any suggestions he may make respecting the working quality of the colour will, as a rule, be considered, if they are at all reasonable. At the same time no printer is expected to interfere with the working of any department outside his own, neither is he justified in ordering a particular colour on his own authority, nor in refusing to give a trial to a "gum" colour simply because it is *apparently thinner* than a "starch" colour that he has just successfully printed with the same roller. It is impossible for anyone by mere inspection to estimate with any degree of certainty the relative printing values of two colours that are thickened with totally different materials. Gum thickenings rarely or never appear to be as thick as starch, flour, or tragacanth pastes; but thickness, considered merely as stiffness, is not the only desirable quality in a printing colour. It must also possess a certain "body," and this, to a great extent, is dependent upon the density and viscosity of its thickening; in other words, upon the percentage of dry thickening material it contains, and upon the nature of that material. Gum solutions often contain three or four times more dry thickening than starch and other similar pastes, and consequently "gum" colours frequently give a much crisper and more perfect impression of the pattern than could be obtained from a "starch" colour *apparently* many times their thickness. Some colours are best thickened with gum, others with paste; and the colour mixer or the chemist is the only person who is sufficiently acquainted with the properties of colour materials to know exactly what to use in a given case.

Colours may, however, be suitably thickened, as far as regards material, and yet not work well in the printing machine. When this happens, the source of the trouble will usually be found to be the consistency of the colour. If too thin, it gives a slovenly, blotted impression of the design: the colour spreads out, by the capillary attraction of the cloth, beyond its proper limits, all the lines and masses of the pattern exhibit soft, spongy edges, the finer details run together, and the whole effect has an unsightly, blurred appearance, due to the general lack of sharp definition.

Sometimes the "blotch" (background) and other large patches of colour in a printed pattern, instead of being uniform in shade, present a peculiar, irregular, mottled appearance, consisting of small spots and other variously shaped objects of light colour, distributed unevenly over the surface of the darker colour in which they occur. This particular form of unevenness is known as "blebbing," and arises from the use of colour that is too thin for its immediate purpose. "Blebbing" mostly occurs with paste colours (starch, etc.), and is not always due entirely to their excessive thinness, but to that, coupled with the unsound condition of the paste itself. On standing for some time starch and other pastes break up into a curdy-looking mass, become somewhat "watery," and lose their smooth, soft, "gummy" feel. If such pastes are let down with water to make thin colour—a procedure often adopted—they further lose what little "body" still remains to them, and, although they may be beaten up and strained into a seemingly smooth paste, become "sloppy" and quite unfit for printing. Even freshly made starch paste is apt to undergo the same transformation when diluted largely with cold water—a fact so well recognised in practice that in all well-managed colour shops extra thin paste thickenings are always specially boiled as required. The actual cause of "blebbing" is that, owing to the lack of viscosity or "body" in the colour, the roller fails to retain a sufficient supply of it to transfer a full impression of the pattern to the cloth; in other words, the thin, slushy colour slips out of the engraving before the latter comes in contact with the cloth, thus causing meagre, uneven impressions.

Colours that are too thick also produce very bare, weak impressions; not because there is any deficiency of colour in the engraving, but because it is too solid to be absorbed freely by the cloth. Delicately engraved patterns printed with *very thick* colour scarcely make a mark on the cloth, and heavy patterns, coarsely engraved, leave an impression which, instead of being full and even, lies on the surface of the cloth, and shows up nearly every line of the engraving. Both these faults are due to the same cause, namely, the inability of the colour to soak into the body of the fabric.

The remedy for printing colours that are either too thick or too thin is obvious.

(4) Frothing.—During the operation of printing, many colours are exceedingly apt to froth, especially if a brush "furnisher" is used in the colour-box. The more a colour froths, the lighter in shade does it become and the more does it increase in bulk, so that, quite apart from causing bad work, it also causes a great deal of inconvenience by overflowing the colour box, and either flooding the floor or dropping into any other colour that may be working along with it. The froth consists of a mass of minute air bubbles mixed with the colour, and is produced by the agitation which the colour undergoes in the colour box, a sort of churning action, kept up continually by the combined motions of the roller, furnisher, and doctor. The colours most liable to froth are those containing a large percentage of gum, albumen, and other elastic thickening agents, all of which, for some ill-understood reason, retain bubbles of air much more tenaciously than do starch and other pastes of a similar nature. With the exception of the acetates and formates, none of the mordants in general use are capable of forming more than a momentary froth when beaten up with air, and the same may be said of the solutions and preparations of most of the colouring matters. Pigment and lake printing colours containing soap solutions or glue-paste in addition to albumen foam up very rapidly unless they are printed at a slow speed, and even then they soon become quite unworkable if the pattern takes up too little colour to allow of the box being constantly replenished. The longer a given portion of colour remains in the box the more will it get churned up, and the sooner will it become utterly useless.

In order to reduce the tendency of certain colours to froth, it is customary in practice to add to them small quantities of benzine, turpentine, or oil, and in the case of albumen colours, to further supplement these with a little ammonia. What rôle exactly these substances play in preventing the retention of air bubbles by gum and albumen colours has not yet been thoroughly explained, but it is probable that they reduce the surface tension of the thickenings, and thus enable the air to escape more readily. In any case, although they are not perfect preventives, they at least preserve the colour in working condition for a considerable time, and keep down all excessive frothing.

(5) "Sticking-in" of Colours.—It often happens that some portion of a colour settles in the engraving of a printing roller, and persistently refuses to

leave it when the cloth is pressed into it, the result being a weak and uneven impression of the pattern. This serious defect—known as "sticking-in"—is most frequently encountered in pigment colours, Indigo, Aniline black containing insoluble salts of copper or lead, and in the numerous "discharges" and "resists" that contain china clay, zinc dust, zinc oxide, chalk, lead sulphate, and other insoluble matters; but it is also liable to occur in many printing colours which have been kept in stock too long, and in which a precipitate has been formed either by some of the constituents coming out of solution, by the combination of the mordants and colouring matters, or by the reaction of the latter on the thickening. The colours most subject to spontaneous decomposition of this sort are old Alizarin colours, basic aniline colours, Logwood and iron blacks, "steam" mineral colours and Catechu browns, etc.,—in short, just those colours in which the colouring matters and mordants are mixed together, and especially those that contain easily dissociable compounds or mixtures which readily form more or less insoluble lakes when allowed to stand for any length of time.

The "sticking-in" of pigments, and the like, is generally due to faulty mixing; either the pigments are too granular, or the thickening is too thin. In either case, or both combined, the cloth only absorbs the soluble part of the colour, leaving the insoluble part in the engraving, where it accumulates until the whole is almost filled up to the level of the smooth surface of the roller. A thick colour naturally prints better than a thin, watery one, since it holds the insoluble matter in suspension better, and thus prevents it, in a great measure, from settling; but thick colours cannot always be used in pigment printing, nor are they always effective when they can, so that where 'sticking-in" does happen with a pigment colour, the best remedy is to regrind it until it is in too fine a state of division to settle easily in its thickening. All *strong* pigment colours and others that contain, of necessity, *large* amounts of insoluble matter, are liable to "stick-in," however carefully they may be made, and from all points of view they are perhaps the most difficult to print. The "sticking-in" may be overcome almost entirely by replacing the ordinary wooden "furnisher" roller in the colour box by a revolving brush; but while this keeps the engraving clear of deposited colour, and thus does away with one inconvenience, it tends unfortunately to give rise to another, namely, frothing—a defect which is, as previously pointed out, extremely likely to be developed in "albumen" and "gum" colours when a brush furnisher is used.

As regards the "sticking-in" of other colours, very little can be done to remedy it. Sometimes the addition of a little oil will improve matters, but usually when a mordant colour works badly from this cause it is useless, since the precipitate which ought to have been produced in the fibre of the cloth already exists in the colour. Old basic aniline colours may be rendered workable sometimes by gently heating them with a little acetic and tartaric or citric acids, which re-dissolve the colour lake, but, as a rule, it is safer to make a fresh lot of colour, especially if it be a light shade, and cheap in consequence. Dark and expensive shades can be treated as above, and worked off little by little with newer colour. Old Alizarin reds are often mixed with Logwood black or Persian berry yellow and a little iron mordant, and then used up as dark chocolates: sometimes they work well, but usually they "scum" and "streak" badly, and cause more trouble than they are worth.

Very finely divided precipitates are often quite workable, even when they are unintentionally present in a colour; and if the lakes they consist of are only loosely combined with the mordants (that is not completely developed), they occasionally yield a colour very little, if at all, inferior in brightness and fastness to that which would have been yielded had the printing colour been in perfect condition to start with. The cloth takes up the fine precipitate, and subsequent processes complete the reaction which started in the colour itself, converting the partially formed lake into an insoluble compound which adheres firmly to the cloth. On the other hand, however, a partly decomposed colour more often than not produces bad work, either by "sticking-in," by giving a lighter shade than was intended, or by washing out of the cloth unevenly during the final soaping operations which effectually remove any loosely fixed insoluble bodies that have been transferred to the cloth along with the thickening and which become detached when the thickening is washed out. It is therefore better to avoid, as far as possible, the introduction of precipitates, however fine, into colours that are not intended to contain them, inasmuch as such precipitates cannot be relied upon to work well, and in most cases represent a dead loss of colour.

Alizarin, Anthracene brown, and other colouring matters, which are of necessity applied to the cloth in the form of finely divided powders, ground up into a paste and then thickened, often cause a good deal of trouble by "sticking-in," and this can be obviated only by thoroughly sieving them through fine silk cloth before mixing them with their mordants and thickenings, and afterwards straining the made-up printing colour through the finest of "jean" cloth before sending it in to the printer. If the colour works badly after this careful preparation, the fault lies with the colouring matter itself; some brands of Alizarin and similar pasty colours resist all efforts to strain them; they settle into a dense, clay-like mass, which clogs the straining cloth and refuses to pass through by any means whatsoever. When this is the case it is useless to attempt to make workable printing colours of them; the only thing to do is to return them at once to the maker,—they are absolutely unfitted for printing purposes, and, as a rule, too expensive, or the wrong shade for use in the dye-house.

Unworkable precipitates are also formed in printing colours by the irrational mixing of two or more colours to produce a compound shade. While it is true that many colouring matters and mordants, of widely diverse properties, may be and are mixed together with excellent effect, it is also true that many others mutually react upon each other, with disastrous results. If the colouring matter is not destroyed entirely, it is at least diminished in tinctorial strength, or is altered in such a way as to be incapable of proper fixation upon the cloth; and if the mordants have been precipitated, they are liable either to "stick-in" or to scratch the roller. In order to avoid these accidents the most competent colour mixers utilise, as far as possible, for their compound shades, only such colours as are fixed by the same mordants, and possess a strong family likeness as regards fastness to light and washing. In this way they obtain mixtures which not only work as well as any one of their constituent colours, but which have the further advantage of behaving as a single colour when subjected to the action of soap or light; that is, they fade or wash out evenly, without undergoing any very great alteration in general tone. On the other hand, mixtures of "fast" and "loose" colours can never be depended upon to give regular results; and as they usually belong to quite different classes of colour stuffs, they are apt also to combine with each other, forming insoluble bodies which are difficult to work; in consequence, colours differing widely in general properties ought not to be mixed together unless the effect aimed at cannot be obtained in any other way.

From the foregoing rough outline of the "generalia" of colour mixing it will be seen that, apart from all questions of correct shade and colour harmony, the technical perfection of a calico print depends in a great measure upon the proper preparation of the colour paste; that is to say, upon its physical nature—thickness, softness, freedom from grit, etc.,—as distinguished from its chemical composition.

With a view to avoiding the various mishaps brought about by faulty printing colours, it is usual to observe the following precautions:—

(1) All water used is examined for dirt and fine sand, and, if not free from

these impurities, is filtered or allowed to settle. Condensed water should be used wherever available.

(2) Gum thickenings, especially natural gums, are allowed to settle as long as possible before use. They invariably contain fine gritty particles of one sort or another which cause damage.

(3) Starch and flour, known to contain grit and sand, or bodies that form gelatinous or flocculent precipitates on boiling, should be mixed with cold water into a thin milky fluid, and then "jigged" (strained or sieved by shaking) through fine straining cloth before being used for thickening purposes. Such impurities are most difficult to strain out after boiling.

(4) Pigment colours and other insoluble constituents of a printing colour must always be ground to the finest state of division possible, otherwise they are liable to "stick-in."

(5) Soluble bodies ought to be completely dissolved: if colouring matters, they are also passed through a fine silk sieve into the thickening paste, so as to avoid "specks."

(6) Colours thickened with dry starch or flour must be well boiled first and then thoroughly cooled before the mordants (if any) are added: neglect of these two points results in a badly-working colour.

(7) When a small quantity of one colour is added to a large quantity of another it must not be thrown in bodily, but gradually diluted with successive small portions of the larger bulk, until it can be safely mixed in without any fear of its being unevenly distributed throughout the mass.

(8) All colours must be thoroughly well strained and stirred up before being given into the hands of the printer.

(9) All colour tubs, etc., must be thoroughly cleansed and well rinsed out with clean water before receiving their contents.

These simple workshop precautions appear to be considered by most writers on calico printing as insignificant details, unworthy of even passing mention, but they are none the less important on that account. They may be regarded, and justly so, as mere "commonplaces" of colour mixing, but at the same time their observance constitutes one of the fundamental conditions of success in all calico printing, and forms an essential part of the routine work connected with the preparation of every single printing colour. No matter how perfect a colour may be in other respects, if it be compounded without due regard to its working qualities it is practically certain to possess one or other of the defects already noted; haphazard, careless colour mixing, done in ignorance of what to expect in the way of faults, and of how to avoid them, always results, sooner or later, in bad work, damaged rollers, spoiled cloth, and a general loss of time and material.

In fine, a good colour is the *first* essential to good work, and a good colour can only be obtained by paying the utmost attention to every detail of the many consecutive operations which are involved in its preparation.[1]

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[1] For information concerning the making of compound shades from ready-made "standard" colours reference must be made to the section on "Styles of Printing." It is impossible to give any details until the actual composition of the colours in question has been dealt with.

PART V.

TREATMENT OF GOODS AFTER PRINTING.

TREATMENT OF GOODS AFTER PRINTING.

Before proceeding to a fuller consideration of the question of "colour mixing"—a question to which it will be necessary to return when dealing with the practical details of the application of the various classes of colouring matters to the different "styles" of printing—a few general remarks on the after-treatment of printed calicoes, as compared to that of the products of an apparently similar manufacture, may not be out of place at this stage.

From the fact that the mechanical means employed for the printing of coloured designs on wall-papers and textiles is, to all intents and purposes, identical, it might be surmised that some analogy also existed between the composition and modes of fixation of the colours applied to them respectively. Such, however, is not the case: no such analogy exists or is possible; for although wall-paper is like calico in that it consists essentially of cellulose, its physical structure precludes any possibility of its being treated in the same way as a textile fabric. In fact, all resemblance between the technique of the two manufactures begins and ends with the printing of the design. Moreover, the uses to which a wall-paper is put do not require its colours to withstand the same wear and tear as those of a calico print. Without discussing this point, it may be interesting to note that in wall-paper printing a ready-formed colour (along with suitable vehicles, such as size, paste, or varnish) is applied to the surface of the paper, that it is sufficiently fixed thereon by the simple process of drying, and that it consists in its finished state of a mechanical mixture of colouring matter and vehicle or thickening; whereas in calico printing (excluding pigments) of the highest class a colour of requisite permanency or "fastness" can only be produced on the fibre itself by some process of local dyeing, and that a calico print in its finished state is freed, as far as possible, from all thickening matters which have been used during the printing, and which, if allowed to remain, would only impair the beauty of its colours.

With a few exceptions, the colours appearing on a piece of calico as it emerges from the drying apparatus attached to the printing machine do not exist as such, but consist of various substances, or mixtures of substances, which are capable either of attracting colouring matter from a dye bath, or of reacting upon each other, under suitable conditions, to form an insoluble colour lake. From this it is clear that the final process of wall-paper printing corresponds exactly to the initial stage in the production of a printed pattern on calico; for while a wall-paper is practically ready for the market immediately after printing and drying, a calico print in the same state requires further treatment before its colours are either developed or "fixed." Of course a piece of calico can be printed in precisely the same colours as a piece of wall-paper if need be; but in that case it would not possess that quality of resisting the action of soap which has come to be looked upon as characteristic of a good "print," and in consequence such a procedure forms no part of the practice of calico printing, although it is true that "loose" work of a different kind is produced for some markets.

The object of this perhaps somewhat irrelevant comparison of wall-paper printing and textile printing is to show (*a*) that, in general, colours of the requisite permanency cannot be obtained on textiles by the mere evaporation of a solvent or of the soluble parts of a vehicle; (*b*) that the colouring principles best suited to textile printing are those which are capable of penetrating into the fibres of the material, and of being converted therein, by chemical means, into insoluble compounds and colour lakes; and (*c*) that the development of the colour proper on textile goods is dependent upon some process of dyeing, which, whether it be performed during or after printing, must of necessity be followed by a thorough washing of the pieces, in order to remove from the *unprinted* parts all loosely adhering colour, and from the printed parts as much as possible of the thickening material used in the original printing paste.

The purpose in making this digression from the main subject of the present chapter is to point out that the printing of a design in "fast" colours on a textile fabric may be regarded broadly as involving two separate and distinct series of operations: the first leading up to, and completed by, the printing process; the second connected entirely with the development, fixation, and brightening of the printed colours, and with the removal from the cloth of all thickening agents, and of the dye stains, and various by-products that have been formed in the course of working. Hence, the printing process, forming, as it were, a dividing line between two quite distinct sets of operations, all work put into a piece of cloth after printing comes under the comprehensive heading of "after-treatment."

As might be expected from the immense number and diverse properties of the different colouring matters now employed in calico printing, this "after-treatment" varies according to the class of work in hand. Sometimes it is simple and short, sometimes long and complex, and at all times most important, especially in its earlier stages, since these cannot be repeated when once the cloth has been dyed or washed.

All after-treatments, with one or two unimportant exceptions, consist of various combinations of two or more of the following processes:—

(1) Ageing.
(2) Dunging.
(3) Dyeing.
(4) Steaming.
(5) Fixing.
(6) Raising.
(7) Cutting.
(8) Washing.
(9) Soaping.
(10) Clearing.
(11) Drying, etc.

These several processes do not each correspond to one limited and definite mode of working, but each represents a distinct group of similar operations, which differ from each other in detail rather than in principle.

The same operation may be performed in different types of machine, and the same machines may be equally well used for widely different purposes. Such modifications as relate to the practical manipulation of the above processes will be dealt with in a general way here, but all discussion respecting the *rationale* of particular "after-treatments" will be deferred to a later section of this volume, in which typical examples of the more important "styles of printing" will be considered in detail. It would be out of place at this point to dwell on the chemistry of the subject; in fact, it is unnecessary to do so, as each "style" will be treated as a whole later on, and adequate reasons will be given for every step in its production. In order to avoid useless repetition, therefore, the following remarks will be confined to a general description of the principles and methods of working the above processes.

(1) AGEING.

Strictly speaking "ageing" consists in exposing certain printed goods to the more or less prolonged action of a warm, moist atmosphere. Experience has shown, however, that equally good results can be obtained in most cases by running the goods through hot steam, and, in consequence, the meaning of the term "ageing" has been extended to include all such improved processes.

The objects of "ageing" printed goods are many and various. Amongst them, the following may be mentioned as the most important:—(1) to bring about such changes in printed iron and aluminium mordants as will enable them to undergo the dyeing operation without spreading or "bleeding" into the unprinted parts of the cloth; (2) to promote the oxidation of Aniline black, Catechu brown, Manganese bronze, etc.; (3) to effect the reduction of Indigo and similar colours by one process, and their subsequent re-oxidation by another; (4) to provide the necessary conditions under which certain oxidising and reducing agents are capable of discharging the colour from those parts of an uniformly dyed fabric upon which they are printed; and (5) to assist generally in the formation and fixation upon the fibre of numerous colours and mordants which require either to be run rapidly through hot steam or to be exposed to air, under certain conditions of time, temperature, and humidity, for their proper development.

These various effects are produced by four different methods of "ageing": (1) by hanging the goods in large, specially constructed "ageing" or hanging rooms; (2) by passing them through a continuous ageing apparatus, wherein regular conditions of temperature and moisture are maintained; (3) by a short steaming in the Mather & Platt continuous steam "Ager"; and (4) by a recent modification of the last, in which damp steam is replaced by dry, superheated steam. Each of these systems of ageing possesses qualities which render it peculiarly adapted to certain classes of work, and therefore the choice of the particular one to employ must be guided by the requirements of the style of work under treatment.

(1) **"Ageing" or "Hanging Rooms."**—Ageing was at one time carried out in immense brick or wooden chambers, heated at first by fire-brick or iron flues from furnaces beneath, and later by rows of steam pipes arranged underneath the grated floors. In the days when block printing was the only available means of impressing patterns on calico these chambers were known as "stoves"; and as it was generally believed that heat was the only factor required to convert the iron and aluminium mordants into a fit state for dyeing, no provision was made for the introduction of moisture. This is easily understood when it is remembered that the printed pieces were allowed to hang in the printing room until they were sufficiently dry to be transferred to the stoves without any fear of the colours "marking-off" or smearing. During this hanging in the printing room the processes of drying and "ageing" went on simultaneously; and as good results were obtained, in dyeing, after the subsequent "stoving," it was only natural to infer that dry heat was all that was required to effect the necessary changes in the printed mordants. With the introduction of roller printing, however, this theory had to be abandoned. It was at once found that goods dried over steam-heated cylinders, or in hot-air machines, required several days' exposure to cool air before they could be made to take a full, deep shade in the madder dye-bath. The result was that the stoves were converted into cooling or "ageing" chambers by withdrawing the heat. To a great extent this was an improvement, but still irregularity in dyeing was of constant occurrence, and it was noticed that the poorest and weakest colours were always obtained during very dry or very frosty weather. The outcome was that many chemists undertook researches on the subject; but it was not until 1828 that D. Koechlin finally set at rest all doubts as to the proper conditions under which regular "ageing" might be ensured independent of climatic variations. In the published report of his investigations (*Bulletin de la Société Industrielle de Mulhouse*, 1828), he not only points out that moisture, no less than heat, is an absolutely essential factor in "ageing," but also that a more or less definite relationship should exist between the degrees

of temperature and humidity, and that these should be kept as constant as possible during the whole operation. The temperature varies between 22° C. and 36° C., the moisture being regulated to show about 3° C. lower on the wet bulb thermometer than on the dry bulb thermometer.

In consequence of D. Koechlin's determination of the most suitable conditions under which "ageing" could be performed, the "cooling rooms" were re-arranged to conform to them, and no further trouble was experienced in the production of "madder-dyed" work printed by machine. In these chambers, which are from 25 to 40 or more feet in height, the printed goods are hung in long loops from a series of wooden bars or rails which form a sort of secondary skeleton ceiling, between which and the roof proper sufficient space is allowed for the workmen to move about whilst hanging the cloth. The floor may be either of wood, stone, or iron grating, and the windows, doors, and roofs must all be double in order to conserve the temperature, and to avoid the condensation of the moisture in the form of drops which play havoc with the marketable value of any goods they fall upon. The necessary heat is supplied from steam pipes arranged around the base of the walls, and at frequent intervals across the floor or under the gratings; and the moisture is obtained from the same steam pipes through funnel-shaped jets, provided with taps for regulating purposes. The funnels are covered with wool or calico to prevent the accidental splashing of the pieces if the taps happen to be open too wide or the pressure of the steam increases suddenly.

The regulation of the moisture is based upon the well-known scientific fact that the closer the atmosphere approaches to the point of saturation with aqueous vapour, the more closely does the temperature registered by the wet bulb thermometer creep up to that indicated by the ordinary dry-bulb thermometer. If, therefore, the predetermined difference between the two thermometers tends to decrease, too much moisture is present in the ageing chamber, and the steam supply must be diminished until the original conditions are restored; if, on the other hand, the mercury in the wet-bulb instrument drops, the moisture is deficient, and must be increased by opening the taps in the funnel-shaped steam jets.

The goods are allowed to hang in these chambers for from one to six days, according to circumstances. If they are simply printed in aluminium mordants, one day may be quite sufficient to fully "age" them; but if they also contain iron mordants or Aniline black or Catechu, a much longer time will be required as a rule, since these latter must undergo a veritable oxidation, whereas the alumina mordants only lose acetic acid. In the case of Aniline blacks developed by this method of slow "ageing," it may be noted that great care should be taken to avoid exposing them to cold currents of air during the period that elapses between the time of printing and the time of hanging, cold air preventing the formation of a full shade. The exposed parts present a more or less grey appearance, and no amount of either steam or chromic acid oxidation will afterwards convert the grey parts into black.

The end and aim of "ageing" by hanging in a warm, humid atmosphere is to fix, as far as may be, the various colours and mordants that are used in the well-known *Madder style* of printing. A great many eminent chemists and calico printers have devoted a vast amount of time to the study of the ageing process, with a view to explaining the real nature of the chemical and physical changes that take place in mordants, etc., under the combined influence of time, temperature, and moisture. This study has been of inestimable value to the industry, but so far has failed to supply any incontrovertible evidence as to whether the mordants, etc., are actually combined chemically with the cotton fibre, or whether they are merely fixed thereon mechanically. What is definitely known is that large quantities of acetic acid are liberated in the ageing rooms, and that the mordants are left upon the fibre in the form of insoluble basic salts; that iron mordants, *i.e.* ferrous salts, are oxidised or converted into mixtures of basic salts of uncertain composition; and that colours capable of absorbing atmospheric oxygen do so in varying degrees, according to the length of time they remain in the chamber. Apart from the temperature and moisture of the atmosphere of the "ageing room," the amount of acetic acid and other vapours present exercises a considerable influence upon the speed and effectiveness of the ageing. It stands to reason that if the chamber is overcharged with free acetic acid vapour its efficiency will be reduced, by reason of the fact that the evolution of the acid still retained as acetate by the mordants on the cloth will be retarded, if not prevented altogether; and further, if heavy patterns, printed with strong iron mordants, are hung in a closed chamber, they rapidly absorb all the available oxygen, or at least most of it, before they are sufficiently "aged," with the result that irregular work is produced. The same obtains with such colours as Aniline black and Catechu brown when used in conjunction with the mordants for madder colours. The remedy for these disadvantages is obvious, viz. ventilation. This can be obtained either by fixing suitable hoods in the roof of the chamber, or, better, by blowing-in a mixture of fresh warm air and steam through a fan, the old air and acid vapours being thus driven out through any conveniently arranged flue or hood. The introduction of a constant current of fresh air and steam into an ageing chamber filled with cloth requires very careful management to avoid causing sudden changes of temperature, and is only successful when carried out without giving rise to any appreciable fluctuations of heat and humidity. Given a sufficiently spacious chamber, provided with doors, windows, and a few ventilators in the roof, and the "ageing" ought to proceed in a regular manner, without the necessity of an artificial draught; in fact, very few "ageing rooms" in England are fitted up with any such appliance.

Where "ageing rooms" still exist, they are used to advantage; but to a great extent they have been superseded by a modification of Thom's Continuous "Ager," and in many works they have been put to other uses, being transformed into ordinary departments by the addition of intermediate floors, etc.

(2) **Thom's Patent Ageing Chamber.**—To John Thom, of Mayfield, belongs the credit of having first devised a machine for the continuous "ageing" of mordants printed on cotton cloth. For this purpose it was necessary that the moisture should be introduced into the apparatus in a systematic manner, and that all excess of acid vapours, etc., should be enabled to escape. These conditions were successfully fulfilled in Thom's patented machine (Eng. Pat. 22610, 1849), a sketch of which is shown in fig. 52.

The ageing chamber, A, A, consists of a wooden cottage with gable ends, the roof being pitched at an angle of 45°. Inside, it is furnished with top and bottom guide rollers R, R, over and under which the goods are drawn. Beneath the chamber a stone cistern C is situated in the brickwork foundation. This cistern is partly filled with water into which a steam pipe S dips, and is provided with an overflow pipe O, so as to maintain the level of the water. Immediately above the water, a double series of planks P, P are so arranged that the upper ones come over the spaces between the lower ones, and thus prevent any chance of the cloth getting splashed when the water is heated by the steam entering through the pipe S. Ventilation is obtained by means of the outlet pipe E fixed at the peak of the gable. The cloth K to be aged enters and leaves the chamber over the woollen-covered rollers M, M, situated in slits cut in each end of the chamber. In operation the water in the cistern is heated to 180° F., at which temperature it gives off aqueous vapour; this gradually fills the chamber above by escaping between the planks P, P, and when the requisite temperature is attained the goods are passed through slowly, and, on emerging, are either plaited down or bundled up loosely. In either case they are allowed to lie about, a day or two, in pile in the room where the ageing machine is situated,

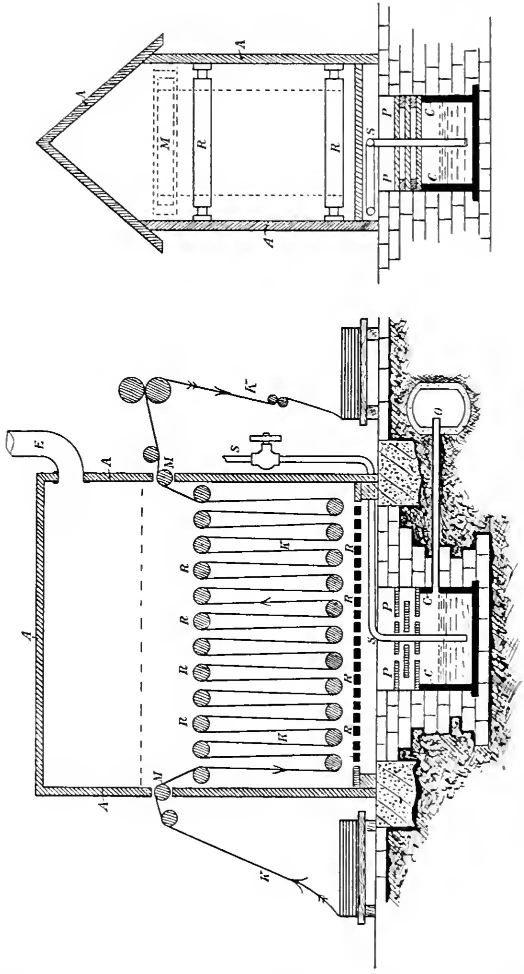


Fig. 52.—Thom's ageing machine.

and in which is maintained a suitable degree of heat and humidity. Goods treated in this way may sometimes be sent forward to the dye-house at once, but, as a rule, it is preferable to let them "age" for a day or two in pile before dyeing. The piles are turned over once or twice to equalise the "ageing."

Walter Crum, of Thornliebank, adopted Thom's principle of continuous working, but enlarged the chamber, and introduced the same system of heating and supplying moisture as is used in the old-fashioned "hanging rooms" already described. By this means he was enabled to deal with a much larger quantity of cloth at a time, and, in addition to obtaining more satisfactory results, he effected (as did Thom also) a considerable saving of valuable floor space, since goods in bundle or in pile take up much less room than when suspended from bars in single folds.

A diagram of a machine based upon Crum's improvements is given in fig. 53.

In Crum's original machine the chamber was of wood, but in the instance given (fig. 53) it consists of a brick room 40 feet long, 24 feet high, and 17½ feet wide. It is situated inside the works, an advantage which cannot be overestimated when condensation of moisture is in question. The width allows of three widths of ordinary cloth being treated at one time; and as most "madder work" is done on 30″ material, the space allowed is more than ample. If need be, broader cloth can easily be run; but if it exceeds the length of the guide rollers these will require to be replaced with wider ones—a simple matter if broad work is a regular article of production. Three separate sets of top and bottom rollers R, R are installed; and heat and moisture are obtained from the steam pipes S, S, and the cloth-covered funnels F, F, respectively. In other respects the working of the apparatus is identical with Thom's, except that the cloth is arranged to emerge on the entrance side. For the purpose of preventing the formation of drops, the ingress and egress slits are furnished with copper steam pipes C, C, between which the cloth passes over the rollers M, M. The fumes disengaged during the operation are drawn off by a small fan B, through the exhausts A, A, A; the fan only works when required, or it may be allowed to revolve slowly and continuously if unusually large amounts of acid are given off from heavy patterns printed in strong mordants. According to the class of work under treatment, the temperature of the "ageing chamber" varies from 25° C. to 36° C., with a constant difference of about 3 degrees between the indications of the wet- and dry-bulb thermometers. The time occupied by the pieces in passing through the chamber depends upon the nature of the mordants and the weight of thickening in the printed parts of the cloth. Strong mordants, somewhat basic in character, require less time to "age" than weaker mordants, to which extra acetic acid has been added to overcome their liability to dissociate; and fine patterns printed from lightly engraved rollers absorb the moisture more rapidly than heavy patterns printed from deep engraving, which deposits a much larger quantity of thickening on the fibre. This thickening presents a hard, dry surface to the air, and prevents the moisture from reaching the fibres of the cloth unless sufficient time is allowed for it to become softened in the moist atmosphere of the "ageing chamber." For the majority of madder styles the goods are run at such a speed as to be 18 or 20 minutes in passing through the chamber, but in special cases the time may be increased to 35 minutes.

As a rule, if the goods are found to contain 6 per cent. to 7 per cent. of moisture, evenly distributed throughout, they may be regarded as having been sufficiently "aged," that is, if they were quite dry to start with. On leaving the "chamber" the goods are plaited down, and allowed to lie a day or so before dyeing. Iron mordants ought always to lie three or four days in a warm, moist atmosphere after "ageing," in order to enable them to absorb as much oxygen from the air as they are capable of taking up, otherwise they exist on the piece in various states of oxidation, and dye up unevenly in consequence. The only real drawback to Thom's system of "ageing" is that Catechu browns printed along with iron and aluminium mordants cannot be fully oxidised by so short an exposure to the atmosphere of the "ageing chamber." In all other kinds of madder-dyed work this exposure is sufficient to carry the *ageing* to a point from

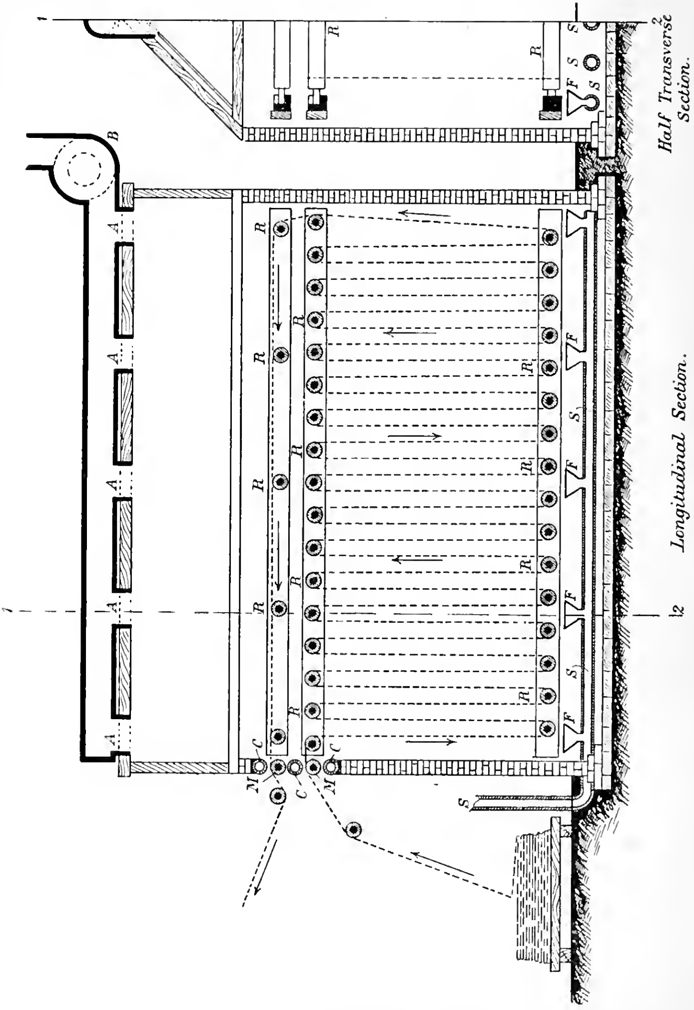


Fig. 53.—Crum's ageing machine.

which it proceeds to completion by natural means during the time that the goods are stored in bundle previous to dyeing; but in the case of Catechu the colour can only be fully developed by a rather prolonged exposure to freely circulating, warm, moist air, and for this reason it is preferable to hang goods printed with Catechu in single folds in one of the old-fashioned "ageing rooms" for four to five days. However, at the present time this one drawback is not of much moment, since Catechu and madder-colour effects can be easily and successfully matched in other ways that give equally good results. Before leaving the subject of ageing chambers it may be remarked that the atmosphere of the rooms in which they are situated, and in which the goods are stored after passing through the chamber, ought to be maintained in a condition corresponding, as near as possible, to 24° C. dry-bulb and 21° C. wet-bulb thermometers.

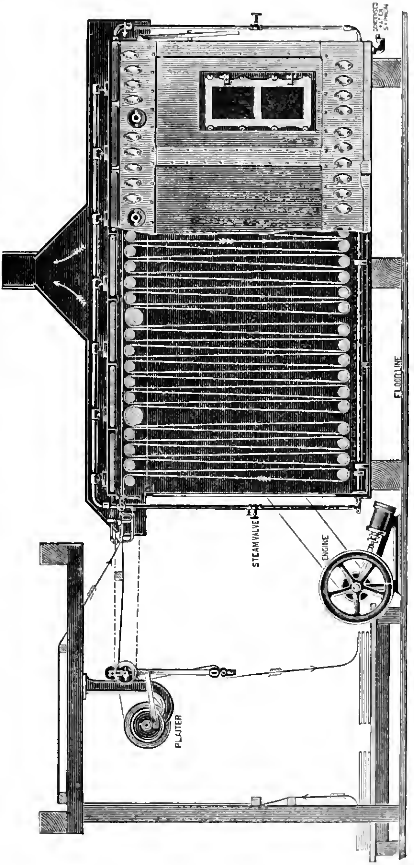


Fig. 54.—Mather & Platt's rapid steam ager.

(3) **Mather & Platt's Rapid Steam "Ager."**—This machine, known throughout the calico-printing world as the "Mather & Platt," was brought out in 1879, and at once achieved a well-merited and lasting success; so much so, in fact, that it is now an indispensable piece of plant in all modern printworks.

From fig. 54 it will be seen to consist of a comparatively small iron chamber, inside which top and bottom rollers are fitted. The top of the chamber consists of a wooden hood, arranged to carry off the gases disengaged during the operation of ageing. A pipe from the top of the "ager" runs into this hood, the ventilating shaft of which communicates with the outer air; and the ventilation required may be obtained either by the current so induced or by means of a fan working in the shaft itself. The cloth enters and leaves the machine through the same aperture, which is provided with two steam pipes, fixed longitudinally, to prevent drops of condensed water forming and falling on the cloth.

The apparatus is supplied with low-pressure steam through a perforated pipe situated beneath the lower set of guide rollers. Where a steam engine is used for driving, its exhaust steam may be utilised for this purpose; but in general better results are obtained from a special supply pipe, which can, of course, be used to keep the chamber in working condition whilst the engine is stopped. Any condensed water formed runs down the sides of the chamber, and is drawn off by a syphon situated at the bottom. If the apparatus occupies a position in which it is exposed to cold draughts, it is usually boarded round in order to keep it hot, thus avoiding an undue condensation of the steam.

The great variety of purposes to which the rapid ager is adapted, combined with its high rate of production, has enabled it to take the place of both the preceding forms of "ageing" in all cases where rapidity of oxidation is not detrimental. For "madder styles" it is not so well adapted as are the older and slower methods, but, all the same, large quantities of this style are produced by its means, especially if they contain Aniline black; and if proper precautions be observed, the final results leave little to be desired. Aniline blacks, which formerly took at least six hours to oxidise in the "hanging rooms," can be fully developed in the rapid ager in half the number of minutes; and styles such as the printing of Indigo by the Schlieper & Baum and hydrosulphite processes, the alkaline discharge of Turkey-red and tannin mordants, and many other discharges, both by oxidation and reduction, all of which were impossible under any conditions previous to the invention of the rapid ager can now, by its means, be produced with ease and certainty. So that, quite apart from the great advantage it has in increasing the output, the rapid ager has been instrumental also in increasing the resources of the textile colourist by rendering possible the practical application of many processes that were previously of scientific interest only.

The temperature at which the Mather & Platt Steam Ager is worked varies from 65° C. to 95° C. with the dampness of the steam regulated to show 3° C. less on the wet-bulb thermometer. The lower temperature is employed for Vanadium and Copper aniline blacks, either alone or in combination with iron and aluminium mordants, and the higher temperature for Prussiate blacks in all styles. The Prussiate black will stand still greater heat than 95° C., but without exhibiting any improvement in shade. The goods are usually run at a speed of 60 yards per minute, and at this speed take 3 minutes to pass through the chamber.

From a practical colourist's point of view, the "rapid ager" has two great advantages over all other systems of "ageing." In the first place, it permits of the important Prud'homme style of Aniline-black discharging being produced to the utmost degree of perfection; and secondly, it allows of Indigo and other vat dyes being reduced on the fibre in presence of caustic soda. Neither of these processes can be carried out in any other apparatus or by any other means. If Prud'homme blacks printed in coloured discharges are "hung," the black is poor and the colours are dull; and all processes in which caustic soda, as such, plays an important part must, of necessity, be completed before the caustic has time to become converted into carbonate, by the absorption of carbonic acid from the air.

When the "rapid ager" was first introduced for the oxidation of Aniline blacks and other printing colours containing free mineral acids, a good deal of trouble was experienced from the extreme liability of the cloth to become "tender." This defect was found to be caused not by any inherent defect in the machine, but by the too great percentage of acid in the colours themselves. In the "hanging rooms" these same colours came out very well, but when subjected to the energetic oxidising action of the "rapid ager" the free acid liberated rapidly destroyed the cloth at the temperature at which the operation was performed. A modification of the composition of the printing colours was all that was required to remedy the defect, and nowadays, when "tendering" of the cloth occurs, it may safely be attributed to one of three causes:—(1) the acidity of the colour; (2) too great a heat in the "ager"; and (3) to the goods being allowed to stay too long inside—that is, not passing through the "ager" quickly enough. If these three points are attended to, the Mather & Platt rapid ageing and steaming chamber will be found to give perfectly reliable results, and to possess all the many advantages claimed for it.

(4) **Ageing with Superheated Steam.**—The only reason for including this system under the heading of "Ageing" is that it is carried out in a chamber that is, to all intents and purposes, an obvious modification of the ordinary rapid ager.

It was found that the powerful reducing properties of the comparatively recently introduced solid "hydrosulphites" could only be utilised to the best advantage when goods upon which these salts were intended to act were exposed to the action of dry, superheated, air-free steam. For this purpose the ordinary ager is unsuited, and in consequence it became necessary to modify its construction and arrangements. The result of numerous experiments is that various types of the "hydrosulphite ager" are now on the market—all more or less efficient. Amongst these, the most generally useful perhaps is the combined "hydrosulphite, Aniline black, and Indigo ager," made by Messrs Mather & Platt of Salford. This exceedingly convenient machine (fig. 55) fulfils all the conditions essential to the successful production of each of the above three styles, namely, a high working temperature, the least possible admission of air, and an arrangement for supplying the moisture that is requisite in the steaming of Indigo and other vat-dye prints.

The walls of the chamber consist of flanged iron plates, accurately machined on their edges, so as to fit together perfectly air-tight All the roller-bearings and fixings are machined so that the rollers run perfectly truly and freely, and the rollers are mounted in such a way as to allow of their being oiled from the outside whilst the machine is running—a great advantage. The roof of the chamber is made up of cast-iron steam chests, which, in conjunction with a serpentine coil-pipe, supplied with high-pressure steam, at the bottom, serve to maintain the chamber at the requisite temperature for "hydrosulphite" work, viz. about 104° C. The steam used in the chamber enters through two perforated pipes running along the length of the upper part of the chamber, and before entering it passes through a steam trap, where any water it may contain is removed.

The steam supply pipes are furnished with suitable guards to prevent any possibility of the cloth being damaged by drops and splashes.

The cloth enters and leaves the chamber through a narrow slit close to the bottom—an arrangement whereby the exclusion of air is best secured. As cold, damp cloth passing into the chamber would reduce its efficiency, the goods to be treated are passed round a steam-heated drying cylinder before entering the steam. All undue tension on the cloth whilst travelling through the chamber is avoided by driving several of the rollers over which it passes by power.

Ventilation of the chamber, in so far as it consists in removing the gases disengaged during the operation of ageing, is secured by means of a perforated suction pipe situated at the bottom, beneath the serpentine heating-coil.

This improved ageing apparatus may be used for the reduction of Indigo printed by either the glucose or the "hydrosulphite" process. For this purpose it is provided with a water tank in the bottom of the chamber, for use when the former process is employed; for the latter, the ordinary method of working the

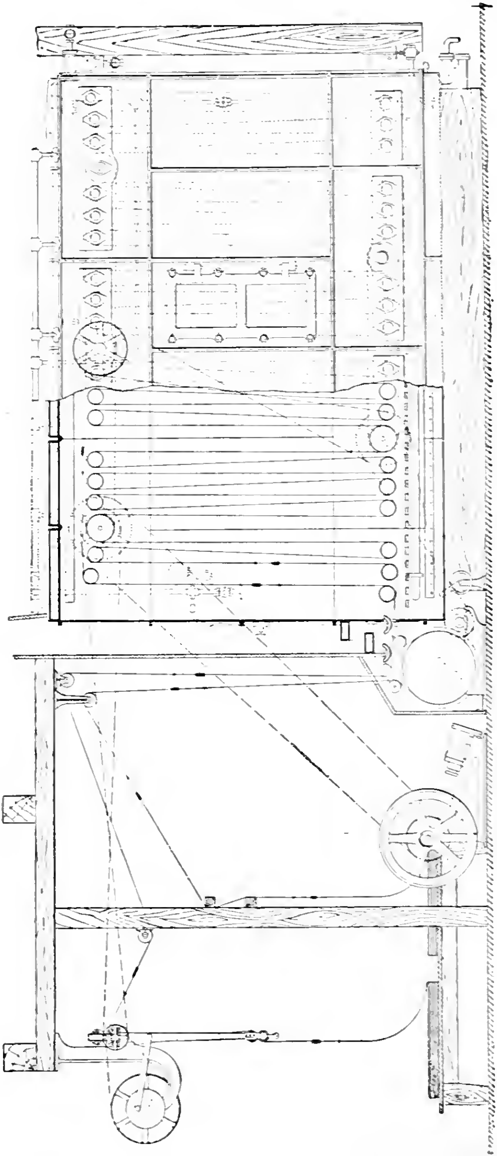


Fig. 55.—Hydrosulphite ager (Mather & Platt)

"ager" is sufficient, as excess of moisture is not conducive to good results in any hydrosulphite work.

If desired, the machine can be arranged for the steaming of two superposed pieces of cloth simultaneously, thus doubling the output of certain styles of work.

Superheated steam "agers" are indispensable in all works where processes depending on the reducing action of the hydrosulphite-formaldehyde compounds are in use. The discharging of certain azo colours cannot be effected in any other apparatus, but Indigo may be reduced by hydrosulphite in the ordinary type of "rapid ager" if care be taken to keep the temperature up and to avoid the presence of too much moisture. On the other hand, the glucose process of Indigo printing absolutely requires the presence of moisture, and therefore cannot be carried out in superheated steam agers unless they are specially adapted to its requirements.

(5) **Indigo Ager** (for the glucose process).—The ordinary "ager" used for this process is much simpler in construction than the combined "hydrosulphite, Aniline-black, and Indigo ager" just described; it resembles in some respects Thom's ageing machine, the main differences being in its smaller size, in the chamber being filled with steam as free as possible from air, and in the passage of the cloth being reduced from about 20 minutes or more to from $\frac{1}{2}$ to 2 minutes only. A glance at fig. 56 will show clearly the arrangement of a special Indigo ager for the glucose process.

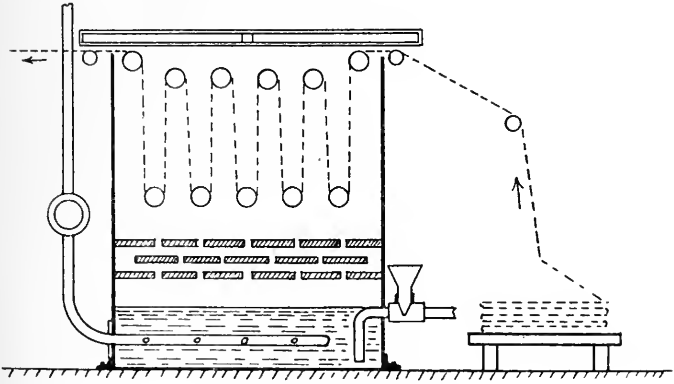


FIG. 56.—Indigo (glucose-alkali) ager.

The chamber itself is made of iron plates; the lower part is arranged to serve as a cistern; and the roof, as in all the best modern agers, is composed of cast-iron steam chests, the heat of which precludes any possibility of drops of condensed water forming on its under side, and dropping therefrom on to the pieces passing through beneath. The steam enters the chamber through the water in the cistern, and thus becomes charged with the necessary moisture. Above the cistern an arrangement of overlapping plates is provided to prevent the cloth from getting splashed by the boiling of the water below; suitable precautions are also taken to avoid drops of water condensing on the edges of the slits through which the goods enter and leave the chamber.

This apparatus ensures the rapid and even reduction of Indigo; and although it is not absolutely essential to success, it is perhaps the safest system to adopt for the purpose. In many works the ordinary ager can be made to yield equally good results if properly handled and supplied with damp steam; in fact, many firms who print indigo by the Schlieper & Baum process make no other arrangement for its steaming beyond providing for the introduction of plenty of moist steam into an ordinary ager.

(2) "DUNGING."

Dunging is an operation specially connected with the after-treatment of goods printed in iron and aluminium mordants, and derives its name from the fact that cow-dung enters largely into the composition of many "dunging" liquors. It consists in passing the "aged" cloth through cow-dung let down with water or through a solution of cow-dung substitutes, and occasionally, for delicate work, through a bath of bran and chalk. Dunging constitutes one of the most important steps in the production of the "madder style," and demands the utmost care in its performance, since upon the state of the cloth as it leaves the final dunging beck depends the ultimate success of the work.

The function of "dunging" may be described as threefold, namely, (1) to complete the "fixing" (already partly accomplished in the ageing chamber) of the mordants on the cloth; (2) to combine with and render insoluble any undecomposed mordant that may dissolve out of the cloth while it passes through the liquor; and (3) to remove, as perfectly as may be, all the thickening material used in the printing colour; in short, its function is to prepare the printed cloth in such a manner as to enable it to take up evenly the requisite quantity of colouring matter from the dye bath.

The necessity for "dunging" is almost too self-evident to call for explanation. However, it may be noted that if cloth plastered with thickening and containing unfixed mordants were entered into a dye bath, the thickening, by acting as a mechanical resist, would prevent the dyestuff from penetrating into the fibres of the material, and thus give rise to irregular dyeing; and the unfixed mordants would dissolve off in the hot dye liquor, and not only cause uneven dyeing, but also attach themselves and attract colour to the white unprinted portions of the cloth, thereby staining them beyond remedy. Besides, the presence of soluble mordants in a madder dye bath is productive of great loss of dyestuff: the mordant combines with the colouring matter to form insoluble lakes, which simply float about in the dye liquor, only to be thrown away after spoiling the goods. Imperfectly "dunged" goods are subject to these same mishaps in a less degree, so that, from all points of view, the thorough cleansing ("dunging") of printed goods from all foreign matters, other than those that go to form part of the ultimate colour, is an operation of extreme importance.

The use of cow-dung as a cleansing agent is the outcome of practical experience alone. The nature of the chemical and physical changes that take place in the "dunging" process has never yet been ascertained definitely. All that is known is that it "fixes" the greater part of the mordant which has already been partially converted into an insoluble basic salt by the action of the "ageing" process; that it prevents the unprinted parts of the cloth from becoming mordanted, and thus subsequently attracting colouring matter from the dye bath; and that it removes effectually all thickening agents, leaving the cloth in the best possible state for being dyed up fully and evenly. Fresh cow-dung is slightly alkaline, and contains, besides water and some phosphates, a fair percentage of albumen and a considerable amount of insoluble organic matter. The alkali and albumen both precipitate iron and aluminium mordants, and the insoluble matter also has a powerful attraction for them, so that any mordant that may dissolve out of the cloth immediately enters into combination with it, and, in being thus rendered insoluble, is prevented from injuriously affecting the unprinted parts of the cloth—the "whites."

Although cow-dung is generally acknowledged by practical men to be superior to any other dunging agent, it requires careful application to secure the best results. An excess impoverishes and dulls the colours, and imparts an unpleasant greenish tinge to the "whites." It also varies considerably in composition; and in working requires to be emptied out and thrown away at frequent intervals, by reason of the large amount of thick sediment formed, which, if allowed to act upon the goods, would inevitably ruin the "whites." As a rule, one charge of cow-dung cannot be used for more than 200–300 pieces of calico without causing trouble.

With a view to overcoming the disadvantages of cow-dung, many substances have been suggested as dung substitutes. Amongst them the most commonly used and most important are the following:—

(1) Sodium Phosphate ($Na_2HPO_4.12H_2O$).—This salt is extremely useful for the fixing of mordants that are too delicate to stand the energetic action of cow-dung, and in cases where a weak mordant is printed in combination with a strong one, *e.g.* the "red and pink madder-style."

(2) Sodium Arsenate ($Na_2HAsO_4.12H_2O$).—This salt is perhaps used more than any other as a dung substitute in England. It acts like sodium phosphate in all respects, and in countries where it is not prohibited it is generally preferred on account of its greater efficiency. The poisonous nature of goods "dunged" with arsenate is very much exaggerated. As a matter of fact, it is either removed from the cloth during the many subsequent washings it undergoes, or is combined with the mordant and colouring matter in an insoluble and quite innocuous form. The only danger to be apprehended from its employment is, that it may possibly contaminate the stream into which the effluent of the works runs; but nowadays this danger is reduced to vanishing point, since most river and canal authorities insist upon all poisonous substances being eliminated from the effluent before it leaves the works. A good sample of arsenate of soda ought to contain at least 50 per cent. of the pure salt.

(3) Silicate of Soda ($Na_2Si_4O_9$).—This salt occurs in the solid form as "soluble glass," but it usually comes into commerce as a thick, colourless, syrupy liquid. It finds but limited use as a dunging agent, on account of its liability to contain an excess of either caustic soda or carbonate of soda, both of which "strip" the aluminium mordants off the cloth at the temperature of the dunging bath. Basic salts of aluminium readily dissolve in warm alkali, and in consequence the use of silicate of soda is attended by some risk, especially if applied to the "red and pink style." On the other hand, iron and chromium mordants, not being soluble in weak alkalies, can be fixed in silicate with safety. Although freshly and properly prepared silicate of soda is not open to the above objections, it nevertheless decomposes into silicic acid and a basic salt if kept long in solution. The main drawback to the use of silicate, however, is that aluminium mordants "fixed" by its means yield poor and dull shades of red when dyed up in Alizarin.

(4) Sodium Carbonate ($Na_2CO_3.10H_2O$) and "crystal carbonate" ($Na_2CO_3.H_2O$) are only used for the fixation of iron and chromium mordants in certain cases.

(5) "Ammonium Carbonate" [$(NH_4)HCO_3.(NH_4)CO_2.(NH_2)$] in the dry state is a mixture of the bicarbonate and carbamate, but when dissolved in water and ammonia it is converted into the normal carbonate $(NH_4)_2CO_3$. It is an excellent "dunging" agent for aluminium mordants, but hitherto has not found much employment on the large scale, probably on account of its price.

(6) Silicate of Lime, recommended by Higgin as a cow-dung substitute, is little used. It is a sparingly soluble salt, which is employed as a saturated solution, the strength of the bath being kept up by always allowing an excess to remain in suspension in the dunging liquor.

(7) BRAN.—This substance cannot be regarded as a dung substitute proper, although it is frequently used along with a little chalk for treating weak aluminium mordants which are so far "fixed" upon the fibre in "ageing" as not to require a more drastic treatment. The diastase ferment in the bran converts the starchy matters in the thickenings into soluble glucose, which easily washes out of the cloth, while the chalk serves to neutralise any traces of acid that still remain after the ageing process. Chalk is a regular constituent of all dunging liquors; it combines with all acids liberated by the dunging agents, and acts generally as a weak and useful, though harmless, alkali.

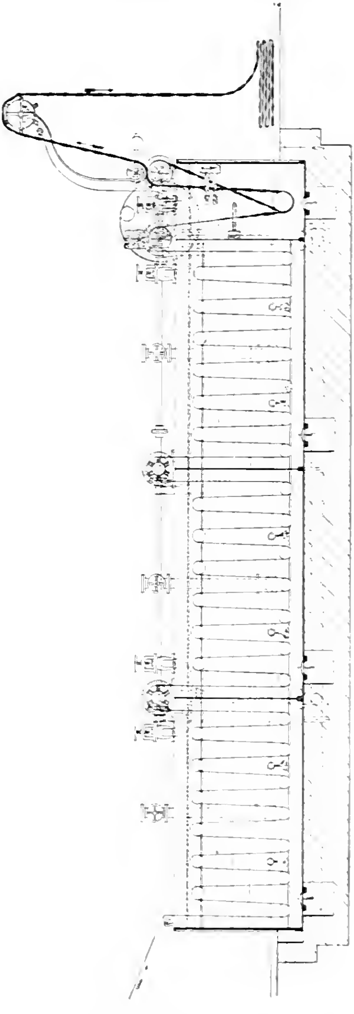


FIG. 57.—"Fly" or first dunging becks (Mather & Platt).

The advantages accruing from the use of "dung substitutes" lie in the direction of increased cleanliness, convenience, and regularity of working, rather than in the better fixation of the mordants and the more perfect removal of thickening materials. Dung substitutes effect neither of the latter two objects any better than cow-dung, if as well; but being colourless, regular in composition, and, with the exception of bran and chalk, quite soluble, they neither stain the cloth, give rise to irregularities in shade, nor require to be thrown away every few hours, as is the case with cow-dung. A dunging machine set with sodium phosphate, etc., can be worked a whole day without emptying out, whereas with cow-dung a considerable amount of time is lost owing to the necessity for emptying out and re-charging the machine with fresh cow-dung at frequent intervals, the length of which varies according to the class of work under treatment. Heavy patterns require fresh liquor oftener than light patterns, and the kind of thickening used also governs the working of the dunging process to some extent, since starch and flour are more difficult to remove than the various gums.

A dunging liquor made up from any of the foregoing "substitutes" may often be used continuously for several days if it be replenished regularly with a little fresh solution. The amount to be added is easily calculated when it is borne in mind that the cloth usually abstracts its own weight of solution from the bath: the bath, however, should be kept as much as possible at the same height during the whole time of the operation, and therefore it is advisable not to allow too many "pieces" to pass through it before "freshening it up" with a few gallons of new dunging liquor from a storage cask kept conveniently at hand.

Most of the dunging substitutes in common use can be mixed in any proportion either with each other or with cow-dung. Indeed, cow-dung, phosphate of soda, and chalk is a very general mixture for the "first dunging" of ordinary madder styles, the "second dunging" consisting sometimes of "phosphate" alone, and sometimes of a dilute solution of cow-dung and one or other of its above substitutes, together with a little chalk or bran.

As a rule, it is essential to "dung" all madder styles twice at least in order to ensure the perfect removal of the thickenings used in printing the mordants. The "first dunging" is known as "fly dunging," and is performed in a series of three or more becks, through which the cloth passes, in the open width, over a system of rollers. The "second dunging" is carried out in one of the many types of spiral washing or dyeing machines, and the goods are, of course, treated in the rope form.

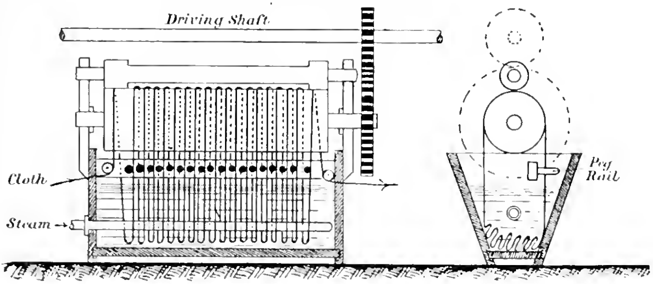


FIG. 58.—Spiral or second dunging becks.

In fig. 57, which represents a section of Mather & Platt's "fly dunging machine," the first compartment is filled with the required liquor at a strength a little above that of the similar contents of the second and third compartments. This difference in strength is not absolutely necessary, but it is found to give the best results in many works. The cloth enters as shown, passes through each beck in succession, and in the last or washing beck is drawn through an earthenware ring or "pot eye," which throws it out of the open width into the rope form, in which form it proceeds to the "second dunging." The temperature of the dunging liquor varies from 60° to 100° C. according to circumstances that will be mentioned later. The usual duration of the "first dunging" is from 2 to 5 minutes.

The "second dunging" occupies 20–30 minutes at 60°–65° C. It is performed in a spiral machine, similar to dyeing and washing machines, and sometimes two machines are run in combination, the goods passing from one to the other in a continuous manner. On emerging from the "second dunging" the pieces must be thoroughly washed, and are then ready for dyeing.

Fig. 58 will give an idea of the working of a spiral "dung beck."

(3) DYEING.

The dyeing of printed calico, either before or after printing, is performed in at least four distinct ways, each of which may be modified according to circumstances.

For dyeing in the *open width*, use is made (1) of "jiggers," (2) of continuous dyeing machines constructed on the same principle as the "fly dung becks," (see fig. 57), (3) and of slop-padding mangles (see figs. 49 and 50).

In the *rope form*, cloth is nowadays invariably dyed in spiral dye becks, of which various types exist.

Fig. 59 shows a section of the "jigger," a machine largely used for dyeing plain shades, but which does not find very extensive employment in printworks where the output is confined to printed goods. It may, however, be used with advantage for small quantities of certain "discharge styles," such as the alkaline discharge on tannin-mordanted cloth. In this style, when the same design is required in small lots of different colours, the "jigger" affords an economical means of dyeing the comparatively short lengths into which the order is split up.

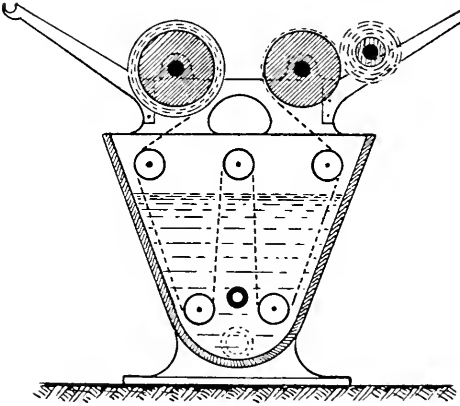
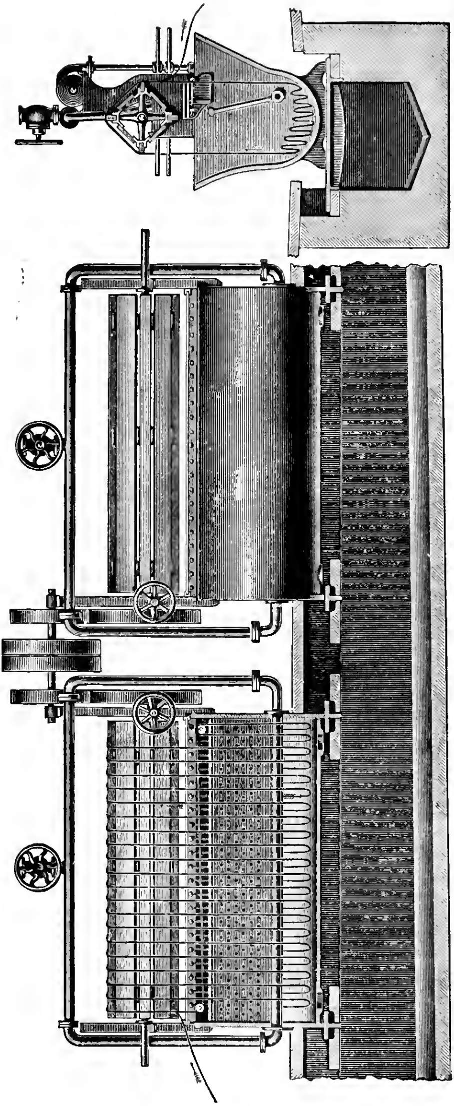


Fig. 59.—Jigger.

The "jigger" consists of an iron or wooden dye beck fixed between two cast-iron supports, which carry bearings in which two fixed rollers revolve. To each bearing an oblique arm is attached for the purpose of supporting a loose roller in such a way that it is capable of revolving in contact with the fixed rollers. The goods to be dyed are sewn end to end and wound on a loose shell, which is then placed upon one of the arms. The goods are now threaded by hand under and over the guide rollers immersed in the dye liquor until sufficient has been pulled through to be wound on the fixed roller at the opposite side of the jigger. The machine is then set in motion, and as soon as the whole length of cloth has passed through the dye liquor the motion is reversed, so that the pieces pass back again and are wound on the opposite fixed roller. These to-and-fro passages are continued until the cloth is fully dyed, at which point, *i.e.* during the last passage, they are wound on a second loose shell instead of on a fixed roller. The dye liquor may then be replaced,



Dyebecks.

if desired, by water, and the goods washed in exactly the same way. In some machines the reversing motion takes place automatically. Jiggers are driven by bevel gearing, acting directly on the axles of both the fixed rollers; and their contents are heated by either open steam pipes or by steam coils situated beneath the guide rollers.

The working of slop-padding machines has already been described, and that of continuous open dyeing machines is the same, to all intents and purposes, as that of "fly dunging machines," except that the operations are carried out under different conditions of time and temperature. In both cases the goods are stitched end to end and run through the dye liquor in a continuous manner.

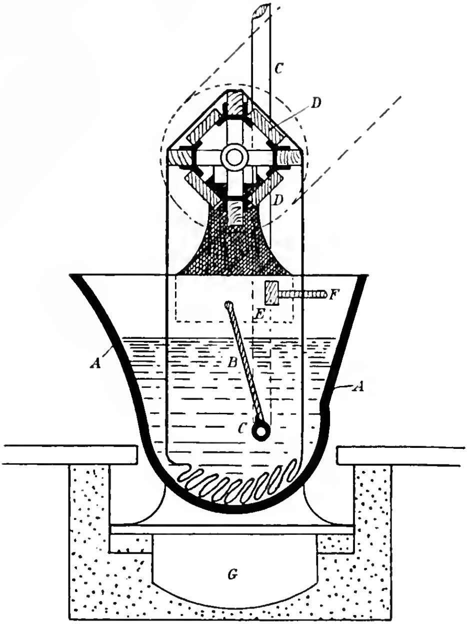


Fig. 60.—Dye beck.

The *spiral dye beck* is the form of dyeing machine most largely used by calico printers. It is convenient, easy to work, gives regular results, and is capable of dealing with from 24 to 40 pieces of cloth at a time. In principle it is similar to the washing machine previously described (fig. 44), but differs from it in detail and general arrangement, a winch taking the place of the squeezer bowls, and the beck being rather different in shape.

Fig. 60 represents a cross-section of Messrs Mather & Platt's spiral dyeing machine, from which an idea of its mode of action may be obtained. See also Plate V.

A A is a long cast-iron dye beck fixed over the drain G; B is a midfeather or dividing board to keep the strands of cloth from becoming entangled; C is a perforated steam pipe for heating the dye liquor; D is a winch over which the cloth circulates continuously; E is a rail—the peg rail—carrying a series of pegs F, which serve as guides for the rope of cloth, and prevent the separate strands from running together and thus becoming entangled. The dotted circles round the winch represent the driving wheels, which may be actuated in any convenient way—either by cogs, straps, friction gearing, or an electric motor. Clutches, etc., are provided at the side of the machine for the purpose of knocking it in or out of gear as required.

The pieces of cloth to be dyed are first of all stitched end to end, so as to form a rope some 700 yards in length. One end of this rope is then introduced at one end of the machine, pulled over the winch and through the dye liquor, then over the winch again and through the dye liquor a second time, and so on until the beck is full. In this way the cloth passes over the winch and through the liquor in the form of twenty to twenty-five huge loops, each of which is kept apart from those on each side of it by being made to run between the pegs F. When the first end of the long rope of cloth has traversed the full length of the dye beck it is brought back, horizontally and above the dye liquor, through two "pot eyes" and over two small pulleys, to the point at which it first entered the machine. Here it is sewn to the last end of the cloth, so that the whole forms an endless rope, passing through and through the machine in a spiral direction and in long slack loops. To guard against any possibility of the loops getting torn asunder by excessive tension, the lower part of each contains a few yards of slack cloth as shown in the diagram; this "slack" falls down the inclined side of the beck in a regular manner, and, if the machine is in good order, it never increases in bulk from the beginning to the end of the dyeing.

Spiral dye becks can be used for a variety of operations, including washing, "dunging," and soaping. When so used, it is almost needless to say that they ought not to be used for dyeing, each beck being reserved for the particular purpose for which it has been set aside.

(4) STEAMING.

Steaming consists in submitting the printed pieces to the action of steam for varying lengths of time and at different pressures.

In the early days of calico printing a very primitive, though to some extent effective, arrangement was used. The pieces were wrapped round a perforated steam pipe covered with printer's blanket to absorb the excess of moisture contained in the steam; they were then enveloped in an outer covering of printer's blanket or other woollen material, and the steam, being then turned on, penetrated through the whole cloth, thus effecting the decomposition of the various mordants, and their subsequent combination with the colouring matter with which they were mixed. This method of steaming is quite unsuited to many modern styles, and is now obsolete, except for the steaming of trial fents where no better system is available. Moreover, apart from the smallness of the output, the pieces were very unevenly steamed, and were subject to many objectionable defects, which need not be specified here, but which led ultimately to its replacement by systems of steaming based on totally different principles.

The earliest of the improved methods of steaming consisted in hanging the goods in iron chambers into which steam was turned, and in which the goods could be treated under low pressure for any length of time. In a still more improved form this system is still used, and is known as "cottage" steaming, the name being derived from the fact that the early "steamers" were shaped like a cottage with gable ends, so as to allow of the condensed steam running down the inside of the roof instead of dropping on the suspended goods beneath. Fig. 61 shows a modern low-pressure steaming cottage made by Messrs Mather & Platt.

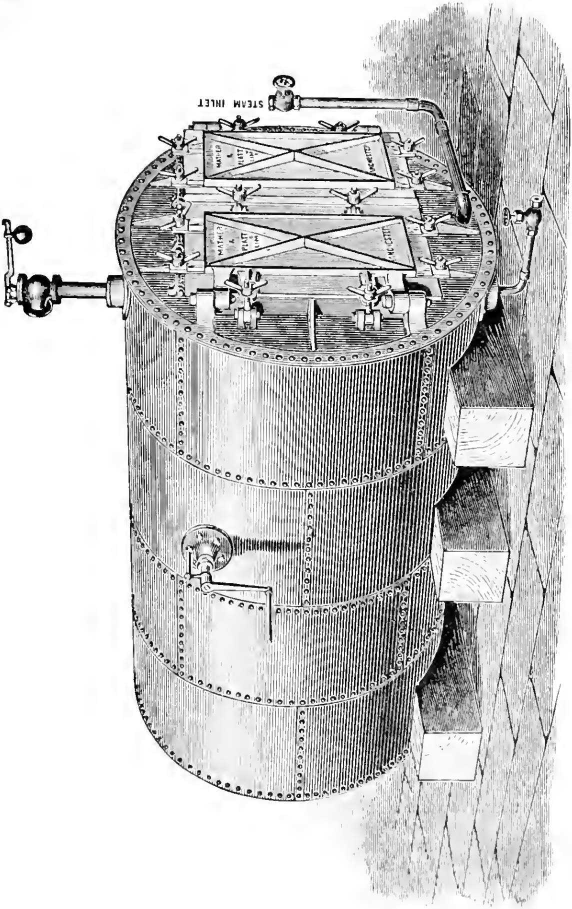


Fig. 61.—Low-pressure steaming cottage.

It consists of a strong cylindrical chamber made of boiler plate, and provided with doors which can be hermetically closed by means of stout bolts. Steam enters beneath a false bottom, so arranged that all chance of condensed water splashing on the pieces is avoided; and the pressure is regulated by a safety-valve placed above. The goods to be steamed are suspended from square wood rollers, the axles of which carry spur-wheels at one end, arranged to gear together when the iron carriage upon which the rollers are mounted is quite full of cloth. Through the side of the chamber extends a short shaft, the inside end of which carries a spur-wheel and the outside end a handle; the spur-wheel gears into one of those on the square wooden rollers, and, when it is turned by the handle, transmits motion to every roller. In this way the position of the cloth on the rollers inside may be varied from time to time from the exterior in such a way as to ensure every part of the cloth being equally steamed. The carriage runs into and rests inside the chamber on rails laid down above the false bottom for its reception. Similar rails are laid down outside, and the two sets are connected, when the door is opened, by a couple of short lengths, so that the carriage can be run in and out with the greatest of ease.

In operation the goods are first of all wound between greys into large open loops of full-width cloth; each loop is then placed on a separate roller, and when the carriage is full it is ready for entering. Meantime the cottage has been heated up by closing the doors and allowing steam to pass through for some time: this is necessary in order to avoid as much as possible the formation of drops of condensed water, and generally to expedite the "steaming." The carriage is then run in, the doors closed, and steam turned on. For a short time it is allowed to pass right through the chamber, escaping by the pipe and valve below; finally the latter is closed and the steam pressure is allowed to rise to the desired extent, as indicated by a pressure-gauge, not shown. From time to time the condensed water (if any) is run from under the false bottom by opening the lowest valve shown in the figure under the doors. The steaming usually lasts from an hour to an hour and a half. The doors are then opened, the carriage drawn out, and the cloth removed from the rollers and unwound. The winding and unwinding are both done on the same machine—a revolving frame with four collapsible arms, something like an ordinary winch when the arms are extended.

In this apparatus steam pressure up to 15 lbs. may be used. High-pressure steaming cottages are similar to the above, but more strongly built. They work up to 30 lbs. per sq. inch. High-pressure "cottages" are the more useful, since they can be worked at any pressure up to their highest limit.

Where small quantities of goods have to be steamed, the "cottage" is the most economical and convenient arrangement to use; and where goods have to be treated by steaming under pressure, it is the only one available for the purpose.

By far the most important system of steaming, however, is that in which large quantities of goods travel slowly through an atmosphere of steam contained in a large brick chamber. This system, known as "continuous steaming," was originally devised by Cordillot, and afterwards improved by Messrs Mather & Platt to such an extent that it is now identified with their names. As will be seen from Plate VI., the appliance consists of a brick chamber, roofed with steam-heated chests, and provided at the bottom with a battery of steam pipes, which, in conjunction with the steam chests above, maintains the atmosphere of the chamber at a high temperature, and prevents the condensation of the steam. The necessary steam is admitted beneath this battery; and in order to avoid the pieces being splashed by any water that may enter along with it, the battery of heating pipes is usually covered with a wooden grating, over which pieces of old calico or of "lapping" are spread. At the top of the chamber two endless chains travel continuously from end to end of the apparatus. These chains run parallel with each other, one at each side of the chamber, and receive their motion from toothed chain wheels, over which they run, and which are

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actuated by power. The centre part of each link of the two chains consists of a forked slot, into which rods drop automatically from time to time as the cloth runs into the chamber. The rods (of brass covered with string or linen) are fed on to the chains at regular intervals by means of a corrugated drum, into the depressions of which they fit. This drum is arranged to deliver them on to a slide leading directly to the moving chains. In this slide they are held until a sufficiency of cloth has entered the chamber to form a long loop, somewhat less in height than the chamber itself; at this point one rod is released, slides into the slots on the chains, and, in travelling forward with the latter, causes the cloth to fall over it, and thereby to begin to form itself into a second loop or fold. Simultaneously with this movement, the first rod carrying the upper loop of the first fold comes in contact with a swinging arm, or rather bar, which nips the cloth between itself and the rod, and thus prevents the weight of the first fold from dragging any more cloth over the first rod. If, for any reason, the swinging bar fails to act, the cloth, instead of hanging in folds, more or less equal in length, runs into the bottom of the chamber, and is dragged along in a tangled mass, with the result that it is unevenly steamed, and in ninety-nine cases out of a hundred is spoiled by absorbing moisture and picking up dirt from the coverings over the steam pipes. The first loop being properly suspended, the cloth continues to run into the machine until the second loop has attained its requisite length; the second rod is then released, falls into position on the chain, and, like the first rod, causes the cloth to commence forming the third loop. At the same moment the first rod, in pushing the swinging bar forward, escapes from under it, leaving it free to swing backwards into contact with the second rod, with which it again nips the cloth exactly as in the first instance, and thus forces the cloth to run into the third loop. These operations are repeated uninterruptedly for every succeeding loop until the chamber is completely filled, as shown in Plate VI. The cloth is fed into the apparatus between two heated draw rollers of brass and falls perpendicularly, until its course is arrested by the entry of the various rods. On reaching the far end of the chamber, the goods are drawn out through a slit in the roof by means of the plaiting-down tackle, of which two sets are shown on the left of Plate VI. The rods leave the chamber at the same time, falling from the chains on to a drum similar to that by which they are introduced at the other end; they are then transported by special travelling bands outside the chamber to the entering end again. In order to avoid the condensation of moisture on their surfaces, which might produce stains on the printed cloth, they are re-heated before they are allowed to enter the chamber again.

In some more modern machines the travelling rod-carrying chains have been discarded in favour of slotted guides, fixed one on each side of the chamber—an arrangement much less liable to get out of order than chains. Into these slots flanged brass rods are inserted automatically, and are pushed forward by a pair of cams at such a speed as to ensure that the cloth is fully steamed. At the exit end of the machine the cloth is drawn out as above, and the rods are automatically picked up by hooks on a pair of endless chains and carried round the chamber to the entering end again, without requiring to be otherwise handled in any way. The advantages of this improved system are that (1) the rods are always at the same temperature; (2) that they are not exposed to the risk of damage, inseparable from constant handling; (3) that any dirty rod can be taken out for cleaning, and replaced by a clean one, without stopping the machine—each rod being simply held in hooks, and not attached permanently to the chain; and (4) the rods cannot well get out of alignment, or fall into the bottom of the chamber, as frequently happens in the older type of "continuous steamer" when the carrying-chains become worn. The automatic cam movement, and indeed all the mechanism of the new system, is extremely simple and durable; and as its installation involves no structural alteration of the steaming chamber, it can be applied without difficulty to existing machines that are at present working on the old chain principle.

Plate VII. shows a section of the improved "automatic continuous steamer," in which four pieces are being steamed together.

For the treatment of printed and dyed goods that require to be aged or steamed for a period intermediate between that given in the "Mather & Platt" Ager and that given in the large continuous steamer, a somewhat similar, but smaller, apparatus is employed. The principle upon which it works is identical with that of the improved "automatic steamer" (Plate VII.), and therefore calls for no detailed description. The chamber is composed of four cast-iron pillars, and the sides are filled in with panels of iron plate; the floor space occupied is very small, and the compactness of the whole machine—a combined "ager" and steamer—enables it to be erected in any convenient part of the works, provided the floor is sufficiently strong and the room sufficiently lofty to accommodate it.

For certain styles of printing it is desirable to steam or age for from five to fifteen minutes, and it is for work of this description that the combined "ager" and steamer has been specially designed. In the full-sized continuous steamer the duration of the exposure to steam is much longer, varying from forty-five minutes to one and a half hours, according to the class of work under treatment. With proper care, both these "steamers" yield excellent results, notwithstanding the fact that the folds of cloth frequently rub against each other before the colours printed upon them are fixed. All the same, accidents are liable to occur if certain precautions are neglected. In the first place, the chamber ought to be heated up thoroughly before any cloth is entered; and in the type of machine where the rods are taken out when they reach the other end of the chamber, they must be heated in order to prevent moisture from condensing upon them when they re-enter the chamber. Moisture, from any source whatever, condensing on the pieces, causes the colour to "run." All parts of the apparatus, therefore, should be perfectly dry and hot before any work is commenced, otherwise mishaps are almost sure to happen. The cloth itself, too, should be warm and dry previous to entering the chamber. These conditions are usually fulfilled by storing the goods in a warm room contiguous to the "steamer," and further, by passing them into the steaming chamber between the heated brass rollers already mentioned. Apart from condensation on the rods and fittings of the machine, it frequently happens that drops of water fall on the pieces from holes in the steam chests which form the roof of the chamber; if the hole is comparatively large, the drops produce large spots; but if it is very minute, the condensed water is forced out as fine spray by the pressure of steam behind it, and causes the colour to run into irregularly-shaped patches, extending over a considerable space. These various faults are easily distinguished from each other; their shape and general appearance afford a clue to their origin. If the colour has run from side to side of the piece in a straight line, the defect may be safely attributed to a damp rod; if drops appear irregularly distributed over the piece, general condensation is taking place on the roof of the chamber; if, however, the drop-marks always occupy the same relative position, they will, as a rule, be found to proceed from a perforation in the roofing steam chests, and the same may be said of the effect of spray, the only differences between the two faults being (1) in the extent of the space over which the colours "run," and (2) that drops produce spots with light centres, whereas a spray gives a more or less cloudy patch. Another fault to guard against is the "marking off" of the colour from one fold of cloth to another. Many colours contain an appreciable quantity of oil and fatty matters, and these are very apt to "mark off" on anything they happen to come in contact with. Again, soluble or hygroscopic bodies which absorb a large amount of moisture in steaming, and oxalic and other acids

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which exercise a decomposing action on starch, etc., are all exceedingly liable to "mark off" during the steaming operation, unless the laps of the cloth upon which they are printed are prevented from rubbing against each other in the "steamer." In practice, therefore, all such goods are steamed along with a piece of "grey cloth," so arranged that the printed sides of the goods (hanging in loops) are separated from each other by two folds of the "grey cloth," which receives any colour that would otherwise be transferred to the printed pieces themselves. Very heavy patterns penetrating through to the back of the cloth and reversible prints are steamed between two "greys" if their colours are in any way likely to "mark off"; and when two pieces are steamed together they are run, printed face to printed face, with a "grey cloth" between them. In this way all danger of "marking off" is avoided. When very light patterns are steamed, four pieces may be run together, without any special precautions, provided the colours on each piece do not contain anything detrimental to each other.

A further important point to be taken into account is the condition in which the goods are sent up for steaming. If they pass directly from the printing machine to the steamer, the colours, being hard and dry, require a much moister steam for their development than if they had been allowed to lie for an hour or two to cool down. During the cooling they absorb a certain amount of moisture from the atmosphere, and then if they are exposed to the action of steam that is too moist they absorb a still further amount, becoming so damp that the colours run at the edges of the design and tend to "mark off" whenever two laps come in contact with each other. It is obvious, therefore, that the working of a steaming apparatus requires experience and no little attention if the best results are to be secured. No matter how perfect the machine may be mechanically, no good work can be executed by it unless the foregoing simple precautions be observed to the letter, and due regard be paid both to the state in which the cloth is presented to the action of the steam and to the humidity of the steam itself.

(5) FIXING.

The term "fixing" in its widest sense may properly be applied to all operations connected with the precipitation of mordants and colouring matters on the fibre; and in this sense it would include ageing, dunging, steaming, etc. As generally understood in printworks, however, "fixing" consists in passing printed or mordanted goods (other than "Madder styles") through solutions of various salts, etc., which either precipitate the mordant in the form of an oxide, hydroxide, or insoluble salt, or increase the complexity and insolubility of an already formed colour-lake. For example, the lakes produced by the combination of tannic acid with basic aniline colours are too soluble to withstand soaping, but if they be treated with a solution of tartar emetic they are converted into insoluble double or compound lakes, consisting of the tannates of antimony and of the colour-base; and as these compound lakes are insoluble in water and soap solutions, the colouring matter is said to have been "fixed" by the tartar emetic. In the case of goods prepared in, say, chromate of chromium, the mordant is "fixed" upon the fibre as an insoluble hydroxide by passing the pieces through a boiling solution of sodium carbonate. In this way, by using suitable fixing agents, many colours and a few mordants are easily capable of being attached to the fibre in such a manner as to resist washing in water, alkaline solutions, or soap; in a word, they are "fixed," and become either "fast" colours or the bases upon which fast colours are dyed.

The methods of effecting this fixation vary considerably. Cloth printed in basic colours is passed in the open width, after steaming, through a solution of tartar emetic or other antimony salt, contained in a small box or "beck" attached to, and forming part of, the "open soaping" and washing machine;

chromium and lead salts are precipitated either in jiggers or becks provided with top and bottom rollers over which the cloth passes continuously—and sometimes in the "open soaper," the first compartment of which is filled with sodium carbonate, sodium sulphate, milk of lime, etc., as the case may require; and basic lead mordants, padded on the cloth, are fixed in a chamber filled with ammonia vapour. But no definite instructions can be given for any and every method of fixing, as the machinery used for the purpose differs in different works; as a rule, any plant will do if the cloth can be passed through it in the open width under the requisite conditions of temperature, and without entailing any waste of material.

Most of the "fixing agents" in general use have been given when treating of the dunging process, so that it only remains here to mention the antimony salts.

TARTAR EMETIC, OR ANTIMONY POTASSIUM TARTRATE [$K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$] is the best known of these salts. It is only sparingly soluble in water, but is nevertheless the most largely used of all fixing agents of its class, and as a precipitant for tannic acid it gives excellent results, especially in the presence of chalk, common salt, and other neutral salts. It is worthy of note that tartar emetic dissolves much more readily in a solution of common salt than in water. Tartar emetic contains 43 per cent. Sb_2O_3.

In using tartar emetic as a fixative for tannic acid, it is important to remember that the bath gradually becomes acid through the formation of acid potassium tartrate by the abstraction of antimony. If allowed to accumulate, this salt dissolves the tannate of antimony or colour-lake, as the case may be, and thus not only prevents its fixation on the fibre, but actually "strips" or dissolves it from the cloth. A little chalk added to the bath neutralises the acidity, and allows of the goods being run through continuously.

DOUBLE OXALATE OF ANTIMONY AND POTASSIUM [$K_3Sb(C_2O_4)_3.4H_2O$] is an efficient and cheap substitute for tartar emetic. It only contains 25 per cent. Sb_2O_3; and although it is weaker in antimony, it yet produces the same result, weight for weight. This is due to the fact that it dissociates more easily, and thus gives up its antimony more readily than tartar emetic. Another advantage is that it can be used longer than an equally strong bath of tartar emetic without injuring the goods.

SODIUM TARTAR EMETIC [$Na(SbO)C_4H_4O_6.\frac{1}{2}H_2O$] is much more soluble than the potassium salt, but it is not much used as a fixing agent, its chief employment being for the production of reserve effects under basic colours.

ANTIMONY SALT [$SbF_3(NH_4)_2SO_4$] contains about 47 per cent. Sb_2O_3, is fairly soluble, and can be used in place of tartar emetic for all purposes. About nine parts of antimony salt equal ten parts of tartar emetic.

ANTIMONY SODIUM FLUORIDE ($SbF_3.NaF$) contains an amount of antimony equal to about 66 per cent. Sb_2O_3, and is therefore half as strong again as tartar emetic; it is very soluble, and can be used for most of the purposes for which tartar emetic is used.

LACTATE OF ANTIMONY, OR ANTIMONIN, comes into the market as a moist yellow mass, or in soft lumps, with the unpleasant smell of decayed cheese. It contains about 15 per cent. Sb_2O_3, the whole of which is available; consequently, as a "fixing agent" it is equal to the same weight of tartar emetic. In practice it is dissolved in water with the addition of a little acetic acid, otherwise it gives a turbid solution.

Freshly prepared *antimony hydrate* is stated by Hummel to be an economical fixing agent for tannic acid, and to possess the advantage of not leaving the bath acid. It is doubtful whether it is used in practice for this purpose.

Details respecting the preparation of "fixing liquors" will be found in the part on "Styles of Printing," where they will be given along with the processes of which they form a part.

(6) RAISING AND DEVELOPING.

Raising or developing only differs from "fixing" in that the colours are not merely fixed on the fibre, but are actually produced thereon at the same time. Amongst the colours so produced, the most important are the mineral pigments, Chrome yellow, Iron buff, Prussian blue, and Manganese brown. Salts of lead, iron, and manganese are printed on or otherwise applied to the cloth, and the colours are "raised" from them by simply passing them through the following solutions:—bichromate of potash for chromate of lead yellow; caustic soda for Iron buff; a ferrous or ferric salt for Prussian blue; and caustic soda and bleaching powder for Manganese brown.

The development of Catechu brown and other vegetable dyestuffs, and also of Aniline black, by running through a hot solution of bichromate of potash, may also be looked upon as a species of "raising," though, strictly speaking, in the case of the vegetable colours it is a true mordanting process, and in that of Aniline black an oxidation process. At the same time it is performed exactly like "fixing" and "raising," and in a similar apparatus, and might therefore be classed with either of those operations.

The development of the azo colours is a subject apart, and will be considered separately; and all other information concerning "raising" will be given under the heading of "Raised Styles" in a future chapter.

(7) CUTTING.

"Cutting" is a technical term used to denote the effect produced by discharging agents on dyed colours. If the dyed ground is discharged perfectly it is "well cut"; if only partially, it is "badly cut." In this sense "cutting" is a general term, but when applied specifically it is usually understood to refer to a particular stage in the production of coloured patterns discharged on Indigo-dyed cloth by the chromic acid method. The cloth is printed with a paste containing chromate of soda, dried, and passed through a warm solution of sulphuric and oxalic acids—the "cutting bath"—when chromic acid is liberated and oxidises, and so destroys the colour of, the Indigo wherever the chromate was originally printed.

Caustic soda may also be classed as a "cutting" agent for Indigo-dyed goods when the latter are printed in ferricyanide of potash, according to O'Neill's process of Indigo discharging. Oxymuriate of tin was also called a "cutting liquor" in the days when Madder or "Swiss" pinks formed an important article of manufacture.

Neither of these two latter styles are at present in vogue—nor ever again likely to be; and in consequence "cutting" may be considered (when used to designate a distinct process) as an essential operation connected with one particular class of work, namely, "Indigo discharge."

(8) WASHING.

The thorough washing of the cloth, after almost every operation through which it goes in the course of being transformed into a *printed* fabric, constitutes one of the most important branches of calico printing.

Formerly the output of printed goods was so small, and the streams upon which the printworks were situated so clear, that the necessary washing of the goods was done by simply allowing them to float in the stream, or in specially constructed stone or wooden troughs and channels, through which the stream was caused to run. For the class of work then produced, this primitive system was perhaps efficient; but as the industry advanced and new processes were introduced, a more rapid and more thorough method of washing was required, in order to cope both with the increased demand for printed goods and with the necessity for removing as perfectly as possible the thickening materials used in printing.

One of the oldest washing machines devised for this purpose, and still used to some extent where existing, is the "dash wheel." It consists of a large revolving wooden drum, mounted on bearings, fixed on each side of a drain, in which the wheel works. It is divided inside into four or more compartments, separated from each other by wooden gratings, and each compartment has a round opening in the side for the introduction of the goods. Jets of warm or cold water are arranged to play on the cloth through slits in the sides and circumference of the wheel and the dirty water escapes through the same slits and holes into the drain beneath. Each compartment is large enough to hold 3–4 pieces of cloth loosely bundled up, and during the revolution of the wheel they are "dashed" from side to side, and from centre to circumference. The process is slow, but the washing is good, and the thickenings get loosened and removed by the constant tossing about of the cloth.

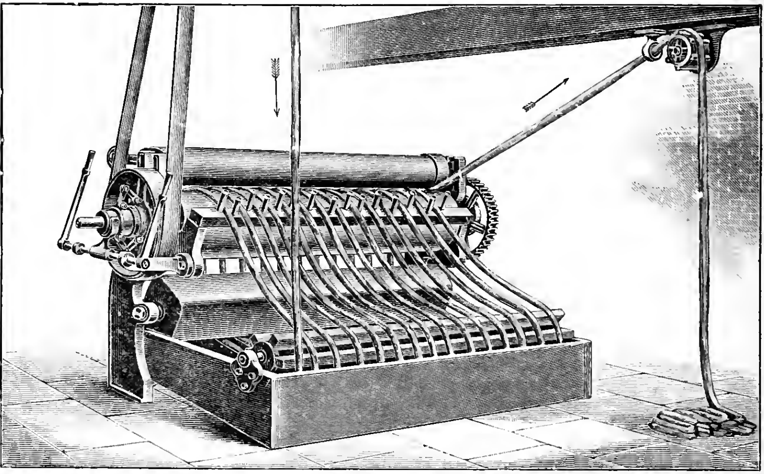

FIG. 62.—Square beater washing machine.

Figs. 62 and 63 represent the elevation and section of one of the most useful, most inexpensive, most largely used, and simplest washing machines. It consists of a long and wide shallow water trough, provided with a square beater and lagged winch. Immediately above the beater is a pair of squeezing bowls of pine. In the machine here shown the cloth is only squeezed as it leaves the machine, the end of the upper bowl being furnished with a white metal ring, between which and the lower bowl the cloth is nipped. The pieces travel spirally through the machine between the rollers; and the action of the square beater, which revolves in a direction contrary to that of the pieces, is to open out the cloth from the rope state to almost its full width as it passes along the surface of the water, so that every part of it receives a flapping motion which effectually beats out all loose particles and dyestuff, etc.

The square beater machine washes at a high speed, and serves admirably for many classes of work in which the cloth requires a thorough and energetic cleansing.

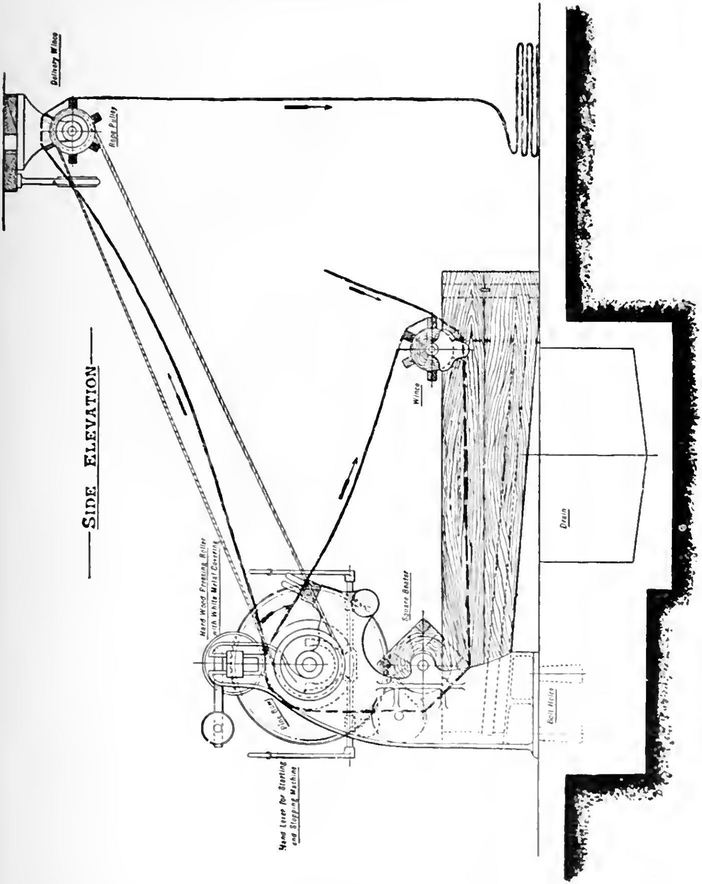

Fig. 63.—Square beater washing machine (section).

Fig. 64 represents another useful and efficient washing machine made by Messrs Mather & Platt of Salford.

It is known as the "slack washing machine," and can be used in either the dye-house or the bleach-house in all cases where it is important to avoid putting any tension on the cloth. The goods pass through, as usual in most up-to-date machines, in a continuous manner, and spirally, and receive a very efficient wash from the water expressed by the squeezing bowls.

The washing machine shown in fig. 43 is also largely used for all purposes of cleansing printed goods in all stages of manufacture. Two pieces of cloth may be washed at the same time if desired, and when this is possible the production of the machine at full speed is 400 yards per minute. The same type of machine is employed for "souring" and chemicking in the bleach-house, and if fitted with beating arrangements may be used for a variety of other purposes—raising, etc.—apart from washing.

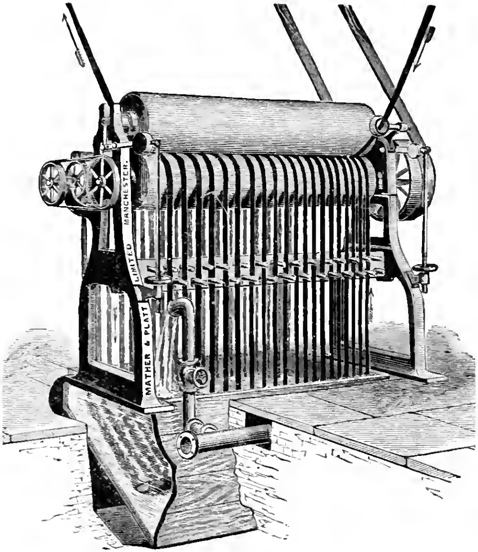

Fig. 64.—Slack washing machine.

Excess of water is usually removed from the washed calico by passing it between a pair of squeezing bowls. A machine suitable for this purpose is shown in fig. 65.

As will be seen, it consists of a wooden water trough and a pair of sycamore, cocoa-fibre, or compressed cotton bowls, mounted in a strong framework. The pressure of the top bowl on the bottom one is adjusted by powerful compound weighted levers. The cloth, after undergoing a final rinsing in the water trough, passes through two "pot eyes" between the pressure bowls, and emerges on the other side free from all surplus water, and in a fit state for opening out and drying over steam-heated cylinders. In this machine two strands of cloth are treated at the same time, and the unequal wearing of the bowls is provided against by giving the "pot eyes" through which the cloth passes a transverse motion, whereby the cloth is made to travel from side to side continually during the whole time that it is passing between the bowls.[1]

In Birch's "squeezer" the plain pressure bowls are replaced by grooved rollers. The cloth is compressed in the narrow grooves of one roller and squeezed by the projecting corrugations of the other, which fit into the grooves of the first.

"Squeezing" machines are for the most part confined to bleach-house work; printed and dyed colours would "mark off" on the white ground and on each other if passed in the rope state between pressure bowls.

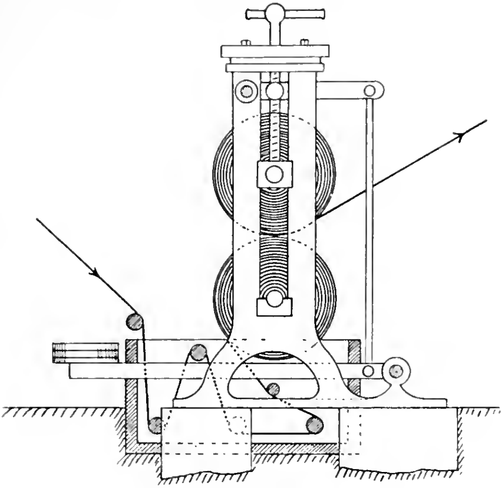

FIG. 65.—Dye-house squeezer.

(9) SOAPING.

Soaping is another important operation connected with the final cleansing of dyed and printed goods.

Its object is twofold: (1) to clear the white unprinted ground of the cloth; and (2) to brighten the colours by removing all extraneous matters and the by products resulting from the lake-forming reactions. These objects are attained by means of two different types of machine:—the *Open Soaping Machine* and the *Spiral Soaping Machine.*

The advantages of soaping printed goods in the full open width are too obvious to mention; in fact, they are so generally recognised that an "open soaper" of some sort is to be found in every printworks.

(1) The machine illustrated in fig. 66, and made by Messrs Mather & Platt of Salford, consists of separate cisterns, and may be used for a variety of purposes, including raising, fixing, "cutting," chroming, developing naphthol colours, and,

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[1] The travelling "pot eyes" have been omitted inadvertently in fig. 65. They occupy a position in front of the lower bowl.

of course, the washing and soaping of these styles. In fig. 66 the machine shown consists of six cisterns only, but any number may be added if required. Each cistern is fitted with brass top and bottom guide rollers, and at suitable intervals heavy squeezing bowls of brass and rubber, or brass and sycamore, are provided to express the excess of dirty water, soap liquor, or other solutions. With the exception of the first cistern, all the cisterns are fitted with patent non-corrodible metal beaters, placed partly immersed in the liquor and between each lap of cloth; they are driven, independently of the guide rollers, at a high speed, and being extremely simple in construction, are very durable and not liable to get out of order. The effect of these beaters is to dash the liquor with great force upon both sides of the travelling cloth, and thus thoroughly cleanse it by loosening and removing all thickening agents and any fixing or raising liquors that may have been used in the first cistern—and this without injuring in the slightest degree the most delicate fabric. The jets of water from the spirt pipes (fixed in front of the two last pairs of bowls) further aid in removing the last traces of soap, etc., from the cloth.

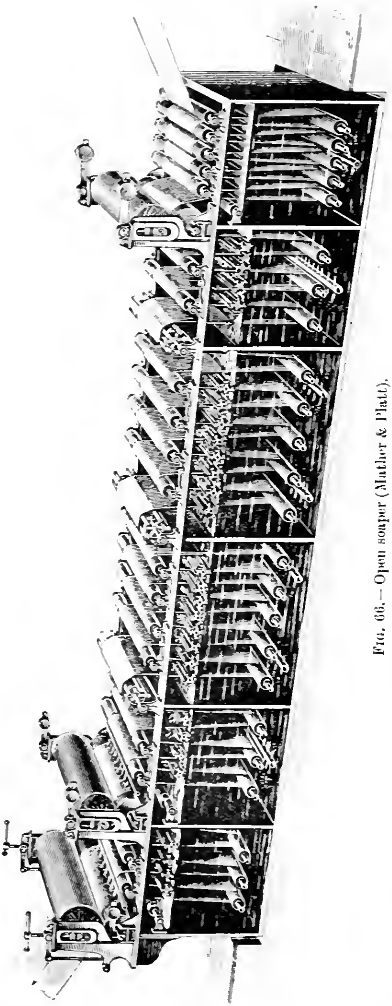


FIG. 66.—Open soaper (Mather & Platt).

The great convenience of the "opening soaping range" for styles of work in which several operations can be performed in unbroken succession is best illustrated by the following outline descriptions of the most common applications to which it is put:—

FIXING OR RAISING AND SOAPING.—For this purpose the first cistern (that on the right) is charged with a solution of tartar emetic or other salt; the second with hot water; the third and fourth with soap; the fifth with clean fresh soap or water; and the sixth with water again. The cloth passes through the first cistern, and then between the squeezing bowls into the washing and soaping cisterns successively; out of the last of these latter it passes through the squeezer bowls into the final washing beck, and thence through the last mangle directly on to the drying machine.

Indigo Discharging or "Cutting."—In this case the same series of operations is gone through, except that the first cistern is filled with "cutting liquor"—a solution containing sulphuric and oxalic acids.

Chroming Aniline Blacks and Raising Lead Yellows.—For this class of work the first cistern contains a hot solution of bichromate of potassium, and the other cisterns, water and soap.

Developing Naphthol Colours.—In the absence of a special machine for this style, the open soaper may be utilised with advantage, but care ought to be taken to avoid filling the first cistern too full of the diazo solutions, since these rapidly decompose, and not only become useless, but spoil the work past repair. For this reason, therefore, it is advisable to attach a smaller and portable cistern or trough to the open soaper, so that a constant supply of fresh diazo solution can be kept up without any undue waste of material. The cloth, prepared with β naphthol and printed in suitable resists, is first passed through the diazo solution, wherein the background is instantaneously dyed, and then in succession through the washing and soaping cisterns, after which it is ready for drying and finishing.

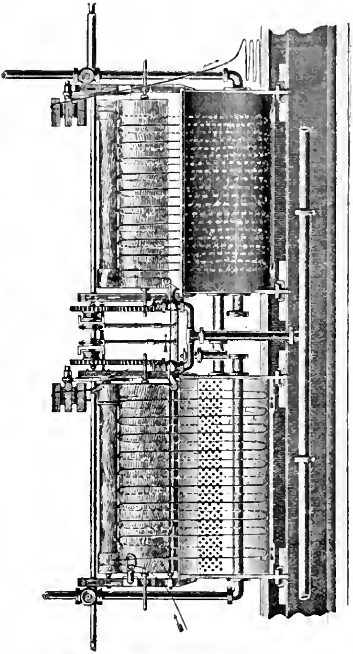


Fig. 67.

Soaping becks (Mather & Platt).

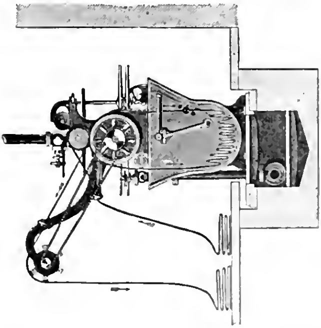


Fig. 68.

Manganese Bronze.—In developing or raising these colours in the open soaper two methods may be adopted at will: either the first cistern may contain a solution of caustic soda and the second a solution of bleaching powder, or the first cistern alone may contain a mixture of the two. In either case the course of the cloth is as already described, *i.e.* through water and soap. If Endler's process for Manganese bronze is employed, the raising solution consists of an ammoniacal solution of bichromate of potash, or a mixture of the chromates of potassium and ammonium.

Prussian Blue may also be "raised" in a similar way with suitable iron salts, but in this case the soap must be replaced with water, since Prussian blue is destroyed by hot soap solutions.

The heating of the various liquors, water and soap solution is effected by means of steam pipes, and the whole machine is driven by bevel gearing connected through a clutch to any suitable engine or motor. The soap solution enters the machine at the end opposite to the cloth, and therefore the latter, in its passage, always meets with a cleaner solution.

(2) THE SPIRAL SOAPING MACHINE is based upon the same principle as the spiral dye beck, and is worked in the same way, except that the cloth passes straight through it or through a series of soap becks arranged together. The soap enters the last beck first and overflows in the others, so that, as in the "open soaper," the cloth passes forward through a cleaner and cleaner solution, until it finally meets with perfectly pure soap as it nears the end of the process.

Figs. 67 and 68 represent sections of coupled spiral soaping becks.

Spiral soaping is a somewhat drastic operation, especially if conducted at the boil, and it is therefore only applicable to the "fastest" colours, such as dyed reds, chocolates and purples, Aniline black and steam Alizarin pinks, etc.

(10) CLEARING OR CHEMICKING.

It frequently happens that, however well printed goods have been washed and soaped, they still retain an unpleasant (and unsaleable) soiled appearance on their white parts. It is to remove this defect that clearing is resorted to. The machine used for this process consists of a padding mangle, a small steaming box, a water mangle, and a drying machine, the disposition of which parts is shown in fig. 69.

The cloth runs continuously through a weak solution of bleaching powder contained in the padding mangle A; then through the steam box B, where the action of the bleaching powder is assisted by the hot steam; and finally through the water mangle C, where it is washed, and then over the drying cans D.

A method of clearing proposed by H. Koechlin was to print a solution of bleaching powder on the face of the cloth with a fine pin roller, and then immediately afterwards print a dilute acid over it with a second similar roller, but this process is not used now. It not only takes up the time of a printer who can be more profitably employed, but is not so reliable as the above method.

Another method of clearing printed goods is to mix a little bleaching powder solution with the stiffening materials used in finishing. This, however, is very rarely done, and at best is only a makeshift, yielding, on the whole, unsatisfactory results.

(11) DRYING.

Apart from hanging in heated chambers, a practice almost obsolete now except in Turkey-red works, the drying of printed goods is done in three ways: (1) over steam-heated drying cylinders, (2) by passing through hot air, and (3) on the stentering machine.

Drying over "cans" or cylinders is effected by means of the machine shown in fig. 70.

This machine consists usually of twenty-four copper or galvanised iron cylinders, heated by steam, and driven by bevel gearing from any convenient shaft or from a small engine. The journals of the cylinders are hollow, and revolve in "stuffing

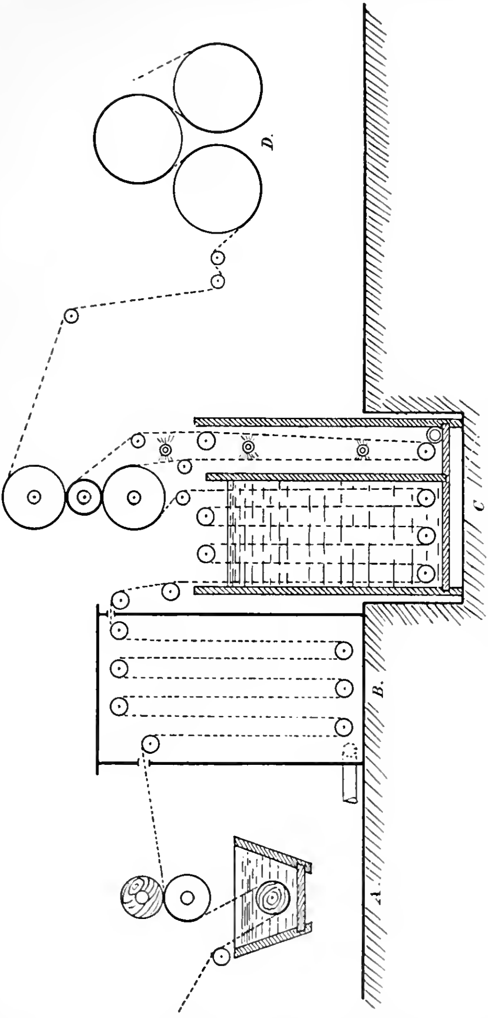


Fig. 69.—Section of chloring or chemicking machine.

boxes" which form part of the hollow brackets bolted on to the hollow framework of the machine. In this way the interior of the cylinders communicates with the steam supply on one side of the machine and with the condensed-water outlets on the other. The steam enters the machine through the hollow uprights and passes into the cylinders by way of the hollow bracket bearings; inside each cylinder is an arrangement of so-called "buckets," which catch the water of condensation and conduct it to the outlet journal of the cylinder, through which it escapes into the hollow uprights at the opposite side of the machine to that where the steam enters.

Cylinder drying machines are made in various patterns; some like the one illustrated, some consisting of fewer "tins" or cylinders, and supported on a single pair of uprights, and others with any number of cylinders, arranged in two tiers horizontally, or, in several groups, vertically. The number of cylinders employed and their arrangement is merely a matter of convenience, depending on the weight of cloth the machine is intended for and the floor space available.

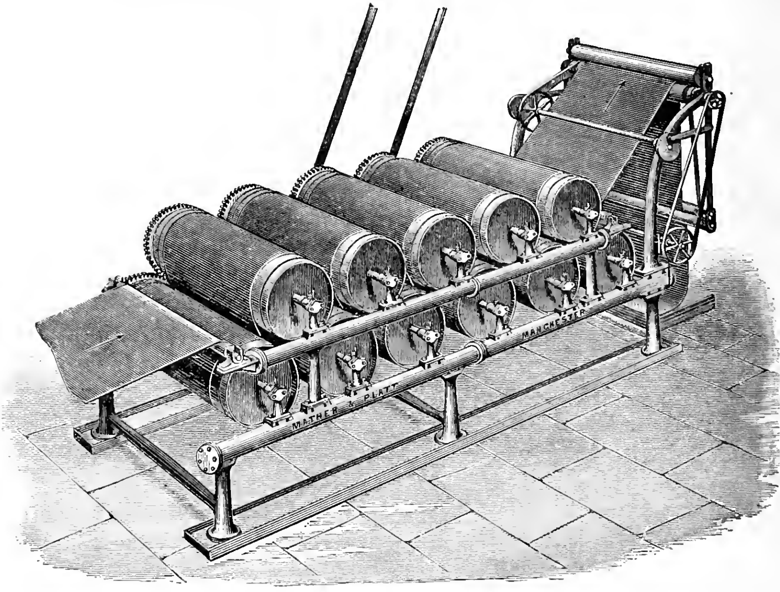
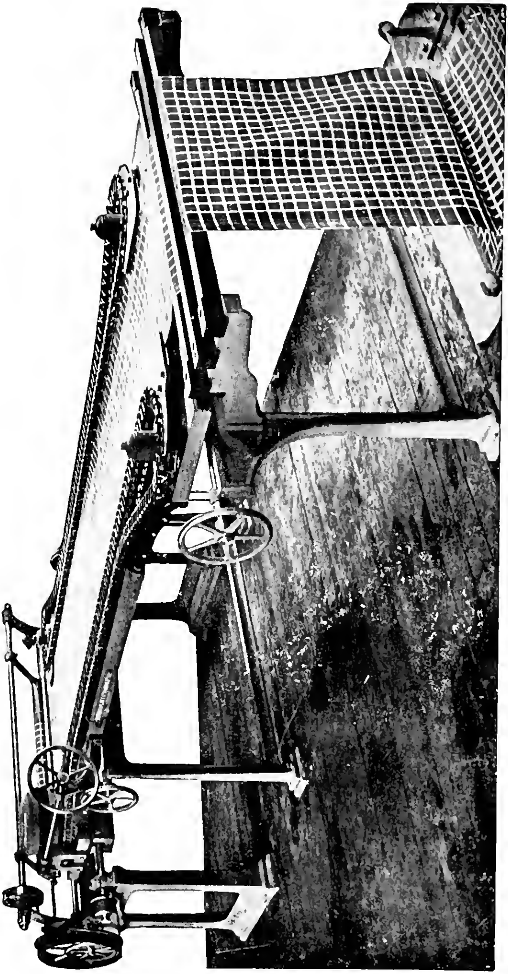


Fig. 70.—Drying machine.

When the cloth is impregnated with substances that are injuriously affected by coming in contact with the hot metallic surfaces of the cylinders, it is dried by being made to pass through a hot-air chamber or "hot flue." Formerly the "hot flue" was actually such, being a long, low, brick chamber, heated by a brick flue communicating with a furnace below. At the present time, however, this "flue" is seldom used; it has been replaced entirely by a system similar to



Short Stenter with Weft Straightener.

that shown in Plate II.—a system more convenient, more reliable, and in every way better. It consists of a large iron or wooden chamber through which the cloth passes over a series of guide rollers made of wood. The chamber is heated by a combination of steam chests and a forced draught of hot air blown in by a powerful fan attached to a tubular heater, through which the air passes before entering the chamber. A reference to Plate II., where the "hot flue" is shown in combination with a printing machine, will explain the working of this improved system of hot air drying.

Aniline black, naphthol prepares, padded mordants, and, in fact, all styles of work that would be injured by hard drying on hot cylinders, are dried in some sort of hot-air apparatus whenever possible. Failing such an apparatus, the best thing to do is to wrap the cylinders of an ordinary machine with several thicknesses of calico, and effect the drying with as little steam as possible.

As already mentioned, when treating of the preparation of cloth for printing, it frequently happens that the cloth has to be dried to a certain width in order that it may fit in with specially designed patterns, such as handkerchiefs, striped curtains, etc. This, of course, takes place before printing, but as the cloth becomes distorted during the subsequent operations of dyeing, washing, soaping, etc., it has to be stretched and straightened again during the processes immediately preceding the final finishing. If this were not done, handkerchiefs and other printed geometrical patterns would be rhomboidal in shape instead of square, and large checks and stripe patterns would undulate instead of running in straight vertical or transverse lines. For these styles, therefore, and also for fancy woven fabrics and all goods that require finishing to a definite width, the cloth, after being dried in the ordinary way over cylinders, etc., is damped and re-dried on a stretching or "stentering" machine, provided with a weft straightening device, whereby the distorted threads of the cloth can be brought back to their original position at right angles to each other.

The modern "stenter" is based upon exactly the same principle as the "mercerising" machine, and works in the same way, except that the cloth, instead of being passed through a solution of caustic soda and then washed, is simply damped and dried. The machine, which is illustrated in Plate VIII., consists of a long frame situated over a damping and drying arrangement. Two endless chains, one at each side, run along the whole length of the frame, and, as in the "merceriser," each link of these chains carries a clip which automatically grips the selvedges of the cloth as it enters, and retains its hold upon them until they are automatically released at the exit end of the frame. For a certain distance after entering the cloth is stretched by the divergent travel of the chains, and at the same time damped by jets of steam which play upon it from beneath. During its passage along the remaining length of the frame, and whilst it is held at the full stretch (the chains now running parallel), it is dried by a strong heat applied under it, either from rows of Bunsen burners, or by means of hot air blown upon it by a fan. As the cloth leaves the machine it is plaited down, and is then ready for any further treatment that will not interfere with its width.

In older types of "stentering" machines the selvedges of the cloth were pushed down on pins carried by the chains; but in most modern calico printworks "pin stenters" have been replaced entirely by the clip machine, which has the advantage of not perforating, and so not weakening, the selvedges. "Pin stenters" are still used for heavy woollen goods, and sometimes also for certain kinds of cretonnes and other heavy cotton cloths, but they are almost out-of-date for ordinary calicoes.

Another system of drying, different from any of the foregoing, consists in drawing the pieces over and in contact with the surface of a series of double-convex copper steam chests. Whatever the merits of this system may be—

and doubtless the drying is efficient enough—it is open to the objection that, if the cloth is saturated with colour or has any colour penetrating through to the back, the colour in question is almost certain to smear badly during its progress over the chests. For lightly-printed patterns it is possible that this method of drying is both rapid and economical, but, taken altogether, it is not so generally useful as those machines upon which all classes of goods can be treated.

The output of drying machines of any type depends upon the amount of water contained in the goods to be dried. It is important, therefore, that they should be freed as far as possible from all surplus water. In the case of white cloth this object is attained by passing the cloth between the squeezing bowls already described, but if printed goods were so treated the colours would "mark-off." To avoid this use is made of the "hydro-extractor," a machine in which all excess of water is driven out of the cloth by centrifugal force. (See fig. 71.)

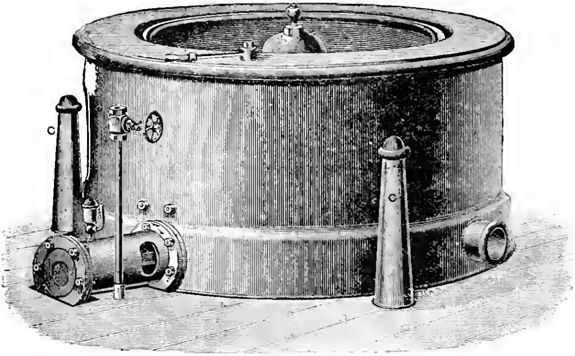


Fig. 71.—Hydro-extractor.

The hydro-extractor consists of a strong circular cage of iron or copper supported on a central pillar, so that it is capable of revolving at a high speed when actuated by the small engine (direct acting) at the side. The cage is enclosed in an outer casing of cast iron, which prevents the water from splashing over the floor and neighbouring machinery. The cloth to be hydro-extracted is loosely bundled up in comparatively small lots, and packed evenly in the cage so as not to upset its balance; the engine is then set in motion, and the water is forced out of the goods by the enormous centrifugal force generated by the high speed of the revolving cage (1500–2000 revolutions per minute).

Even the hydro-extractor can only be used for the fastest colours, and only then after a thoroughly good washing and soaping. Dyed Alizarin colours (Madder style), Aniline black, and a few other colours can be safely treated in the "extractor"; but most steam styles, and discharges and resists in colours, are apt to, and in most cases do, "mark-off," and must be squeezed in the open width before drying—not in the rope or the bundle forms.

The various conveniences attached to all calico printing machinery—such as scrimp rails, opening rollers, tension bars, scutchers, etc.—are so numerous, and vary so greatly in construction, that it would be impossible to go into a full explanation of their varied uses. Moreover they are merely contrivances for doing away with hand labour of a simple sort, and do not form any essential part of the machines to which they are attached, although, at the same time, they add greatly to their efficiency as machines. It may be noted that "scrimp" rails are corrugated bars, with the corrugations diverging from the centre; the cloth in passing over them tends to run in the grooves and is stretched in consequence; that opening rollers and cones are similar in construction, but revolve, either with or against the cloth; that tension rails are a series of bars, between which the cloth is threaded in such a way that it passes over the first, under the second, over the third, and so on, under and over the whole series, until it becomes sufficiently taut to enter the printing or padding machines, etc.; and that "scutchers" are devices for opening out the cloth from the rope state to its full width: this they do by beating a long length of rope as it passes over them, shaking it out and untwisting it so that as it passes over a pair of spiral opening rollers, some distance from the revolving beater, it becomes opened out to its full width.

For further particulars of these and other minor devices for increasing the automatic capabilities of the various machines used in washing, dyeing, and drying, reference must be had to treatises dealing more especially with the mechanical aspect of textile colouring, or to *A Manual of Dyeing*, by Knecht, Rawson, and Loewenthal (to which work this volume is a supplement), in which is described the most important machinery employed for the above purposes.

PART VI.

MORDANTS, ETC.

MORDANTS, ETC.

So enormous is the number of colouring matters now at the disposal of the calico printer, and so diverse are their chemical and physical properties, that, as might be expected, different classes of them affect the fibre in very different ways. Some colours—those belonging to the "direct dyeing" class—possess in themselves the power of dyeing textile fabrics more or less permanently; others, like the basic aniline and the acid dyestuffs, also possess this power as regards the animal fibres, wool and silk, but have scarcely any affinity at all for the cotton fibre, unless the latter is prepared with some substance capable of precipitating the colour upon it in the form of an insoluble lake; and yet other colouring matters (more correctly colouring principles, for any colour they may possess is of no practical value), can only be applied to the fibres in combination with certain metallic salts or oxides which unite with them to form intensely coloured and very insoluble "lakes," which, being produced in the body of the fabric, are in most cases exceedingly "fast" to light, air, water, and soap.

The difference in the behaviour of different colouring matters towards the cotton fibre is readily exhibited in the following simple printing trials:—

(1) Print on a piece of plain, bleached calico three stripes, consisting respectively of a thickened solution of (*a*) Erika (direct dyestuff), (*b*) Magenta (basic dyestuff), and (*c*) Alizarin (mordant dyestuff). Steam the cloth for an hour. The Erika and Magenta will be found to give a pink stripe, while the Alizarin remains yellow. Now wash and lightly soap the cloth; the Magenta and the Alizarin are almost entirely removed, whereas the Erika is but little affected, thus showing that it alone has dyed the cloth permanently. It is not a very fast colour, but still it is capable of dyeing cotton without any addition.

(2) Now add to the Magenta printing colour a little tannic acid, and to the Alizarin a little acetate of alumina. Again print them on white calico and steam for an hour, when both colours will yield a pink. Divide the cloth into two parts, and treat *one-half* in a solution of tartar emetic. Then wash and soap the two pieces together, dry them, and compare them with each other, and also with the first trial. It will be at once evident that the Magenta and Alizarin are now fixed upon the fibre in such a way as to resist soaping; and further, that the Magenta on the half of the second trial, treated with tartar emetic, is more resistant than that on the untreated half, whereas the Alizarin is equally fast in both cases, and remains practically unaltered in all respects.

This experiment shows (1) that some dyestuffs require the addition of other bodies before they can be fixed upon the cloth; (2) that in the case of colours like Magenta (basic aniline colours) a special treatment with a metallic salt is necessary before the colouring matter can be properly fixed, that is, converted into its most insoluble state; and (3) that the tinctorial properties of bodies belonging to the Alizarin family—bodies which when used alone possess no powers of dyeing any fibre—can only be utilised when they are combined with a suitable metallic base which not only unites with them to form a highly-coloured, insoluble body or "lake," but also has the effect of fixing this lake firmly upon the fibre.

The tannates of the colour-bases of Magenta and similar colours, are only partially insoluble in soap solutions; hence the necessity for treating them in a solution of tartar emetic or a tin salt, either of which fix the tannic acid upon the cloth as a very insoluble metallic tannate.

(3) Print two separate pieces of cloth, the one with four Alizarin colours, containing respectively the acetates of alumina, chrome, tin, and iron, and the other with four Magenta colours, containing, in like manner, tannic acid, aluminium acetate and a solution of arsenious acid in glycerine, and albumen, or any other mordant or fixing-agent whatever. After steaming, all the Magenta colours will be found to have yielded more or less the same shade of red, while the Alizarin colours will have given four distinct colours, namely red, claret, orange, and purple, or, if the acetate of iron was strong enough, a deep-purplish black.

(4) Again, print a piece of white calico in stripes of aluminium, iron, chromium, and tin acetates; pass through the rapid ager, and "fix" in a weak solution of ammonia. Dye three separate portions of the cloth thus printed in Erika, Magenta, and Alizarin respectively. The Erika will dye the cloth *all over* in pinks of varying intensity and brightness; the Magenta will only dye the printed parts in different shades of red or pink; but the Alizarin will have dyed the same printed parts in full deep shades of red, purple, claret, and orange—shades so "fast" that they may be severely soaped until the unprinted parts of the cloth are almost white, or at least as free from dye-stains as hot soaping will make them. Treated in the same way, the Magenta and Erika colours would be entirely removed.

Analogous results are obtained when wool or silk are substituted for cotton, or when Logwood, Quercitron bark, etc., are substituted for Alizarin. The colours produced are, of course, different, and they act differently on the different fibres, but the effects obtained are quite as various and distinct as the above, and demonstrate quite as clearly the necessity for treating all colours according to their chemical properties, and according to the nature of the material to which they are to be applied.

From these four experiments it is clear that Erika, Magenta, and Alizarin represent, broadly, three quite distinct classes of colouring matters: (1) those possessing an inherent affinity for the cotton fibre; (2) those which can only be fixed upon it by means of other substances, and even then only yield various shades of one colour; and (3) those which require to be combined with a metallic base, and yield different colours with different bases.

The first and second classes have two qualities in common; they both consist of bodies in which the colour exists as such, and they both dye the fabric in one colour only, which is merely fixed thereon in an almost unchanged state, —in the case of basic colours, tannic acid simply replacing acetic or hydrochloric acid, etc., as the case may be. Such bodies have been aptly termed *monogenetic colouring matters* by the late J. J. Hummel; while such as Alizarin, Logwood, etc., which possess no colouring power in themselves, but yield various coloured precipitates with different bases, are known as *polygenetic colouring principles.*

Although, generally speaking, each class of colouring matters is applied in a special way, it is none the less difficult to draw a hard and fast line between the different groups. Some colours possess the qualities of one, and are applied by the methods of another, and others, again, form a class by themselves. On the whole, then, the simplest and most practical classification is that based upon the methods and means of application; and as many of the mechanical operations employed for this purpose are common to many colours, it is possible to group the latter into "styles"—a term which includes everything connected with the production of a given kind of calico print.

As already observed, this question of style is largely, if not entirely, a question of the behaviour of colouring matters towards the fibre; but, from what has just been said, it will be evident that some classes of colouring matters have no action whatever upon the cotton, wool, or silk fibres, except in presence of certain other bodies which precipitate them as insoluble "lakes." These bodies—such as tannic acid and various metallic salts, etc.—are absolutely essential to the development and fixation of colours in some styles of printing; and as they constitute an actual ingredient of the finished colour in many cases, and in others play an important part as oxidising or reducing agents, some idea of their composition, manufacture, and function is necessary to a proper understanding of the principles underlying each of the many "styles" of printing.

Such bodies as form insoluble compounds with colouring matters are known as *mordants*; all the others, which do not act as mordants proper, but which are used largely as oxidising, reducing, brightening, and cleansing agents, are known under various names, and may be classed as "assistants."

MORDANTS.

By far the greater number of the fastest colours known, though capable of solution or suspension in water and other solvents, and of penetrating in this state into, and staining the fibres of, various textile materials, do not alone possess the property of attaching themselves thereto so permanently as to withstand the action of hot soap solutions or of light and air. In order to render them capable of resisting these influences, they must be combined with mordants, or otherwise converted into insoluble bodies.

Mordants are a numerous class of substances. They comprise acids, neutral salts, basic salts, and hydroxides, and may or may not possess colour. In any case their colour is not an essential feature, their sole use being to precipitate the colouring matter upon the fibre in an insoluble state. To this end they are applied in various ways, according to their nature, to the state of the fibre under treatment, and to the style of work in hand. In calico printing they are either precipitated and fixed upon the cloth previous to dyeing (dyed style), or they are applied to it, by printing, at the same time as the colour (mixed with it, in fact), the printed cloth being afterwards steamed, during which process the mordant is decomposed, and, under the influence of the heat and moisture, its metallic base combines with the colouring matter to form an insoluble compound, which is deposited within the fibres of the cloth, and fixed there more or less permanently at the same time.

In wool and silk printing this latter process is also employed, but the method of mordanting these animal fibres is quite different and much simpler than that of mordanting cotton, which is a particularly inert substance, and has but little natural attraction for most mordants.

In mordanting wool, it usually suffices to boil it in dilute solutions of metallic salts, containing either free sulphuric, formic, lactic, and other acids, or acid salts like bisulphate of soda and "cream of tartar." Under the combined action of heat, dilution, and of the acid additions, the "mordanting" salt, in presence of the wool, dissociates, and its base, or at least its metallic constituent, unites with the fibre in some way that, up to the present, has not been definitely ascertained.

Silk is mordanted in the same manner as wool, except that it is rarely heated beyond tepidity. It possesses the property of absorbing metallic salts (especially if they be at all basic) from cold concentrated solutions, and these salts, which it takes up in a more or less unchanged condition, are subsequently dissociated when the silk is washed in water. Hence silk is usually steeped in strong solutions of various basic salts, then squeezed and washed in water, the mere dilution with which is sufficient to bring about the dissociation of the salt, and to precipitate it in and upon the fibre in a still more basic and insoluble form.

Cotton, on the other hand, requires much more elaborate treatment before it can be satisfactorily mordanted. Unlike silk and wool, it has no power of decomposing metallic salts by mere steeping and boiling in their solutions, nor does it possess any affinity for mordants, except tannic acid, which it absorbs readily and retains fairly tenaciously. In mordanting cotton, therefore, the aim is to precipitate insoluble bodies within the substance of the fibre, and when this is successfully accomplished the fibre retains them almost as firmly as if they were chemically combined with it.

The salts used by the calico printer for mordanting cotton comprise (1) those which are easily dissociated by exposure to warm, moist air after printing; (2) those which form insoluble salts with various acids; and (3) those the metallic bases of which precipitate certain colouring matters as insoluble lakes, under suitable conditions.

To the first class belong the acetates, sulphate-acetates, and basic acetates of alumina or iron. The cotton is impregnated with their solutions, dried, and exposed to warm, moist air in an "ageing" apparatus. The greater part of the acid is driven off during this process, leaving a basic salt on the fibre. Any remaining acid is then neutralised by ammonia, chalk, etc., or replaced by an acid such as phosphoric, silicic, arsenic, or in some cases tannic acids, which precipitates the iron or alumina. With the exception of the last mentioned, these acids are employed in the "dunging process" as salts of sodium.

To the second class belong mordants like basic ferric sulphate, basic sulphates of alumina, and various chromium salts, any of which can either be precipitated by tannic acid, arsenates, phosphates, or silicates, or simply be converted into hydroxides by alkalies and sodium carbonate.

The third class includes all salts whatsoever that are used in the so-called "steam styles." The mordant and colouring matter are mixed together and printed on the cloth, which is then subjected for an hour or so to the action of steam, as already described (see Steaming). In the cold, the mordant and colouring matter do not react upon each other; but under the influence of hot steam the former decomposes, its acid or acids are liberated, and its base combines with the latter, which it precipitates as an insoluble coloured lake in the body of the cloth. Amongst the most important mordants of this class are the acetates of alumina, iron, chrome, tin, zinc, and nickel, the nitrates, the citrates of alumina, sulphocyanide of aluminium, zinc sulphate, oxalate, and even hydrate, of tin, acetate of lime, and various other salts and double salts which act in the same or similar ways.

On the whole, the acetates are the most generally useful of all mordants. They are stable in the cold (many of them can be boiled without decomposing if they are not too basic); their acid is readily removed in "ageing" and "steaming," or in "dunging," and other after-treatments; and, above all, they neither tender the fibre nor does the liberated acid injuriously affect the colours. The same may be said of the formates, but hitherto these salts have found but occasional use in practice, though they are well worthy of more attention, since in many cases they give brighter colours than the corresponding acetates. Nitrate of alumina is chiefly employed to impart a more fiery tone to Alizarin reds, and most other special salts are used for obtaining some particular effect, or in cases where experience has shown that they are the most suitable for the purpose intended.

In mordanting cotton with acetates of alumina and iron it generally happens that only a portion of the acetic acid is driven off in "ageing," the residue remaining in the cloth as a soluble basic acetate, or even as a normal acetate, either of which would dissolve off in the dye bath and cause stains if allowed to remain. In order, therefore, to remove the last traces of acid, the cloth is "dunged" either in ammonia, carbonate of soda or chalk, or in phosphate, arsenate, or silicate of soda. If the first three are used, the mordant exists on the cloth as a hydroxide; if the latter three, as a basic salt, or a mixture of basic salts and hydroxide. In any case it is insoluble, and thus gives rise to no bad work during the subsequent dyeing operation.

Cow-dung, when used as a fixing agent, produces the same effect as the above substances, and for printed mordants is by far the most effective of this class of bodies, since it not merely precipitates the unchanged mordant, but removes at the same time, and very rapidly, the thickening material that has been used in printing.

When mordants are printed on calico, a good deal more is applied than the cloth is capable of absorbing; the result is that the excess adheres loosely to the surface of the cloth, and, if not removed by a thoroughly good "dunging," will combine with the colouring matter in the dye bath and form a superficial crust of colour lake, which not only obstructs the penetration of the dye liquor into the body of the cloth, thus preventing the latter from being properly dyed, but also causes immense damage by rubbing off on to the unprinted portions of the cloth, which are intended to remain white. Moreover, when such imperfectly "dunged" pieces are soaped after dyeing, the surface crust of colour washes off in patches, leaving the goods in an unsaleable condition, owing to their irregularity in colour.

Although most mordants are applied as neutral, or slightly acid, solutions of various salts, they may also be applied in alkaline solution in all cases where the base is either soluble in caustic soda, or where it plays the part of an acid, *e.g.* stannate of soda, aluminate of soda, plumbite of soda, and alkaline iron, and chrome mordants. When applied in this way they are usually fixed in a bath of weak mineral acid, or passed through a salt which neutralises their alkalinity—ammonium chloride, for example—or by being allowed to decompose spontaneously in contact with the fibre, and afterwards washed in water. Most alkaline mordants are only stable in strong alkaline solution, and even then are very liable to spontaneous decomposition: dilution with water, therefore, precipitates the dissolved oxides, and acts as a veritable fixing process when applied in the form of wash-water.

Mordants are not confined to metallic compounds, for, strictly speaking, any substance that is fixed upon the fibre in combination with a colouring matter is a true mordant—that is, if it forms an essential constituent of the colour lake. In this connection β-naphthol, tannic acid, and oleic and other fatty acids are all, in a sense, mordants, since they are all important agents in the development and fixation of an enormous number of colours on the cotton and other fibres. It is true that tannic acid and the fatty acids are usually present on the fibre as metallic salts in most cases, but their metallic bases are not necessarily their essential features, and usually act as mere fixing agents, or at most are introduced for the purpose of making the final colour lake more complex—it being a general rule that the more complex the lake the faster the colour. The property possessed by the tannic and fatty acids of combining with metallic bases is utilised in many styles of printing. For instance, goods printed in aluminium acetate are frequently dyed, after "ageing" and "dunging," in a solution of tannic acid, and can then either be dyed up again in Alizarin, or treated in the same way as goods mordanted in tannate of antimony, namely, dyed up in any basic aniline dyestuff. Similarly, fatty acids in the form of soda salts are combined with alumina mordants in Turkey-red dyeing, and are absolutely essential to the production of a fine, bright, fast red.

At the same time, cloth prepared in either pure oleic acid, or oleate of tin, lead, alumina, etc., can be dyed in many artificial dyestuffs. The shades obtained in this way are very bright, but will not stand much washing.

The great variety of mordants, together with the great diversity of their chemical and physical properties, makes it impossible to formulate any general rule for their application to the fibre. At all times they must be chosen and applied with due regard to the nature of the colouring matter and material to be dealt with: and as each individual colouring matter possesses its own characteristics, these will, to a great extent, determine the mode in which it is to be fixed. Then, too, the appliances at hand modify in many cases the composition and application of mordants, and must therefore be taken into account if the best results are to be secured. Very often the process of drying adopted makes all the difference between success and failure: a mordant or a colour that comes out satisfactorily when the cloth is dried in hot air may be utterly ruined if the drying is done on steam-heated cylinders. In such cases the composition of the mordants, etc., must be modified in order to adapt them to the altered conditions: so that, quite apart from all other questions, that of machinery enters largely into all calculations respecting the production of a given "effect."

As a rule, the drying of cloth impregnated with mordants that readily dissociate should be conducted at as low a temperature as possible: if dried too sharply, the mordants are apt to become *dehydrated* (technically "burned"), and in this state they yield exceedingly poor colours on dyeing.

It is important, too, that aluminium and iron mordants should be "aged" *gradually*, and under suitable conditions of temperature and humidity, otherwise they fail to penetrate the fibre sufficiently. The mordant lies on the surface of the cloth, and any colour dyed on it afterwards is thin and uneven, lacks body and brightness, and, above all, is not fast to soaping, during which operation it "runs" or "marks off" when the goods are squeezed or wrung out.

Iron mordants used for the "dyed style" of printing are especially sensitive to high temperatures in drying and ageing, and require the most careful treatment after printing to prevent them from oxidising too rapidly.

Some mordants act as such by virtue of their acids, others by virtue of their bases: the former are fixed by means of metallic salts whose bases form insoluble salts with them, and the latter either by alkalies which precipitate them as hydroxides and basic salts, or by salts with whose acids they combine to form insoluble salts.

In the following account all the more important mordants and assistants used by the calico printer are given, together with a brief description of their preparation, modes of application, suitability for special purposes, and behaviour under varying conditions.

(1) Aluminium Mordants.

Salts of aluminium were known to and used as mordants by the Hindoos, Chinese, and Egyptians in very early times; and their value is such that at the present time they still constitute perhaps the most generally useful group of this class of bodies. They are cheap, easily prepared, and can be applied to all fibres.

Alum.—Alum comes into the market in two forms, viz. *Potash Alum* [$K_2Al_2(SO_4)_4.24H_2O$], containing 10·8 per cent. of Al_2O_3, and Ammonia Alum [$(NH_4)_2Al_2(SO_4)_4.24H_2O$], containing 11·9 per cent. of Al_2O_3. The importance of the alums has been diminished considerably by the introduction of a comparatively pure aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, but they are still preferred by some calico printers on account of their regular composition and high state of purity.

Application.—The application of alum to the cotton fibre depends upon the fact that when cotton is impregnated with basic aluminium sulphate and then dried, a more basic, and more or less insoluble, salt is precipitated upon it.

The basic salts are made by adding varying quantities of sodium carbonate or bicarbonate, chalk or hydrate of alumina to solutions of the normal salt. The degree of basicity desired may be obtained by working according to the following equations:—

(1) $K_2Al_2(SO_4)_4 + 2NaHCO_3 = Al_2(SO_4)_2(OH)_2 + K_2SO_4 + Na_2SO_4 + 2CO_2$.

(2) $2K_2Al_2(SO_4)_4 + 6NaHCO_3 = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 2K_2SO_4 + 6CO_2$.

(3) $K_2Al_2(SO_4)_4 + 4NaHCO_3 = Al_2(SO_4)(OH)_4 + 2Na_2SO_4 + K_2SO_4 + 4CO_2$.

The behaviour of these salts varies considerably on boiling and dilution. Solutions of the normal salts are unaffected, but the more basic they are made the more readily do they dissociate. For instance, according to Liechti and Suida, the basic salt $Al_4(SO_4)_3(OH)_6$ begins to dissociate at 68° C., or when diluted with water to three times its original volume, and when dried on the cotton cloth it gives up to it 58 per cent. of its alumina. The salt $Al_2(SO_4)_2(OH)_2$ is much more stable; it can be diluted with fourteen times its volume of water or be boiled for half an hour before it commences to deposit a more insoluble basic sulphate and yields 50 per cent. of its available alumina to the fibre. The normal salt only yields 13 per cent. of its alumina to the fibre, and consequently is of little value except as the raw material for the manufacture of other mordants.

The presence of potassium and sodium sulphates in basic aluminium sulphate solutions increases their liability to dissociate on boiling, but in the case of the salt made according to the first equation the precipitate re-dissolves on cooling.

Basic sulphates of alumina are only used by the calico printer for Turkey-red dyeing, other salts being found much more suitable for printing by roller or block.

The cloth is slop-padded in the basic mordant, then dried and fixed in either carbonate of ammonia, phosphate, silicate, or arsenate of soda, or in ammonia. It is then well washed, and may be dyed up in any suitable colour.

In Turkey-red dyeing the usual procedure is first of all to impregnate the cloth with an oil mordant; then pass it through a solution of basic sulphate of alumina corresponding to the formula $Al_2(SO_4)_2(OH)_2$ and dry it. The oil and alumina mutually fix each other on the fibre, and the resulting red is much more brilliant than if no oil entered into its composition. Turkey-red dyeing will be described later.

The other methods of fixing may be employed for dyestuffs other than Alizarin, although this can be equally well dyed up in the absence of oil, yielding on subsequent oiling and steaming a very bright and fast red.

The deposition of alumina from basic sulphates can also be effected by "ageing"; but this method is rarely adopted in practice, since the liberated acids are apt to tender the fibre unless it contain oil; besides which, "ageing" offers no advantages over other methods of working.

A basic sulphate in use at one of the most important Turkey-red dyeing establishments is made as follows:—

{ 30 kilos. of potash alum.
{ 300 ,, boiling water.

Dissolve and add gradually, stirring all the time,

{ 10 kilos. soda crystals ($Na_2CO_3.10H_2O$).
{ 100 ,, water.

Allow to cool, and set at 8° Tw.

Cloth prepared in a solution of sulphated oil equal to 5 per cent. fatty acids is run through the above basic sulphate at 32° C., then dried and stored until required for dyeing in Alizarin. Just before dyeing, any unprecipitated alumina is finally fixed on the cloth by a passage in open width, through a series of "dunging" becks containing a weak solution of sodium binarseniate and chalk. It is then washed and entered into the dye bath.

Other basic sulphates of alumina may be used in a similar way.

Sulphate of Alumina.—This salt [$Al_2(SO_4)_3.18H_2O$] occurs in commerce in the form of irregular lumps, having a granular surface and of a fused appearance. It was originally manufactured from bauxite, and used to contain an appreciable amount of iron. It also varied a good deal in composition, and on these two counts it was regarded with disfavour by most calico printers of a few years ago. At the present time, however, it is prepared on the large scale from the alumina obtained as a by-product in the manufacture of soda from cryolite. This alumina is practically free from iron, and when dissolved in sulphuric acid and evaporated down it yields a remarkably pure sulphate of alumina.

Aluminium sulphate has two advantages over the alums. In the first place, it contains more alumina (15·5 to 19 per cent.); and in the second, it is entirely free from the sulphates of potash and soda, which are not only useless but add to the cost of production. It also contains less water in proportion to its percentage of alumina, so that, taken all together, it is much cheaper as a raw material than either of the alums.

Basic sulphates of alumina are made from the normal commercial sulphate in exactly the same way as they are made from alum; but since less sodium and potassium sulphates are present, they are somewhat more stable, though, when heated and diluted, they produce precipitates analogous to those already mentioned.

The mordants made from aluminium sulphate are applied to cotton in the same manner as the basic alums. They are also largely used for the mordanting of wool and silk by the ordinary methods. It is usual, however, to employ the normal salts for wool, the basic sulphates being apt to go on the fibre irregularly.

Acetates of Alumina.—These salts are the most important to, and are most largely used by, the calico printer. They are easily prepared, either by dissolving the hydrate in acetic acid or by the double decomposition of aluminium sulphate and lead acetate:—

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + 3PbSO_4.$$

Solutions of the normal salt always smell of acetic acid, and this fact led Crum to assert that its real composition was $Al_2(C_2H_3O_2)_4(OH)_2$, which body remains when solutions of the normal salt are evaporated to dryness under reduced pressure and at a low temperature. He regarded the solution as containing the free acid.

Normal acetate of alumina is neither decomposed by boiling nor by dilution, but it deposits the hydroxide on standing for a long time; and, in common with the basic acetates, it is precipitated when boiled in the presence of sulphates, whether of alumina, soda, or potash. On cooling, however, the basic salt precipitated re-dissolves in the case of the normal acetate, whereas in the case of the basic acetates it does not.

In preparing aluminium acetates for printing it is usual to leave a portion of the aluminium sulphate undecomposed. The presence of a soluble sulphate prevents the solution of lead sulphate which is dissolved in appreciable quantities by pure acetate of alumina. Where the pure acetate is found to give the best results or is essential, and where the presence of lead sulphate is detrimental—as, for instance, in steam Alizarin pinks—it can be prepared either by the double decomposition of acetate of lime and sulphate of alumina, or by dissolving aluminium hydroxide in acetic acid.

It has been found by experience that in most cases it is inexpedient to replace the whole of the sulphuric acid in aluminium sulphate by acetic acid; hence most of the acetates technically known as "red liquors" are strictly speaking *sulphate-acetates.*

The sulphate-acetates, besides being cheaper than the normal acetates, are better in that they give up practically the whole of their alumina to the fibre during the "ageing" process. This is probably due to the fact, already noticed, that in the presence of soluble sulphates a basic salt is precipitated on heating, and as all the water has been driven off in the drying operation after impregnation or printing, this basic salt cannot re-dissolve, and so remains on the fibre in an insoluble state until it is finally fixed thereon permanently by the "dunging" process.

Basic acetates of alumina can be obtained by adding sodium carbonate, or bicarbonate, to the *normal salt*, in which case no soluble sulphate is present:—

$$(1)\quad Al_2(C_2H_3O_2)_6 + 2NaHCO_3 = Al_2(C_2H_3O_2)_4(OH)_2 + 2Na(C_2H_3O_2) + 2CO_2$$

or

$$(2)\quad Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2Na(C_2H_3O_2) + CO_2 + 3PbSO_4.$$

It makes no difference to the ultimate result at what stage the sodium carbonate is added so long as there is sufficient lead acetate used to combine with the whole of the sulphuric acid in the aluminium sulphate—an acetate of soda is always in solution when this is the case.

If, however, one molecule of lead acetate is replaced by a molecule of sodium carbonate the same basic acetate of alumina is produced, but at the same time sodium sulphate is also a product of the reaction and remains in solution:—

$$Al_2(SO_4)_3 + Na_2CO_3 + 2Pb(C_2H_3O_2)_2 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2PbSO_4 + CO_2 + Na_2SO_4.$$

The only difference between the results of the two sets of reactions is that basic acetates containing *sodium acetate* are not precipitated by dilution with water, whereas those containing *soluble sulphates* are so precipitated. Heat causes precipitation in both instances.

The basic sulphate-acetates are obtained in the same manner as the above, and act in the same way in most respects. On heating a basic sulphate-acetate it dissociates, but the precipitate re-dissolves on cooling if its basicity does not exceed that represented by the formula $Al_2SO_4(C_2H_3O_2)_3(OH)$.

The basic acetates and sulphate-acetates are only employed for dyeing, the best for this purpose being the last mentioned, viz. $Al_2(SO_4)(C_2H_3O_2)_3(OH)$, which is sometimes used to replace basic sulphate of alumina in the mordanting for Turkey-red.

Many other basic acetates and sulphate-acetates can be prepared by adding calculated amounts of various alkalies. The normal sulphate-acetates are simply made by using a deficiency of lead or calcium acetate, and can be varied in composition as occasion dictates:—

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 = Al_2(SO_4)(C_2H_3O_2)_4 + 2PbSO_4.$$

Most of the commercial "red liquors" are crude sulphate-acetates of alumina. They differ greatly in composition, no two makers adopting quite the same proportions, or even exactly the same ingredients. The value of a "red liquor" can only be determined by a practical trial; its analysis affords but the slightest of clues to its suitability for the given purpose, and consequently its behaviour can only be ascertained by the results it gives on a practical basis. What is known as "tin red liquor" approximates closely to a true normal acetate, though it possess the reddish-brown colour of all red liquors—a colour they derive from the presence of organic matter in the crude calcium acetate, from which they are usually manufactured.

That the composition of "red liquors" varies within wide limits is shown by the following formulæ, all of which represent "receipts" that are or have been used in practice:—

	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.
Water	1740	2000	1500	1000	1000	1000	1200	..	...	3600
Lead acetate (brown)	660	1140	945	400	400	300	500	...	...	1590
Potash Alum	...	...	...	400	400	400	600	...	400	1908 (or
Sulphate of alumina	600	665	665	...	...	...	...	70	...	1336)
Sodium carbonate (10 aq.)	...	...	...	40	...	35	...	..	...	150
Chalk	...	...	...	...	35	...	...	7	25	...
Calcium acetate 24° Tw.	...	...	...	...	...	...	...	250	1000	...
	1	2	3	4	5	6	7	8	9	10

Of the above, Nos. 1, 3, 4, 5, and 10 are perhaps the most reliable in practice, though the most basic are only suited to mordanting by slop-padding in a mangle, since they would be liable to dissociate if boiled up with thickenings for printing. For the latter purpose Nos. 1 and 3 are the most useful, and both have given good results on the large scale, when printed, "aged," etc. No. 4 without the soda also yields excellent results, and was at one time used very largely in England under the name of "4/4 liquor."

Aluminium acetates play an important part in the "steam style" of printing. In a steam Alizarin red, for instance, the mordant is simply added to the thickened Alizarin, upon which it does not act in the cold. When printed on calico, however, and "steamed," it decomposes, combines with the Alizarin to form a red lake, and at the same time fixes this lake on the fibre.

A good aluminium acetate for steam work is made as follows:—

Dissolve 60 kilos. of sulphate of alumina in 174 kilos. of water.

Then add

66 kilos. *white* lead acetate.

Stir until the lead salt is dissolved; allow to settle, and then decant the clear liquor, which will stand at about 15° of Twaddell's hydrometer. The precipitated sulphate of lead is then washed twice with 80 litres of water each time, and as the wash-waters contain a large amount of aluminium acetate they are saved and utilised for the preparation of the next batch, for which smaller amounts of alum and lead salts are taken, viz.—

160 litres of weak $Al_2(C_2H_3O_2)_6$ = (wash-waters).
14 ,, water.
50 kilos. sulphate of alumina.
55 ,, acetate of lead.

Nitrate-acetates of alumina are also used extensively in calico printing for giving a more brilliant and fiery tone to Alizarin oranges and scarlets. Either of the following recipes may be employed in their preparation:—

(1) 200·0 kilos. water.
133·4 ,, sulphate of alumina
157·2 ,, acetate of lime 23° Tw.
177·2 ,, nitrate of lime 66° Tw.

Settle, and decant the clear liquor.

(2) Nitrate-acetate of alumina.

6,670 grms. of sulphate of alumina dissolved in
10,000 ,, water, then add
4,000 ,, lead acetate.
2,000 ,, lead nitrate.
20,000 ,, water.

Settle, and decant.

The above sulphate-acetates and nitrate-acetates may be used for most purposes of calico printing in the "steam style," but when "steam colours" are thickened with the natural gums—*e.g.* gum Senegal, gum arabic, etc.—it is often found preferable to make use of a pure acetate of alumina. This is prepared as follows:—

PURE ACETATE OF ALUMINA.

3000 grms. of aluminium hydrate 12 per cent. paste.
2000 ,, acetic acid 9° Tw.

Warm until the hydrate is dissolved, then filter, cool, and set at 15° Tw.

ALUMINIUM HYDRATE.

66·7 kilos. sulphate of alumina dissolved in
200 ,, water and precipitated with
240 ,, caustic soda 23° Tw. = 10 per cent NaOH.

Wash the precipitated hydrate several times to free it from sodium sulphate, and then filter it until it contains 12 per cent. of dry hydrate.

Application of the Acetates of Alumina to Cotton.—These salts are not used at all in wool dyeing, and are only applied to silk (and wool) in printing. But for cotton they are employed more extensively than any other mordants in all branches of printing and dyeing, and are capable of yielding a great variety of effects. Cotton is most simply mordanted by their means, by being passed in the open width through their solutions, dried, and then "aged" and "dunged" as already described. For ordinary plain shade dyeing, however, they are rarely used, not because they are not suitable, but because they can be advantageously replaced by the basic sulphates of alumina, which are both cheaper to prepare and much more easily manipulated. On the other hand, the acetates and sulphate-acetates are the mordants *par excellence* for printing, since they may be applied in different ways, and in combination with many colours and other mordants.

The most important of their applications in printing is to the "Madder style"—a style in which the mordant is applied locally, as a pattern, and afterwards combined with Alizarin by dyeing. To produce this style (details of which will appear later) aluminium acetate thickened with starch flour or British gum is printed on plain bleached calico, and dried, preferably in hot air, to avoid all risk of its being dehydrated or "burnt." The printed cloth is then "aged" under suitable conditions, and after "dunging," to fix finally any unchanged acetate and to remove the thickening, it is dyed up in Alizarin, which only attaches itself to the printed parts of the cloth, leaving the rest white, or at most only tinted with an easily-removed stain. By varying the strengths of two or three printing "colours" that may be worked together in a multicolour printing machine it is possible to obtain shades varying from the darkest red to the most delicate pink; and by adding a little acetate of iron to the acetate of alumina in the "red colour," any shade of maroon or chocolate can be added to the combination, each member of which is produced simultaneously during a single dyeing operation.

Alizarin is not the only colouring matter that can be used in conjunction with printed aluminium mordants. The vegetable colours—Persian berry, Quercitron bark, Logwood, etc.,—and artificial dyestuffs of the Alizarin group

—*e.g.* Alizarin orange, Alizarin yellow, Gallopurple, etc.,—can be equally well applied in the dye bath. Even basic aniline colours may be successfully employed if the "dunged" cloth be previously "dyed" in a solution of tannic acid. The aluminium mordant in this case acts as fixing agent for the tannic acid, which is precipitated on the printed parts of the cloth as an insoluble tannate of alumina, and, as such, acts in every way as an efficient mordant for basic colouring matters of all descriptions—Methylene blue, Rhodamine, Auramine, Methyl violets, Methylene green, and Safranine.

For colours that are fixed and developed on the fibre by "steaming," the value of the acetates, sulphate-acetates, and nitrate-acetates of alumina has been already noticed. For Alizarin red they are used in connection with other substances that are essential to the production of the brightest kind of red, and this is true also of their application to the fixation of other colouring matters. At the same time they play the part of true mordants in every case, and the various other additions are made for the sole purpose of modifying or increasing the brilliancy of the ultimate colour.

"Red liquors" are occasionally used to neutralise the acid liberated from Aniline black, but their suitability for this purpose is somewhat doubtful, seeing that aluminium chloride itself is dissociated under the influence of hot steam.

In Turkey-red dyeing the various "red liquors" are sometimes used instead of the basic aluminium sulphates, but they offer no particular advantages over them commensurate with the extra work entailed by the necessity for "ageing" and "dunging."

Aluminium Nitrate [$Al_2(NO_3)_6$].—This salt is prepared by saturating nitric acid with aluminium hydrate, or by the double decomposition of aluminium sulphate and lead nitrate. The latter method is that usually adopted in practice.

ALUMINIUM NITRATE, 23° Tw.

$\left\{\begin{array}{l}\text{22 kilos. sulphate of alumina.}\\ \text{75 ,, boiling water.}\end{array}\right.$

Add gradually

30 kilos. lead nitrate (finely ground).

Stir till dissolved, allow to settle, and decant the clear liquor. Set at 23° Tw.

Basic salts may be obtained in the usual way by adding calculated amounts of alkaline carbonates to the solution of the normal salt.

Nitrate of alumina is only used as a mordant for certain "steam" Alizarin red and oranges, to which it imparts a much livelier and more fiery tone than can be obtained from the use of any other alumina mordant.

The basic nitrates of alumina are not precipitated either on boiling or by dilution with water. They may be prepared in the following way directly, instead of working with the normal salt:—

BASIC ALUMINIUM NITRATE (Depierre):—

$1\left\{\begin{array}{l}\text{1080 grms. potash alum (= 756 sulphate of alumina).}\\ \text{2000 ,, water.}\end{array}\right.$

Add

$2\left\{\begin{array}{l}\text{1000 grms. water.}\\ \text{505 ,, bicarbonate of soda.}\end{array}\right.$

Boil solutions 1 and 2 together and then add

400 grms. nitric acid 64° Tw.

Make up to 10,000 grms. with water.

The above solution contains both sodium and potassium sulphates; its formula is $Al_2(NO_3)_3(OH)_3$, and it is equal to 1·6 per cent. Al_2O_3.

Aluminium Sulphocyanide.—This salt is prepared by the double decomposition of aluminium sulphate and barium sulphocyanide thus:

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = Al_2(CNS)_6 + 3BaSO_4,$$

or by the similar reaction with $Ca(SCN)_2$, calcium sulphocyanide.

The following recipe has given excellent results on the large scale:—

8·5 kilos. barium sulphocyanide. 10 ,, water.	8 kilos. aluminium sulphate. 10 ,, water.

Mix the two solutions together, stir well, allow to settle, and decant the clear liquor. If necessary, a little chalk may be added to neutralise any free acid that may be present.

Lauber recommends the following method, but it gives no better a product than the above:—

(2) ALUMINIUM SULPHOCYANIDE.

5 kilos. aluminium sulphate.
5 ,, water.
250 grms. chalk.

Dissolve and add

11½ litres calcium sulphocyanide 30° Tw.

Settle, and decant the clear solution for use.

The basic sulphocyanides are not dissociated by mere dilution with water, but all, with the exception of $Al_2(CNS)_5(OH)$ decompose on boiling. The basic salts are not used in either dyeing or printing.

As a mordant for "steam" Alizarin reds and pinks, aluminium sulphocyanide is of paramount importance. Unlike the acetates and nitrates, it is not an acid salt; hence it does not take the "doctor edge," in other words it does not attack the steel cleaning "doctor" by dissolving off small quantities of iron; and therefore the reds, pinks, and pale salmon and terra-cotta shades made with sulphocyanide of alumina as mordant are not dulled by admixture with dissolved iron salts, to which they are extremely sensitive. Iron dulls these delicate colours by forming a purple lake with the Alizarin.

The use of sulphocyanide of alumina is limited to the above purpose.

When heavy masses of dark red and light pink are printed in combination it is advisable to pass the goods through the rapid steam ager before subjecting them to the operation of steaming. If this is not done, the large quantity of acid liberated from the mordant fills the "chamber" and prevents the pinks from developing. The same effect is observable in other colours and with other mordants than sulphocyanide of alumina; in fact, it is always better to pass goods containing much acid through the rapid ager previous to steaming, since excess of acid in the "steaming chamber" naturally interferes with the decomposition of the mordants, and in many cases destroys the colours besides, so that re-steaming is of no use.

Aluminium Citrate [$Al_2(C_6O_7H_5)_2$].—This mordant is used sparingly for the production of Alizarin pinks along with the above sulphocyanide of aluminium. It is prepared by dissolving aluminium hydrate in citric acid, and is usually kept on the acid side, as a little free acid affects the brightness of the pink beneficially.

ALUMINIUM CITRATE 10° Tw.

500 grms. 15½ per cent. aluminium hydrate paste.
220 ,, citric acid.
200 ,, water.

Stir until dissolved, and set at 40° Tw.

If too acid, add a little soda ash, say 25 to 30 grammes.

Aluminium Chlorate [$Al_2(ClO_3)_6$].—Aluminium chlorate finds a limited use in certain discharge styles. It is a powerful oxidising agent and must be used with care, otherwise the fibre is easily tendered. It is usually made by the double decomposition of aluminium sulphate and barium chlorate, but it may also be prepared by replacing the latter salt with potassium chlorate.

(1) ALUMINIUM CHLORATE 40° Tw.

I. { 40 kilos aluminium sulphate.
30 ,, water.
II. { 60 ,, barium chlorate.
70 ,, water.

Mix I. and II. together hot, stir well, allow to settle, and when cool, set at 40° Tw.

When potassium chlorate is used the following amounts are taken:—

(2) ALUMINIUM CHLORATE 40° Tw.

I. { 45 kilos. aluminium sulphate.
30 ,, boiling water.
II. { 49 ,, potassium chlorate.
100 ,, boiling water.

Mix the two solutions together hot, then allow to stand until the potassium sulphate crystallises out.

Chlorate of alumina is not often used alone at full strength, on account of its energetic action on the cloth. As a rule, it is mixed with the milder chlorate of soda, unless the colour to be discharged is very dark and the pattern printed very lightly engraved, when chlorate of alumina and red prussiate of potash, with a little citrate of ammonia added, may be employed without fear of damage to the fabric.

Aluminate of Soda [$Na_2Al_2O_4$].—This mordant, more generally known as "alkaline red mordant," is only employed in the printing of dyed styles. It is thickened with maize starch, printed, and after drying, the alumina is fixed either by exposing the pieces to air from which they absorb carbonic acid, or by passing them through a solution of ammonium chloride, or a solution of a phosphoric acid made by decomposing commercial "superphosphate" with sulphuric acid

Aluminate of soda is most readily prepared by dissolving dry aluminium hydrate in caustic soda. It may also be prepared directly from alum by adding strong caustic soda until the precipitate at first formed just re-dissolves. If potash is substituted for soda a purer mordant is obtained, as the sulphate of potash formed during the reaction crystallises out on standing. In the last case the mordant is, of course, aluminate of potash.

(1) ALUMINATE OF SODA.

{ 44 kilos. dry aluminium hydrate.
225 ,, caustic soda sol. 52° Tw.

Heat until the hydrate is dissolved; then cool and set at 36° Tw. The caustic soda is better added in two separate portions. Heat the first before putting in the aluminium hydrate; then add the second and heat the whole.

(2) ALUMINATE OF SODA (from alum).

Precipitate 25 kilos. of alum with
107 ,, caustic soda 14° Tw.

Wash the precipitate well, filter it to a stiff paste, and then dissolve it in—

14 kilos. caustic soda 52° Tw.

Set at 36° Tw.

An excess of alkali is not detrimental to the mordanting properties of aluminate of soda, and it increases the stability of the solution.

The great drawback to the use of aluminate of soda as a general "red mordant" is that its nature prevents it being employed in combination with Aniline black, and other acid colours and mordants that are usually included in the "madder style."

For plain red and pink prints, however, it is perfectly adapted, and can be used with conspicuous advantage in the printing of handkerchiefs which are required to be as good on one side as on the other. In fact, for all red and white styles it is a most useful and reliable mordant; it can be dried at a high temperature on steam-heated cylinders without any fear of the final colour being weak, as is the case with the acetates of alumina under similar conditions; and it is not possible for it to contain soluble iron salts, so that in this respect it is to be preferred to the acid mordants whenever circumstances allow of its employment.

Aluminium chloride has been suggested as a constituent of certain oxidation colours, and a chloride-acetate of alumina has been proposed as a suitable mordant for steam Alizarin reds. The latter may have yielded satisfactory results in the estimation of its inventor, but it certainly cannot compare with the other, and better known, mordants for Alizarin, and ought not to be regarded as even a moderate substitute for them.

(2) Iron Mordants.

In common with the aluminium mordants, the iron mordants have been in constant use from time immemorial; they are still amongst the most important substances employed by the dyer and calico printer, and are applicable to all textile fibres.

Iron salts exist in two states of oxidation—the *ferrous* and the *ferric* the corresponding salts of which are both used as mordants. The ferrous salts pass into ferric salts by simple exposure to air, and are easily converted by oxidising agents, such as nitric acid, potassium chlorate, etc. As a rule, the ferrous salts are the most generally used by the calico printer, since it has been found by experience that the best results are obtained, in most cases, when the mordant exists on the fibre in a state intermediate between ferrous oxide (FeO) and ferric oxide (Fe_2O_3)—that is, as ferroso-ferric oxide (Fe_3O_4) or its hydrate [$Fe_3(OH)_8$] —and this state can be best attained by regulating the air-oxidation of ferrous salts. The ferric compounds find occasional application for the production of "steam" Logwood blacks on delaines and half-wool goods, but even here the ferrous compounds are quite as often used, and give on the whole a more pleasing shade of black. Ferric salts are also used for *dyeing* plain shades of Iron buff; but when the same shade is produced by *printing*, the ferrous salts are again the most generally preferred on practical grounds.

The following are the most important compounds of iron employed in calico printing:—

(1) **Ferrous Sulphate** [$FeSO_4.7H_2O$].—This salt, known as "copperas" and "green vitriol," forms the basis for the manufacture of most iron mordants, except the "pyrolignite" or "black liquor." It is manufactured on the large scale by dissolving scrap-iron in dilute sulphuric acid; or by the gentle oxidation of iron pyrites. By whichever process it is made it comes into the market in the form of light-green crystals, generally coated with an insoluble basic ferric sulphate, due to surface oxidation, if the crystals have been exposed to air for any length of time. A good quality of ferrous sulphate ought to be bright green, and free from contamination with copper or alumina.

Application to Cotton.—Copperas is rarely used as such for mordanting cotton in any way. It may be employed for the Iron buffs already mentioned, and is sometimes used for darkening basic colours dyed on a tannin mordant; but in general it oxidises too rapidly in solution to be of much value, except in cases where no better compound is available at the moment. It plays an important part as a reducing agent in Indigo dyeing, but otherwise its value in printing depends on its usefulness as the raw material for the preparation of other salts.

(2) **Ferrous Acetate** [$Fe(C_2H_3O_2)_2$].—For the printing of "Iron buffs" or "Chamois" this salt is invariably prepared by the double decomposition of ferrous sulphate and either acetate of lead or acetate of lime. The reaction is as follows:—

$$FeSO_4 + Pb(C_2H_3O_2)_2 = Fe(C_2H_3O_2)_2 + PbSO_4,$$

but, as in most mordants, molecular proportions are not strictly observed in practice, experience having shown that an excess of ferrous sulphate gives the best results. Prepared in this way ferrous acetate is really a mixture of the acetate and the sulphate, and is known as "buff mordant."

FERROUS ACETATE (BUFF MORDANT) 18° Tw.

68 kilos. of ferrous sulphate.
196 „ „ water.

Dissolve and add

36 „ „ acetate of lead.

Stir until all the lead acetate is dissolved, then settle, decant the clear liquor, and set at 18° Tw. by the addition of water.

The above mordant, reduced in strength according to the shade desired, is thickened with starch or dextrin, printed and passed through the rapid steam ager. The goods are then "raised" through tepid caustic soda or sodium carbonate, and then allowed to lie in the wet state until the more or less olive-coloured precipitate of mixed ferrous and ferric oxides is wholly converted into the latter, which is the actual "Iron buff" colour.

By far the most important iron mordant, however, is the well-known "iron liquor," "black liquor," or pyrolignite of iron. This salt is prepared in immense quantities for calico printers by dissolving iron turnings and filings in pyroligneous acid (crude acetic acid). It is a dark-olive solution, standing at 24° Tw. In addition to ferrous acetate, it contains a notable quantity of organic matter consisting of tar and an iron salt of pyrocatechin, both of which retard its oxidation, and prevent its complete conversion into ferric oxide during the "ageing" process.

It is applied by printing in precisely the same way as the "red liquors," and goes through an identical series of operations for its fixation, viz. "ageing" and "dunging."

The "ageing" of "black liquor" printed for dyeing up in Alizarin requires to be conducted very carefully and not too rapidly, otherwise poor and uneven colours are the result. To avoid this, the goods are usually hung in an "ageing" room (where this exists), in preference to being passed through "Thom's Ageing Chamber"; the oxidation proceeds more slowly and regularly, and can be stopped at the right point. The "ageing chamber" can, however, be used if the temperature is adjusted to the required degree; in fact most goods are so treated nowadays, and with proper precautions the results leave nothing to be desired. Very weak iron mordants yield, however, very much better shades of purple with Alizarin if they are allowed to "age" slowly in a "hanging" room at a moderate temperature (70° dry-bulb, 66° wet-bulb thermometers). As already noted, the state of oxidation that is necessary is between ferrous and ferric oxide, consequently it is inadvisable to oxidise the goods rapidly by the ordinary methods of steaming, or of subjecting them to the action of oxidising agents like bichromate of soda, etc. In order further to retard the oxidation during "ageing," it is a common practice to add a mild reducing agent in the form of sodium arsenite, which is dissolved either in water alone or in the "iron liquor" before it is thickened. Arsenious acid dissolved in glycerin, common salt, or ammonium chloride is also used for the same object, and is then known as "fixing-liquor." These additions are chiefly made to weak solutions of "black liquor," such as are employed for the "dyed lilac or purple" style.

The effect of "ageing" is to drive off the greater part of the acetic acid, and at the same time to bring about the required degree of oxidation in the basic compound left on the fibre. Only practical experience can teach the printer or dyer to recognise the point at which the oxidation has proceeded sufficiently far.

After "ageing," the printed goods are "dunged" in the usual manner, after which they are dyed in Alizarin, Logwood, or any other colour that forms a lake with iron.

The most common use of pyrolignite of iron is for the production of black and white, or purple and white goods. At a strength represented by 8° Tw. it will yield a full deep black with either Logwood or Alizarin, and at strengths varying from 4° Tw. down to $\frac{1}{15}$° Tw. it gives a graduated range of purples, beginning with almost a black and going downwards to the most delicate tint of lilac. Simple black and white effects are mostly dyed with Logwood; black, purple and white combinations with Alizarin, since Logwood not only gives dirty greys on *weak* iron mordants, but is also a very fugitive colour to use for anything but dark shades of any description.

Pyrolignite of iron is not used for Iron buffs on account of the solid matter it contains—matter which frequently sticks on the cloth as black "specks." Well filtered, it is used as a mordant in "steam" Alizarin purples, but these have lost a good deal of their former importance since the introduction of the mordant colours fixed with chromium salts. Occasionally it is employed as a fixing agent for tannic acid (with which it gives a blackish grey tannate of iron) in cases where a dark, dull shade is to be dyed with basic Aniline colours. For this purpose, however, the so-called "nitrates of iron" are generally preferred.

Ferrous Nitrate [$Fe(NO_3)_2$].
Ferrous Chloride ($FeCl_2$).
Ferrous Thiosulphate ($Fe_2S_2O_3$).

These salts have not, so far, come into use as mordants proper. The first has been recommended as a "buff mordant," and the last is said to yield good results when dried on the fibre; it decomposes, and on exposure to the air finally deposits a basic ferric sulphate on the cloth.

Ferrous nitrate made as follows is said to oxidise very slowly and to serve as an efficient mordant for Logwood blacks and Iron buffs.

FERROUS NITRATE—

I. 1750 grms. ferrous sulphate.
2000 ,, water.
II. 2080 ,, lead nitrate.
3000 ,, water.

Mix the two solutions together; settle, and set the clear liquor at 50° Tw.

Trials made with the above against the ferrous acetate given previously did not compare favourably with the latter.

Potassium Ferrocyanide [$K_4Fe(CN)_6 + 3H_2O$].—*Yellow Prussiate of Potash.*—This salt occurs as light yellow crystals; it is used occasionally as a mordant for "steam Alizarin purples," and as an oxygen carrier in Aniline blacks and certain oxidation discharges. Goods printed in Iron buff, when passed through an acidulated solution of potassium ferrocyanide, are dyed Prussian blue. For this purpose it was formerly used in large quantities, but Prussian blues are rarely dyed on cotton at the present time.

The sodium salt of ferrocyanic acid is rather cheaper and more soluble than the potassium salt, but it has the disadvantage of not forming so stable a mixture with Aniline when used as a constituent of "Prussiate Aniline black."

Potassium Ferricyanide [$K_3Fe(CN)_6$].—*Red Prussiate of Potash.*—Potassium ferricyanide, like the preceding salt, is used as an oxygen carrier in both Aniline blacks and oxidation discharges. Printed on light, indigo-dyed cloth, it discharges the blue when passed through a hot solution of caustic soda.

Alkaline Iron Mordant.—Unlike aluminium hydrate, ferric hydrate is not soluble in excess of caustic soda or potash, but its precipitation may be prevented by the addition of suitable organic substances, and thus it can be obtained in alkaline solution. Of these substances, glucose, glycerin, and citric or tartaric acids are available; glycerin is perhaps the most effective from the point of view of the ultimate results.

ALKALINE IRON MORDANT.

3 kilos. of ferric sulphate sol. 91° Tw. (= 40 per cent. $Fe_2(SO_4)_3$).
¾ ,, glycerin.
14 ,, caustic soda 70° Tw.

Cloth is padded and dried in the above and then exposed to the air, or simply padded and allowed to remain rolled up for some time, when the mordant decomposes depositing ferric oxide on the fibre; or after standing in batch for a short time the cloth may be passed through a solution of ammonium chloride 10° Tw. and fixed like the alkaline alumina mordant.

A somewhat different compound is obtained by using ferrous sulphate in place of the ferric salt; in other respects its action is similar.

Another alkaline iron mordant is prepared by dissolving the pyrophosphate of iron in ammonia. The ammonia is volatilised on drying, leaving the insoluble phosphate of iron on the fibre.

None of these alkaline mordants are used in practice, though they are said to give satisfactory colours when dyed up in Alizarin.

Ferric Sulphates.—Ferric salts are in general of little interest to the present-day calico printer. They are rarely used for "steam colours," and only very occasionally for the fixation of tannic acid. By dyers, on the other hand, they are employed largely for black dyeing with Logwood—a branch of the industry outside the scope of this volume.

Under the general name of "nitrate of iron," ferric sulphate is prepared by the oxidation of the ferrous salt in presence of free sulphuric acid,

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 2H_2O$$

and

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

Basic salts may be obtained by adding alkaline carbonates to the normal salt, but they dissociate on standing.

FERRIC SULPHATE, 90° Tw.

Mix together carefully:—

15 kilos. nitric acid 66° Tw.
20 ,, water.
7 ,, sulphuric acid 168° Tw.

Then add gradually

40 kilos. ferrous sulphate in powder.

Heat to not above 50° C., and when the evolution of NO is finished add a further

3 kilos. nitric acid 66° Tw.

The above solution contains a little free nitric acid and sometimes about 2 per cent. of nitrous acid. If it be required neutral, add ferric oxide, not metallic iron, which would form a certain proportion of ferrous salt in all probability. At 90° Tw. this "ferric sulphate" contains 40 per cent. $Fe_2(SO_4)_3$.

Numerous other methods of manufacturing "nitrate of iron" are employed, but as none of the products are of present interest to calico printers it is needless to mention them.

The same remark applies to all the other ferric salts:—chloride, nitrate-acetate, nitrate-sulphate, acetate, sulphate-acetate, and a host of others sold under various trade names.

(3) Chromium Mordants.

The employment of chromium salts as mordants for cotton may be dated at the earliest from the introduction of Alizarin. One of these salts was certainly used as a mordant before this time, but it was considered rather as an oxidising agent than as a mordant, or as, in a sense, a colouring principle. Bichromate of potash, the salt in question, was employed for "developing' Catechu brown, for "raising" Chrome yellows, and for the mordanting of wool, but no other salt of chromium appears to have been used as a regular mordant until comparatively recent times. For one thing, no other salt was applicable to wool; and for another, the iron, aluminium, and tin mordants satisfied the needs of dyers and printers of the pre-Alizarin days.

At the present time chromium mordants are as important as the older aluminium and iron mordants—in fact, they are indispensable in many styles, since they form the fastest and most beautiful lakes with a great number of artificial dyestuffs.

The compounds of chromium exist in two states of oxidation: (1) chromic oxide (Cr_2O_3) and its salts; and (2) chromium trioxide (CrO_3) and the corresponding salts. In the first the chromium plays the part of the base, while in the second it forms the acid element of the salt. In both cases, however, the mordanting depends upon the deposition of chromic oxide (Cr_2O_3) or its hydrate $[Cr_2(OH_6)]$ on the fibre, and therefore the salts corresponding to CrO_3—*e.g.* the chromates and bichromates—must be reduced to the lower state of oxidation (or the basic state) before they can be utilised as mordants. This reduction is effected either before they are applied to the fibre, or on the fibre itself, according to circumstances.

The most important salts of chromium used by the calico printer are the following:—chromium acetate, nitrate-acetate, sulphate-acetate, sulphocyanide, bisulphite, chlorate, chrome alum, the chromates and bichromates of soda and potash, and the alkaline chrome mordants. A brief description of the practical application of each of these will be given, beginning with the bichromates and chrome alum, both of which serve as the bases of most of the other chrome mordants.

Bichromate of Potash [$K_2Cr_2O_7$].—This salt comes into the market in the form of large triclinic orange-red crystals, containing no combined water. Its powerful oxidising property is utilised in the development of Catechu browns, Aniline blacks, Manganese bistres, and in the discharging of Indigo; and its power of precipitating lead salts is used in the production of the brilliantly coloured Chrome yellows and oranges. When treated in presence of sulphuric acid with reducing agents, *e.g.* sugar, starch, oxalic acid, sulphurous acid, glucose, alcohol, or glycerin, it is converted into a mixture of chromium sulphate and potassium sulphate (chrome alum), from which chromic hydrate can be precipitated by any alkali. On this account it is largely employed as the raw material for the preparation of other salts, either by double decomposition or by the solution of the hydrate in suitable acids.

The only application of bichromate of potash, as such, to the fibre for the object of mordanting, is by printing it along with magnesium acetate and sodium hyposulphite (thiosulphate). In the cold and away from strong light these salts have no action upon each other, but when printed on calico and then subjected to the action of steam the hyposulphite, in presence of magnesium acetate, decomposes and reduces the bichromate to chromic sulphate, which reacts in turn with the magnesium oxide (left by the volatilisation of the acetic acid), with the result that chromic oxide is fixed upon the cloth. The following is one of several formulæ used in practice:—

STEAM CHROME MORDANT.

$\left\{\begin{array}{l}\text{16 kilos. bichromate of potash.}\\ \text{20 ,, boiling water.}\\ \text{15 ,, ammonia 20 per cent.}\end{array}\right.$
60 ,, thick starch paste or dextrin.
16 ,, thiosulphate of soda (finely ground).
15 ,, acetate of magnesium 14° Tw.

Print, dry, and steam for an hour. Then fix in a boiling 10 per cent. solution of sodium carbonate, wash, and dye in any suitable dyestuff. The final treatment in Na_2CO_3 (sodium carbonate) is to ensure that the chromium oxide is fully fixed upon the fibre. If the cloth is to be mordanted throughout, it is passed in the open width through a padding mangle containing the above proportions of the various salts, but with the thickening replaced by water. The concentration of the bath may be varied as required.

In the discharging of Indigo a thickened solution of bichromate of potash (or chromate) is printed on the blue-dyed calico. After drying, and allowing to cool a little, the goods are passed through a tepid solution of sulphuric and oxalic acids (cutting liquor). Immediately they enter this "cutting liquor" the sulphuric acid liberates free chromic acid, and this at once oxidises and destroys the Indigo on the printed parts, thus producing a white pattern on a blue ground.

Potassium Chromate (K_2CrO_4) is a bright, lemon-yellow salt which crystallises in rhomboidal prisms. It is easily prepared by neutralising the bichromate with caustic potash, or potassium carbonate; the solution is concentrated to the crystallising point, or it may, if desired, be evaporated to dryness on a water bath, in which state it is usually employed for the making of coloured "Indigo discharges."

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

The chromate of potash is preferred to the bichromate for mixing with albumen discharge colours for Indigo, because it contains no free acid. When the bichromate is used for this purpose, it is always neutralised by the addition of ammonia or sodium carbonate added to the printing paste, otherwise the albumen would be coagulated at once.

$$K_2Cr_2O_7 + 2(NH_4)OH = K_2CrO_4 + (NH_4)_2CrO_4 + H_2O.$$

The ammonium chromate acts in just the same way as the potassium salt when treated with sulphuric acid, namely, chromic acid is liberated and oxidises the Indigo wherever it is printed.

The chromates of lead and barium are insoluble salts. They are prepared by the double decomposition of the soluble salts of either metal, and of the chromate or bichromate of potassium. The lead salt is the well-known *Chrome-yellow*, and can be produced on the fibre by printing a thickened solution of lead acetate, and then running the goods through a solution of bichromate of potash.

Sodium bichromate ($Na_2Cr_2O_7.2H_2O$) and sodium chromate ($Na_2CrO_4.10H_2O$) behave in all respects like the corresponding potassium salts. They are, however, more soluble, and are therefore to be preferred in all cases where concentrated solutions are to be printed. The bichromate of soda is rather hygroscopic, and requires to be kept in a dry place or in a closed-up cask; it is cheaper than bichromate of potash, and is capable of replacing it in all its applications, except in those where it is desirable that the sulphate produced in the manufacture of some chromium mordants should crystallise out. Potassium sulphate is much less soluble than sodium sulphate.

Chrome Alum [$K_2SO_4.Cr_2(SO_4)_3.24H_2O$].—An impure chrome alum, containing calcium sulphate and organic matter, is a by-product in the manufacture of Alizarin. It may be purified by recrystallisation, and in this state it comes into the market as dark purple crystals isomorphous with potash alum. Although it contains no alumina its physical and chemical constitution is almost identical with that of the alums; hence its name *chrome alum*. A solution of chrome alum is frequently made in printworks by reducing bichromate of potash in presence of sulphuric acid. The following proportions may be used for this purpose:—

CHROME ALUM SOLUTION.

20	kilos.	bichromate of potash.
50	,,	water.
26·4	,,	sulphuric acid 168° Tw.

Heat, and add gradually

9 kilos. brown sugar.

Boil until the solution is of a bluish-green colour; if it is of an olive or yellowish-green colour it contains unreduced bichromate. Other substances, *e.g.* starch, glucose, glycerin, or the sulphites, may be used in place of sugar, with the same result. The preparation of chromium salts in this way is utilised in the manufacture of several mordants, the sulphuric acid being replaced by other acids.

Chrome alum dissolves in water to a violet solution, but if this solution be heated to 80° C. it turns green, and is said to contain a mixture of normal and basic salt. Practically speaking, it is immaterial which of these two solutions is used for the making of chrome mordants by double decomposition. They certainly act differently towards certain reagents—ammonia precipitates chromic hydrate from both solutions, but while that from the green solution is insoluble in excess of ammonia, the reverse is the case with that from the violet—and they yield corresponding acetates which form basic salts of different degrees of stability; but as none of these basic salts are used in calico printing, and as the normal salts employed are all sufficiently stable, it is unnecessary to draw a distinction between them here.

Basic chromium sulphates are prepared by adding calculated amounts of chromium hydroxide or of alkaline carbonates to the normal salt. They, of course, contain sodium or potassium sulphates, but these do not appear to affect their dissociation point on heating. The basic sulphates deposit a larger quantity of chromic oxide on the fibre as their basicity increases.

Pure chromium sulphate may be obtained by dissolving the hydrate in sulphuric acid. It has no advantages over commercial chrome alum for the preparation of mordants, and is of no practical interest, as it is not an article of commerce, and requires to be prepared specially if wanted in any quantity for a particular purpose.

Chromium Acetate $[Cr_2(C_2H_3O_2)_6]$.—This salt is the most important of the chromium mordants. Its stability is such that it can be boiled and diluted to any extent without dissociating, and yet it combines easily with various colouring matters to form "lakes" remarkable for their beauty and fastness.

Acetate of chrome is prepared on the large scale in three different ways—*e.g.* (1) by dissolving chromium hydrate in acetic acid; (2) by the double decomposition of chrome alum and lead acetate; and (3) by reducing bichromate of potash or soda in the presence of acetic acid. The following formulæ illustrate the practical application of these three methods. In each case the solution contains a little free acid, which is found beneficial in most instances.

Acetates of Chrome.

I.	1200 grms. of	chromium hydrate 20 per cent. paste.
	1500 ,,	acetic acid 9° Tw.

Heat till dissolved, cool, and set at 25° Tw.

II.	*a*	1200 grms.	chrome alum.
		2500 ,,	water.
	b	1350 ,,	lead acetate.
		1000 ,,	water (or acetic acid at 2° Tw.).

Mix *a* and *b* together, settle, decant the clear liquor, and set at 16°–20° Bé. (25°–32° Tw.). This solution contains potassium sulphate; if 1800 grms. of lead acetate were used it would contain potassium acetate, which promotes the solution of lead sulphate—a circumstance to be avoided.

III.	12 kilos. of	potassium bichromate.
	15 ,,	water.
	30 ,,	acetic acid 9° Tw.

Heat to 180° F. and then add gradually 7 kilos. glucose.

When the reaction has finished, heat the whole until it becomes green Then set at 25°–32° Tw.

Basic acetates are prepared either by the double decomposition of basic chromium sulphate and lead acetate or by adding alkaline carbonates to the normal acetate. They are very rarely used, and then only in cases where the colour is dissolved in weak alkalies. What is known as "neutral acetate" is much more commonly employed.

Neutral Acetate of Chrome.

1200 grms.	chromium hydrate 20 per cent. paste.
1300 ,,	acetic acid 9° Tw.
200 ,,	glycerin.

Heat till dissolved, and add about 80 grms. of 10 per cent. solution soda ash (or until the acetate ceases to show an acid reaction).

It is possible that basic acetates might be used with advantage in many styles of work, but they have never been applied to any extent on the large scale. An acetate made according to the following equation is very stable :—

$$Cr_2(SO_4)_2(OH)_2 + 2Pb(C_2H_3O_2)_2 = Cr_2(OH)_2(C_2H_3O_2)_4 + 2PbSO_4.$$

It will stand a fair amount of heating, and does not begin to dissociate until it is diluted with seventy-five times its own volume of water or starch paste, and then only on heating. When printed and sharply dried it yields something more than 25 per cent. of its available chromic oxide to the fibre, and when steamed and fixed in boiling sodium carbonate it gives up almost the whole. Hence it ought to be a useful mordant for the production of two-colour effects on chrome mordanted cloth which is afterwards dyed.

Nitrate-Acetate of Chrome [$Cr_2(NO_3)_2(C_2H_3O_2)_4$].—The nitrate-acetates of chromium are only used in calico printing for such colours as are improved by a slight oxidation—*e.g.* Logwood black, Quercitron bark, Persian berry yellows in strong shades, and Peachwood.

They are most easily prepared by double decomposition thus :—

$$K_2Cr_2(SO_4)_4 + Pb(NO_3)_2 + 2Pb(C_2H_3O_2)_2 = Cr_2(NO_3)_2.(C_2H_3O_2)_4 + 3PbSO_4 + K_2SO_4$$

NITRATE-ACETATE OF CHROME.

$$a\begin{cases}1000 \text{ grms. chrome alum.}\\ 2000 \text{ ,, water.}\end{cases}$$

$$b\begin{cases}300 \text{ ,, lead nitrate.}\\ 770 \text{ ,, lead acetate.}\\ 1500 \text{ ,, water.}\end{cases}$$

Mix *a* and *b* together, settle, and set the clear liquor at 35° Tw.

A basic nitrate-acetate of chrome is the compound most generally used whenever a nitrate-acetate is required. It may be prepared by adding sodium carbonate to the foregoing normal salt, but the most convenient method to adopt is to make it from bichromate by reduction with glucose.

$$2K_2Cr_2O_7 + 6HNO_3 + 4C_2H_4O_2 + 6H_2 = 2Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3 + 4KNO_3 + 8H_2O.$$

BASIC NITRATE-ACETATE OF CHROME.

$$\begin{cases}3000 \text{ grms. potassium bichromate.}\\ 3000 \text{ ,, boiling water.}\\ 3600 \text{ ,, nitric acid 64° Tw.}\end{cases}$$

Add carefully, stirring all the time, 900 grms. glucose 33 per cent. (or glycerin), and then 5000 grms. acetic acid 9° Tw.

Allow the solution to stand until the potassium nitrate has crystallised out ; then reduce to 40° Tw. with acetic acid at 4° Tw.

The glucose in the above formula may be replaced by 900 grammes of glycerin, which must be added with the greatest care, and in small quantities at a time.

Chromium Sulphate-Acetates [$Cr_2(SO_4)(C_2H_3O_2)_4$].—These salts are made by incompletely precipitating the sulphuric acid in chrome alum or chromium sulphate.

$$K_2Cr_2(SO_4)_4 + 2Pb(C_2H_3O_2)_2 = Cr_2(SO_4)(C_2H_3O_2)_4 + K_2SO_4 + 2PbSO_4.$$

They may also be prepared by a method analogous to that employed in the manufacture of the nitrate-acetates of chrome, viz. by the reduction of the bichromates of potash or soda in presence of the necessary acids.

I. SULPHATE-ACETATE OF CHROME 40° Tw.

3000	grms.	chrome alum.
6000	,,	water (boiling).
2250	,,	acetate of lead.
1200	,,	boiling water.

Add the two hot solutions together; allow to settle and cool, and set at 40° Tw.

II. SULPHATE-ACETATE OF CHROME 40° Tw.

18,000	grms.	bichromate of potash.
15,000	,,	sulphuric acid 168° Tw.
60,000	,,	hot water.
9,000	,,	acetic acid 9° Tw.

Add gradually

9,000	,,	brown sugar and then
9,000	,,	acetic acid 9° Tw.

Heat until the solution turns green. If it persistently retains an olive colour, the bichromate is incompletely reduced, and more sugar, or whatever reducing agent has been used, must be added.

Although the sulphate-acetates of chrome are largely used in place of the normal acetates, it is questionable whether they are equally effective. Comparative trials seem to show that they are not, for of several colours made up with both mordants, those containing the normal acetate invariably gave the darkest shades. On repeating the experiments with the addition of acetate of lime to the colours containing the sulphate-acetate, both sets of colours gave practically identical shades on steaming and washing; so that it would appear that the best results are only obtainable when the sulphuric acid is completely replaced by acetic acid. The only effect of adding acetate of lime to the sulphate-acetate colours was to do this, since the same addition to the acetate colours did not influence them in the least, except in the case of those containing Alizarin, and then both series of trials yielded the same shades.

In many instances, too, the sulphate-acetates of chrome coagulate and render insoluble the gum Senegal thickening used in "blotch" colours for the express purpose of keeping the cloth soft. This sometimes occurs with pure acetate of chromium made from the hydrate, but much less frequently than with the sulphate-acetates, hence it is safer to use the pure salt in all cases where any uncertainty exists as to the behaviour of the gum during the steaming process.

Chromium Sulphocyanide [$Cr_2(CNS)_6$].—This mordant is of only occasional use—chiefly for pale shades of "crushed strawberry" and such colours as are sullied by traces of iron dissolved off the steel cleaning doctor by slightly acid mordants. It is prepared in two ways: (1) by mixing solutions of chrome alum and barium sulphocyanide; and (2) by replacing the latter salt with calcium sulphocyanide. The first is the method generally adopted in practice.

$$K_2Cr_2(SO_4)_4.24H_2O + 3Ba(CNS)_6 = Cr_2(CNS)_6 + K_2SO_4 + 3BaSO_4 + 30H_2O.$$

CHROMIUM SULPHOCYANIDE.

3000	grms.	chrome alum.
6000	,,	boiling water.

Add

2580	,,	barium sulphocyanide (crystals).

Stir until dissolved, allow the precipitate of barium sulphate to settle, and then decant the clear solution. Let the potassium sulphate crystallise out as much as possible, and then set the solution at 32° Tw.

Chromium sulphocyanide is also used as a mordant in the printing of steam Logwood blacks, though the acetates answer quite as well.

Chromium Chlorate [$Cr_2(ClO_3)_6$].—Chromium chlorate is a powerful oxidising agent; it smells strongly of chlorine, and when heated gives off copious fumes of the oxides of chlorine. It has been recommended by Prud'homme for the production of ungreenable Aniline blacks, and has been occasionally used in small quantities as an addition to Logwood blacks. Its employment is somewhat dangerous in any case, since the fibre is exceedingly apt to become tendered by the formation of oxycellulose. According to Lauber, basic chlorate of chrome serves admirably as a mordant for Catechu browns, and this is quite likely, considering the energetic oxidising action of the chlorates in general.

Chlorate of chrome is prepared by the double decomposition of chrome alum and barium chlorate, or by mixing hot solutions of chrome alum and potassium chlorate.

I. Chlorate of Chrome.

a { 3000 grms. chrome alum.
 6000 ,, boiling water.
b { 2890 ,, barium chlorate.
 2250 ,, boiling water.

Mix together, and after settling, reduce to 20° Tw.

II. Chlorate of Chrome.

a { 3000 grms. chrome alum.
 6000 ,, boiling water.
b { 2200 ,, potassium chlorate.
 4500 ,, boiling water.

Mix together, cool, and allow the potassium sulphate to crystallise out. Then set at 20° Tw.

Chromium Bisulphite.—This mordant is of uncertain composition. It may be obtained by mixing bisulphite of soda with chrome alum or chromium sulphate solutions. When padded on calico and steamed, it yields a large amount of its available chromium to the fibre in the form of hydroxide, and a further amount can be fixed by a treatment in hot soda. It is chiefly used for the production of the "chrome mordant dyed and discharged" style, and is also employed as a mordant for certain steam colours—*e.g.* Alizarin greens and Alkaline and Alizarin blues.

Alkaline Chrome Mordants.—These mordants are not used for printing, but only for mordanting cloth that is intended for the "dyed and discharged style." For this purpose the goods are first padded in the open width in an alkaline solution of chromium hydrate, then fixed, dried, and again printed with an acid discharge, which dissolves out locally the chromium hydrate, so that on subsequently dyeing, a white pattern on a coloured ground is obtained. If sodium phosphate (Na_2HPO_4) be printed instead of an acid, a half-discharge effect is the result. The phosphate of chrome has less attraction for the colouring matter than the hydrate or oxide; hence, in those parts where the phosphate of soda was printed, the cloth dyes up a lighter shade.

One of the first and most successful alkaline chrome mordants is that worked out by H. Koechlin. He observed that cotton is capable of absorbing chromium hydrate from alkaline solutions, or at least of becoming mordanted when impregnated with such solutions. The more alkaline the solution, the greater is the quantity of chromium hydrate deposited on the fibre. Koechlin's process, as worked on the large scale by one of the most important English firms, is as follows:—

The cloth is padded in an alkaline mordant as under:

Alkaline Chrome Mordant.

20 kilos. chrome alum.
100 „ water.
60 „ caustic soda 70° Tw.

After padding, the goods are batched and allowed to lie all night; or they are simply plaited down and left exposed to the air for twelve to fifteen hours. At the end of this time most of the chromium hydrate will be fixed on the fibre. The goods are then well washed in water, and after drying are ready for printing.

This alkaline mordant does not keep well; on standing a day or two precipitation takes place. The addition of glycerin tends to lessen this liability, but it also diminishes the mordanting power of the solution. The precipitation is hastened by the presence of the sulphates of soda and potash, and it was the recognition of this fact that led H. Schmid to suggest the preparation of alkaline chrome mordants from the hydrate. Made on these lines the mordant is manufactured as follows:—

Alkaline Chrome Mordant.

{ 3,000 grms. chrome alum.
{ 15,000 „ boiling water.
Cool and precipitate the hydrate with
{ 1,000 grms. soda-ash.
{ 5,000 „ water.
Wash and filter the precipitate and then dissolve it in
150 grms. caustic soda at 50° Tw.
The treatment of the cloth is identical with that in Koechlin's process.

Another alkaline mordant is based upon the fact that bichromate of potash and bisulphite of soda have no action upon each other in the presence of ammonia. On steaming, however, the ammonia is volatilised, and the bichromate is reduced with the precipitation of chromium hydrate on the fibre. In practice this process is worked with the following materials and proportions:—

Alkaline Chrome Mordant.

{ 10 kilos. bichromate of potash.
{ 100 „ water.
Dissolve, cool, and add
20 kilos. ammonia 20 per cent.
30 „ bisulphite of soda, 56° Tw.
Make up with water to 200 litres.

The cloth is padded in this solution, dried and passed through the rapid ager, and then washed.

A mordant somewhat similar to the last has been used with excellent results for the "discharged and half-discharged chrome mordant style." It is prepared as follows:—

Alkaline Mordant.

200 grms. bichromate of soda.
200 „ acetate of soda.
300 „ ammonia.
210 „ hydrosulphite NF (M. L. & B.).
4000 „ water.

Pad the cloth in this solution, dry in hot air, pass through the rapid ager, and then through a boiling 2 per cent. solution of sodium carbonate, wash and dry. This mordant printed in citric acid and di-sodium phosphate gives good white and half-discharge effects when dyed up in Alizarin, Cœrulein, Nitro-alizarin, etc. The fixing in sodium carbonate is not absolutely essential, but it ensures the complete fixation of the chromic hydrate, and, as far as experience goes, yields better results. Rather better discharges are obtained if the padded and dried cloth is printed before ageing, the citric acid itself reducing the bichromate, with the formation of a very soluble citrate.

All the alkaline chrome mordants are prone to decompose on standing, and should therefore only be prepared as they are required.

Chromate of Chromium.—The mordants sent out by Meister, Lucius, & Bruning, under the names of Chrome Mordants Ga I, Ga II, Ga III, consist of various basic chromates of chromium, containing a little acetic or hydrochloric acids. The acetic-acid compound is the one most generally employed for cotton. Under the influence of steam it is completely reduced, and is then fixed in soda. For dark dyed shades the following formula is recommended by the makers:—

CHROME MORDANT Ga II.—

200	c.c.	chrome mordant Ga II, 64° Tw.
30	,,	glycerin.
770	,,	water.
1000		

Pad the cloth in this solution, dry it in the hot-air machine, pass it through the rapid ager, and then fix the mordant by passing the cloth in the open width through a 3 per cent. solution of soda-ash at 80° C. After washing and drying, it is ready for printing in citric acid, or, if intended for a plain shade, for dyeing at once.

The chromate of chromium mordants are prepared by dissolving the hydro-oxide in chromic acid, and then adding suitable quantities of acetic and hydrochloric acids according to circumstances. They were first made and patented by von Gallois, and are now put on the market ready for use by Messrs Meister, Lucius, & Bruning. In using them care must be taken to keep the padded cloth away from the light until after it is steamed, otherwise the chromic acid will oxidise and tender the fibre.

Tartrates and Citrates of Chrome.—These two salts are not capable of mordanting cloth, but as they are largely used as resists under "steam" Alizarin reds and pinks, mention of them will be as convenient here as elsewhere. They have the great advantage of giving a perfectly white resist without "running," like the citrates of soda, and citric and tartaric acids, that are used for the same purpose.

CITRATE OF CHROME 42° Tw. (for pink resists).

{ 125 grms. bichromate of potash.
{ 525 ,, hot water.

Add gradually

350 ,, powdered citric acid.

Cool, and set at 42° Tw. by adding water.

ACID TARTRATE OF CHROME 78° Tw. (For dark red resists.)

{ 585 grms. bichromate of soda.
{ 2000 ,, water.

880 ,, powdered tartaric acid.

Set at 78° Tw.

The application of these salts will be given when treating of "resists" and "discharges."

(4) Tin Mordants.

Various tin salts play an important part in many styles of printing. They act as mordants, brightening agents, and discharging agents, and are altogether an indispensable series of bodies to the calico printer.

Tin occurs in two states of oxidation: stannous oxide (SnO) and stannic oxide (SnO_2). Both these bodies are soluble in acids and alkalies, thus forming four distinct classes of salts, namely, the stannous and stannic salts, in which the tin acts as the base; and the stannites and stannates, in which it acts as the acid. The stannous salts are powerful reducing agents: they have a great affinity for oxygen, and if exposed to air for long they are more or less converted into the extremely stable stannic salts. In practice this property is taken advantage of in the discharging of direct-dyeing colours, Iron buffs, Manganese browns, etc., and in resisting the insoluble azo colours.

Of the acid salts (that is, those in which the base is tin), both classes are used largely; but of the others, only stannate of soda is used to any extent, although the stannite is sometimes employed in the discharging of Turkey-red, and a few special discharge effects on the "direct colours."

Stannous Chloride ($SnCl_2.2H_2O$).—This salt is made by dissolving granulated tin in hydrochloric acid. It comes into the market in the form of moist-looking crystals, and is commonly known as "tin salt" and as "tin crystals." If dissolved in a very small quantity of water a clear solution is obtained, but on adding more water the solution becomes "milky," owing to oxidation and simultaneous precipitation of some oxychloride. Stannic chloride is formed at the same time.

$$3SnCl_2 + O + 2H_2O = 2Sn(OH)Cl.H_2O + SnCl_4.$$

The oxychloride re-dissolves on the addition of a little hydrochloric acid. A similar oxidation product is formed on the surface of "tin crystals" if they be exposed for any length of time to the combined action of light, air, and moisture.

Application.—Mixed in small quantities with thickened "red liquors," "tin crystals" serve to prevent the fixation of iron on the cloth during the "ageing" process, and thus ensure the brightness of the Alizarin red subsequently dyed upon the cloth. When added to the extent of from 3 per cent. to 5 per cent. they enable the red mordant to resist "purple covers" (weak iron mordants) printed over it, and so make it possible to produce a bright red object on a fancy purple ground.

The energetic reducing action of "tin crystals" is utilised in the discharging of many colours, though its importance in this respect has diminished since the introduction of the "hydrosulphites." It is still, however, employed almost exclusively for resisting the fixation of the insoluble azo colours on β-naphthol prepared cloth, and for this purpose it is so far unsurpassed. (See also Oxidising and Reducing Agents.)

As a mordant, "tin crystals," in conjunction with acetate of soda, finds an occasional application in the printing of Persian berries, with which it forms an exceedingly brilliant reddish-yellow lake, very fast to light and soap. Its use as a mordant for "steam" colours is attended by some risk of tendering the fibre, notwithstanding the presence of acetate of soda, and consequently it is generally replaced by other stannous salts, and sometimes by the hydrate, especially when a mixed aluminium and tin mordant is required, as in the case of a particularly brilliant "steam" Persian berry yellow.

Apart from its employment as a discharging and reducing agent stannous chloride serves as the chief point of departure for the preparation of other tin mordants, and this, at the present time, perhaps, is its most important use in the calico-printing industry.

Stannous Acetate $[Sn(C_2H_3O_2)_2]$.—This salt is still largely used in the production of "discharge" effects on grounds dyed with the Benzidine, Diamine, and other series of direct dyeing colours, and, to a slight extent, as a mordant for the vegetable colouring matters.

It is most conveniently prepared by the double decomposition of stannous chloride and lead acetate.

Stannous Acetate (Acetate of Tin) 30° *Tw.*

a { 1390 grms. lead acetate.
800 ,, water.
300 ,, acetic acid 9° Tw.

b { 1125 ,, stannous chloride.
300 ,, water.
600 ,, acetic acid 9° Tw.

Mix *a* and *b*, allow the lead chloride to settle, and then set the clear solution at 30° Tw.

Prepared in this way the solution of tin acetate ought to be quite clear. It contains free acetic acid, but this is no detriment, especially when it is used for "discharge colours" containing tannic acid; moreover, it prevents the precipitation of basic salts, which are apt to stick in the engraving during printing.

Stannous Nitrate $[Sn(NO_3)_2]$ (?).—The composition of nitrate of tin is uncertain. It is made by slowly dissolving rods of tin in cold dilute nitric acid free from the lower oxides of nitrogen. Great care should be taken to regulate the reaction so as to avoid the evolution of NO_2.

NITRATE OF TIN 54° Tw.

5 kilos. of tin rods or small blocks.
40 ,, nitric acid 30° Tw.

Allow the reaction to proceed slowly until the acid is saturated. Then set at 54° Tw. by adding water.

On standing for a lengthened period, stannous nitrate deposits a white insoluble body—probably meta-stannic acid.

"Nitrate of tin" was formerly used as an assistant mordant in steam Alizarin reds, but is now practically obsolete, except in the wool dyeing trade for the production of Cochineal scarlets, etc.

Citrate of Tin.—A mordant under this name is frequently used in combination with acetate of chrome for the production of a quiet lemon yellow from Persian berries extract. As used, it is not a solution, but merely a kind of pasty precipitate, which dissolves when added to the printing colour; probably it exists partly in solution and partly in a "salted out" state, as might be expected from the mode of its preparation.

CITRATE OF TIN.

{ 48 kilos. citric acid.
90 ,, water.

Dissolve, cool, and add

21·5 kilos. crystal carbonate of soda,

and then

33 ,, "tin crystals."

Stir till the mixture thickens, and stir up every time before use.

Oxalate of Tin $[Sn(C_2O_4)_2]$.—Oxalate of tin is one of the most important ingredients in steam Alizarin red, towards which it acts both as a true mordant and as a brightening agent. Without the presence of tin salts it is impossible to obtain a brilliant red in the "steam style," and the oxalate is the best to use for this purpose. As generally made, oxalate of tin is a mixture of the stannous and stannic salts, since it is prepared from "oxymuriate of tin," itself a mixture of nitric acid with "tin crystals." On the large scale the following method is adopted for its manufacture:—

Oxalate of Tin.
10 kilos. "oxymuriate of tin."
40 ,, water.
Precipitate the above with
3 kilos. soda-ash.
20 ,, water.

Settle, run off the supernatant liquor, wash the precipitate three times by decantation, and then filter and press it to a stiff paste (about 15 kilos. in weight). Finally, add to it 1400 grammes of oxalic acid, dissolved in sufficient water to make the whole up to 20 kilogrammes, and heat until the whole is thoroughly homogeneous. The heating is carried out in a deep earthenware pot or mug, placed in boiling water in a colour pan. By substituting 1200 grms. of tartaric acid for oxalic acid the corresponding tartrate of tin may be obtained.

Stannic oxalate is made in the same way, except that stannic chloride is used in place of the "oxymuriate."

I. Stannic Oxalate.
Stannic chloride
5 kilos. stannous chloride.
5 ,, hydrochloric acid 24° Tw.
0·8 ,, chlorate of soda.

The chlorate of soda must be added as rapidly as the reaction permits, and the solution of tin salt in hydrochloric acid must be gently heated at first in order to promote the beginning of the reaction. When the latter is finished the tin hydrate is precipitated by adding soda-ash.

The above solution diluted with 20–30 kilos. of water is precipitated with about 3 kilos. of soda ash dissolved in 30 kilos. of water. Wash and filter the precipitate as above, and then dissolve it in 1400 grammes of oxalic acid and sufficient water to make the whole up to 20 kilogrammes.

Another *stannic oxalate* used for preparing an oil mordant is made by adding a solution of oxalic acid to a solution of stannous chloride in nitric acid, or by adding stannous chloride slowly to a mixture of nitric and oxalic acids. The former is the most rational method, but the latter is almost invariably adopted in practice, and gives satisfactory results, so far as can be judged from the quality of the work produced.

II. Stannic Oxalate.
2 kilos. nitric acid 57° Tw.
1 ,, warm water.
1½ ,, oxalic acid.
Add gradually
6¼ ,, "tin crystals."

In this case the stannic oxalate is in solution, and mixed with hydrochloric acid. Probably the same compound would result from using a mixture of "tin oxymuriate" and oxalic acid, though what actually takes place during these reactions is not easy to explain.

Oxymuriate of Tin.—This product is simply a mixture of nitric acid and "tin crystals," and varies a good deal in composition.

Oxymuriate of Tin.

30 kilos. of nitric acid 57° Tw.
Add gradually
50 ,, stannous chloride.
20 ,, water.
———
100

"Oxymuriate of tin" is thus made in practice. It is only used for the preparation of other mordants in calico printing; it varies considerably both as regards its percentage of tin and its acidity; and unless made on the spot, it is impossible to say exactly in what state of oxidation the tin really exists; in fact it is at all times difficult to ascertain the true composition of an "oxymuriate of tin."

Stannate of Soda (Na_2SnO_3).—In this salt the stannic oxide acts as the acid; and as it is precipitated by dilute mineral acids it is easily applied to the fibre. Stannate of soda is prepared by fusing together metallic tin, caustic soda, and sodium nitrate, and sometimes common salt.

$$2Sn + 3NaOH + NaNO_3 = 2Na_2SnO_3 + NH_3.$$

The "melt" is broken up and sent into the market as white, fused-looking lumps, which, when fresh, are entirely soluble in water, but undergo decomposition when exposed to moist air and become partially insoluble.

Application.—The chief use of stannate of soda is for the preparation of cloth for printing. The cloth is padded in a solution of "stannate" at about 6° Tw.; squeezed and passed without drying (though it may be dried) into sulphuric acid at 3°–4° Tw.; well washed and dried.

$$SnO_3Na_2 + H_2SO_4 + H_2O = Sn(OH)_4 + N_2SO_4.$$

The presence of stannic oxide on the cloth enhances the brightness of the printed colours, and increases their fastness to washing. Formerly stannate of soda was largely employed for the preparing of goods for the "steam style," but it is now usually replaced by "oleine" or sulphated oil. It is still used for making "eosine lakes."

Stannite of Soda (Na_2SnO_2), prepared by dissolving stannous hydrate in caustic soda, is only used in some methods of Turkey-red discharging; and a few other compounds of tin are only employed occasionally for special styles. Most of them are readily replaceable by the mordants already given, and therefore do not call for particular mention.

(5) Nickel Mordants.

The only nickel salts of any practical use are the sulphate, the acetate, and the bisulphite.

Nickel Sulphate ($NiSO_4.7H_2O$) is a green-coloured salt, easily soluble in water. It comes into the market in crystals, and its sole use is for the preparation of the acetate.

Nickel Acetate [$Ni(C_2H_3O_2)_2$] is prepared by the double decomposition of nickel sulphate and lead acetate.

$$NiSO_4 + Pb(C_2H_3O_2)_2 = Ni(C_2H_3O_2)_2 + PbSO_4.$$

Nickel Acetate.

a { 28 kilos. nickel sulphate.
50 ,, water.
b { 38 ,, $Pb(C_2H_3O_2)_2$ lead acetate.
20 ,, boiling water.

Mix *a* and *b* together hot, allow to settle and cool, and set at 20° Tw.

The chief use of nickel acetate is as a mordant for Alizarin blue.

Nickel Bisulphite comes into commerce as a green solution marking 32° Tw. It is often employed instead of the acetate for the printing of Alizarin blue, and also in combination with acetate of chrome for Alizarin green S. and similar bisulphite compounds of the mordant colouring matters.

(6) Zinc Mordants.

The zinc compounds play a not unimportant part in the production of many styles of printing.

Only the acetate and bisulphite are employed as mordants proper, and then they are restricted to the fixation of Alizarin blue, with which they form a very beautiful lake, much purer than that obtained with chrome mordants. Zinc oxide is the basis of several processes for the resisting of prussiate Aniline black (the well-known Prud'homme style), and it not only prevents the development of the black, but also forms simultaneously ferrocyanide of zinc, which acts as a mordant for any basic colours with which it may be mixed.

The following are the most important zinc salts and compounds used in calico printing:—

Zinc Sulphate ($ZnSO_4.7H_2O$).—This salt is employed, like the acetate, for the fixation of Alizarin blue. It is prepared by dissolving zinc in sulphuric acid, and as a commercial product it comes into the market as white crystals, known commonly as "white vitriol." Its chief use is for the preparation of other zinc mordants.

Zinc Bisulphite [$Zn(HSO_3)_2$].—A very rarely used mordant for Alizarin blue, and of very little practical interest. It is sold as a yellowish fluid standing at 30° Tw. Zinc bisulphite is capable of giving good results with Alizarin blue, but on the whole it is a quite unnecessary mordant, since it can be replaced with advantage by either the acetate or the cheap sulphate.

Zinc Acetate [$Zn(C_2H_3O_2)_2$].—Zinc acetate is made by mixing solutions of zinc sulphate and lead acetate.

$$ZnSO_4 + Pb(C_2H_3O_2)_2 = Zn(C_2H_3O_2)_2 + PbSO_4.$$

ACETATE OF ZINC 30° Tw.

3000 grms. zinc sulphate.
5000 ,, boiling water.

Stir in, until dissolved,

4000 grms. lead acetate.

Settle, cool, and set the clear liquor at 30° Tw.

Zinc acetate serves both as a mordant for Alizarin blue and as a resist for Aniline black in cases where the presence of solid substances like zinc oxide, chalk, magnesium carbonate, etc., is objectionable—*e.g.* in many flannelette styles. Used in place of acetate of soda for neutralising diazo solutions, it allows of these colours (the insoluble azo colours) being employed under Aniline black covers (Plusanski's process). It also acts, in common with the sulphate of zinc, as a resist to pigment colours, and it is largely used for this purpose when thickened with dextrin and mixed with china clay.

Zinc Chromate ($ZnCrO_4$).—Zinc chromate finds an occasional use in the production of the indigo reserve style. It is a pale yellow precipitate, obtained by mixing solutions of zinc sulphate and potassium bichromate or chromate.

ZINC CHROMATE.

a { 4 kilos. of potassium chromate.
5 ,, water.

b { 3 kilos. of zinc sulphate.
5 ,, water.

Mix *a* and *b* hot, allow to settle; then wash the zinc chromate by decantation several times and filter it down to 3600 grammes = 50 per cent. paste.

Zinc chromate mixed with a suitable resist paste and printed on *light indigo dyed cloth* constitutes a resist discharge; and if associated in a two-colour pattern with a simple indigo resist paste gives rise to the "two blue and white" indigo reserve style. After printing, the light blue cloth is passed again through the indigo vats; the Indigo only dyes the unprinted portions, and when the cloth is subsequently treated in a bath of sulphuric and oxalic acids, chromic acid is liberated from the zinc chromate and discharges the light blue over which it was originally printed. On washing, the other reserve is removed; and as it contained no chromate, it simply leaves a light blue where it was printed, thus giving an effect of white and light blue on a dark blue ground.

Zinc Oxide (ZnO).—Zinc oxide is one of the most useful resisting agents for prussiate or other Aniline blacks; and as it is easy to work, keeps well in made-up colours, yields very bright coloured discharges, and has no injurious effect on either colours or cloth, it is now generally employed in all Prud'homme styles where solid matter in the material is of no moment. It is also used for the production of imitation "damask effects," for which purpose it is mixed with a little albumen and a gum tragacanth thickening, and printed either as white on white cloth or slightly tinted with any suitable colouring matter. On mercerised sateen the contrast between the dull matt surface of the zinc oxide and the silky lustre of the cloth gives a very pleasing damask effect.

In making printing pastes from zinc oxide, care must be taken to grind it up into the finest state of division possible, and to strain it thoroughly before printing, otherwise "sticking-in" and scratched rollers may be expected.

Zinc oxide, being an exceedingly white substance, and having a good covering power, is largely used in the printing of linings, either as a white on tinted grounds, or as a solid pigment colour mixed with other pigment colours and fixed with albumen.

(7) Copper Mordants.

The function of copper salts in printing is principally to act as oxidising agents or carriers of oxygen.

Copper Sulphate ($CuSO_4.5H_2O$).—This salt, known as "blue-stone" and "blue vitriol," is manufactured on the large scale by roasting copper pyrites, and afterwards dissolving the residue in hot sulphuric acid. The solution is then filtered from the insoluble matter and treated with scrap iron, which reduces any ferric sulphate, and at the same time precipitates the whole of the copper. The copper is collected, well washed, and re-dissolved in sulphuric acid; then concentrated and purified by repeated recrystallisations, finally coming into the market in the form of beautiful triclinic crystals, containing five molecules of water of combination.

Copper sulphate is used as a constituent of indigo reserve pastes; in Catechu, Logwood, and Sapan wood printing colours; and it enters into the composition of many Aniline blacks, although in those applied by printing it has been replaced by the sulphide and sulphocyanide.

Copper sulphate is the raw material for the preparation of other copper salts.

Copper Sulphide (CuS).—The introduction of copper sulphide as an oxygen carrier in Aniline blacks was due to Charles Lauth in 1864. During the oxidation of Aniline black, either by steaming or "ageing" in a warm room, the sulphide, in presence of a chlorate, becomes converted into sulphate, and this in turn assists in the oxidation of the aniline. During the printing process the sulphide of copper is inactive, so that the troublesome mishaps attendant on the use of a soluble copper salt are avoided.

As prepared in the works, sulphide of copper is a black paste usually containing 30 per cent. CuS. Either of the following methods of making it may be adopted with equal success:—

I. Sulphide of Copper.

a { 1,360 grms. caustic soda 70° Tw.
  250 „ flowers of sulphur.

Dissolve carefully.

b { 1,200 grms. copper sulphate.
  10,000 „ water.

Mix the two solutions at 170° F., settle, run off the supernatant liquor, and then wash the precipitate three times by decantation. Filter and press the precipitate until it weighs 1500 grms. = 30 per cent. paste. If filtered to 2250 grms. the paste equals 20 per cent. of copper sulphide, a strength at which it is often used on account of its mixing in the printing paste better than the stiffer and drier mass.

II. Copper Sulphide.

a { 1,200 grms. copper sulphate.
  10,000 „ water.
b { 1,250 „ crystallised sodium sulphide.
  5,000 „ water.

Mix the two solutions at 170° F., and proceed as in the first recipe.

Copper sulphide is practically used for Aniline blacks only, although it may be sometimes employed in oxidation discharges when other oxygen carriers are not available.

Copper Acetate [$Cu(C_2H_3O_2)_2.H_2O$]. — Acetate of copper forms bright green crystals, and can be prepared in solution by the double decomposition of copper sulphate and lead acetate.

$$CuSO_4 + Pb(C_2H_3O_2)_2 = Cu(C_2H_3O_2)_2 + PbSO_4.$$

Copper Acetate 20° Tw.

a { 1000 grms. copper sulphate.
  1000 „ boiling water.
b { 1500 „ lead acetate.
  3000 „ water.

Mix *a* and *b*, allow to settle, and set the clear liquor at 20° Tw., or as strong as required.

Acetate of copper is sometimes used as a mordant for Alizarin blue, with which it forms the reddest lake obtainable—a lake of extreme fastness to soap, and very fast to light; as the oxidising agent in Catechu brown, Logwood, and Sapan wood colours, and Aniline black applied by slop padding; and as a constituent of indigo reserve pastes. With the exception of the first application, however, copper nitrate is capable of replacing it with advantage.

Copper Nitrate [$Cu(NO_3)_2.6H_2O$].—Copper nitrate is a powerful oxidising agent. It forms very soluble bluish crystals, and may be prepared in solution by the following recipe:—

Copper Nitrate.

a { 10,000 grms. copper sulphate.
  25 litres water.
b { 13,200 grms. lead nitrate.
  7 litres boiling water.

Mix the two solutions hot, allow to settle, and use the clear liquor.

The chief uses of copper nitrate are those given under copper acetate. It is rarely used for Aniline black, which it oxidises too rapidly, and at the same time tenders the cloth.

Copper Sulphocyanide [$Cu_2(CNS)_2$].—Cuprous sulphocyanide was recommended by Higgin in 1868 as a suitable substitute for copper sulphate in Aniline black. It is still used occasionally in England for this purpose, but not so much as formerly, the formulæ for other processes having been perfected to such an extent as to render unnecessary any resort to other copper salts than the sulphide. Copper sulphocyanide may be prepared by the double decomposition of copper sulphate and potassium or barium sulphocyanides in presence of a reducing agent like bisulphite of soda. It forms a white insoluble precipitate, generally known as "white paste."

On the whole, the use of copper salts as mordants, in the proper sense of the word, is unimportant. Apart from their application to direct-dyed colours, for the purpose of increasing their fastness to light, and their use for transforming Paranitraniline red into a brown, their value to the calico printer depends entirely upon their oxidising properties; for although, as already noted, Alizarin blue forms a very permanent lake with copper oxide, this particular shade is not in great demand, and indeed the fact of Alizarin blue forming any such "lake" is practically unknown, or at least has, hitherto, not been published.

(8) Lead Mordants.

As mordants proper, lead salts are of no practical value whatever, and are never used as such. Their great importance depends upon their property of forming the brilliant pigments "Chrome yellow" and "Chrome orange," and their usefulness as points of departure for the preparation of other metallic mordants.

Lead Acetate [$Pb(C_2H_3O_2)_2.3H_2O$].—This salt is manufactured by dissolving litharge (PbO) in acetic acid, and is known as "white sugar of lead," or "brown sugar of lead," according to whether pure acid or pyroligneous acid (crude acetic acid) has been used in its preparation.

Basic acetates of lead are obtained by boiling litharge with solutions of the normal salt, and vary in basicity with the quantity of litharge employed. One of the commonest basic acetates of lead is represented by the formula $Pb_2(C_2H_3O_2)_2(OH)_2$. All basic solutions of lead acetate absorb carbonic acid from the air, and become turbid owing to the precipitation of basic lead carbonate.

The basic acetates are for the most part used in the production of plain shades of Chrome yellow on cloth or yarn.

Lead Nitrate [$Pb(NO_3)_2$] is prepared in a similar manner to the acetate, namely, by dissolving litharge in nitric acid. Basic nitrates are prepared by increasing the amount of litharge used, and possess the same properties as the corresponding basic acetates. They give a somewhat redder yellow with bichromate of potash than the latter.

Basic Lead Carbonate.—This constitutes the well-known and largely used pigment white lead. As employed by the calico printer, lead carbonate is prepared by the double decomposition of lead acetate and sodium carbonate.

LEAD CARBONATE.

$$\begin{cases} 34 \text{ kilos. lead acetate.} \\ 200 \quad ,, \quad \text{water.} \end{cases}$$

Precipitate with about

$$\begin{cases} 12 \text{ kilos. soda-ash.} \\ 50 \quad ,, \quad \text{water.} \end{cases}$$

Settle and wash the precipitate by decantation; then filter it to a 50 per cent. paste.

When required for use the above is simply mixed with starch paste and printed; then developed in bichromate of potash and washed and dried. It is a particularly useful lead colour to use in combination with Aniline black, and gives good yellows in practice.

Lead Sulphate ($PbSO_4$).—This salt is a by-product of many reactions that take place during the making of a large number of mordants by double decomposition. Its only use in calico printing is to act as a mechanical resist to Indigo dye liquors, and for this purpose it is exclusively employed in conjunction with lead nitrate, basic lead acetate, copper salts and china clay.

Plumbite of Soda.—Plumbite of soda is formed when lead hydrate is dissolved in excess of caustic soda. Its sole application is in the discharging of Turkey-red by the alkaline process.

In general the lead salts are used as thickened solutions, in which state they are printed. After passing through a bath of warm sodium sulphate, to prevent them from running, they are treated in a bath of hot bichromate of potash, which not only precipitates the lead as lead chromate (chrome yellow), but at the same time completes the oxidation of any Aniline black, Catechu brown, or Prussian blue that may have been printed along with them. In the latter case, of course, the goods are "steamed" previous to their treatment in sodium sulphate and bichromate.

In the absence of Prussian blue, the yellow chromate of lead may be transformed into the basic chromate (Lead or Chrome orange) by running the goods through a boiling solution of clear lime water.

The "yellowing" or "tinting" of dyed red patterns is usually performed, when Chrome yellow is the colour required, by passing the printed and dyed goods through a solution of basic lead acetate. Then, without drying, they are run through a chamber filled with gaseous ammonia, which precipitates the lead hydrate on the fibre, and afterwards into a bath of bichromate of potash, where the colour is developed. In this way a red pattern on a yellow ground is obtained. Other particulars respecting the *practical* application of lead salts will be furnished in another part of this volume.

(9) Manganese Mordants.

Manganese salts are rarely or never used as true mordants; and although they are capable of forming lakes with mordant colours, they have hitherto not been applied to this purpose in practice. It is worthy of note, however, that the Alizarin blue manganese lake is quite as fast in all respects as the corresponding and largely employed zinc and nickel lakes, and is, moreover, a greener shade than either, so that it might very well form a useful addition to the range of blues obtainable from Alizarin blue.

Manganese Chloride ($MnCl_2.4H_2O$).—This salt is the most generally useful of the manganese compounds. It is obtained as a by-product in the production of chlorine from manganese dioxide and hydrochloric acid, and comes into the market as pink crystals, or as "bronze liquor" marking 71° Tw. The crystals are very hygroscopic, and liquefy if left exposed to the air.

Manganese chloride is used in dyeing and printing for the production of the well-known "Manganese brown, bronze, or bistre," as it is variously termed. For this purpose the cloth is padded in a solution of the manganese chloride 10°–20° Tw., then passed through a boiling solution of caustic soda free from carbonate, and finally through a weak solution of bleaching powder, which converts the manganous hydrate into manganic oxide (the actual colour). If now the goods are well washed, dried, and treated with aniline salt, a black is obtained. This method at one time formed the basis of several fancy styles in which coloured discharges were produced on a black ground, but is now quite out of date.

Manganese Sulphate ($MnSO_4H_2O$).—Like the chloride, manganese sulphate is a pink salt. It is also used in the same way for "bronzes," and requires no further description.

The acetate, nitrate, and mixtures of these with the sulphate or chloride may be easily prepared by double decomposition with suitable lead salts, but so far these compounds of manganese are of merely scientific interest to the calico printer.

(10) Calcium Salts.

The only calcium salt used as an assistant mordant is the acetate. This is usually prepared in the works by dissolving burnt lime in acetic acid.

ACETATE OF LIME 23° Tw.
5 kilos. burnt lime (CaO).
25 „ hot water.
Add gradually to about
25 kilos. acetic acid 9° Tw.

Add the lime until the mixture is slightly alkaline; allow to settle, and if the filtered liquor is free from iron, decant it; if not, add more lime, and settle again, after stirring it up well. When satisfactory, decant the supernatant liquor, wash the precipitate, and add the washings to the strong solution. Then acidify with acetic acid (allow about 2 per cent. excess) and set at 23° Tw.

Other compounds of calcium are chalk, the sulphocyanide, bleaching powder, and the oxalate. Chalk finds its chief employment for neutralising purposes, the sulphocyanide is restricted to the preparation of the corresponding aluminium salt, bleaching powder needs no mention here, and the oxalate is employed solely as an addition to the chromate discharge colours on Indigo.

OXALATE OF LIME.—Dissolve 1000 grms. of oxalic acid in water, and neutralise with about 800 grms. of chalk. Wash the precipitate by decantation, and then filter and press it until it weighs 2000 grms. = 50 per cent. $Ca(COO)_2$.

(11) Oil Mordants.

The value of fatty matters in dyeing has been recognised from time immemorial. The particular fatty substance used by the ancient Hindoos in their process of Madder red dyeing was derived from milk. They steeped the cotton cloth in milk and then spread it out in the sun to dry, repeating the operations until it was sufficiently impregnated with fat to fix the required amount of alumina in the fibre when steeped in a solution of alum or some preparation of alum. At the present time an analogous treatment is observed in many styles, and in the modern process of Turkey-red dyeing, the impregnating of cloth with a fatty matter is no less essential or characteristic a feature than in the old Hindoo process. The fatty matters used to-day are vegetable oils, modified in such a way as to render them soluble in water, but their function is the same as that of milk; and although a good deal of profound research work has been carried out with the object of elucidating their exact rôle, the chemical changes that they undergo during the various processes of steaming, mordanting, and dyeing are still subject to contention, and their nature is as yet more or less a matter of opinion.

Whatever the nature of these chemical changes may be, it is beyond all dispute that they enable the oil to attract the mordant and fix it upon the fibre; so that, practically, the fatty matter acts as a fixing agent, and, like other fixing agents, it forms a component part of the ultimate colour lake produced upon the cloth. Further than that, certain oils play the part of true mordants towards basic colouring matters; and if the resulting lakes are not very fast, they are at least a combination of fatty acid with colour bases, and are fixed upon the fibre in a similar way to all other colour lakes. Sometimes, as in the last instance, the oil, or at least the fatty acid, acts the part of mordant, the metallic salt with which it is combined simply acting as a fixing agent; at other times the reverse is the case, the metallic base playing the rôle of mordant, and the fatty acid that of the fixing agent. In Turkey-red the fatty matter forms an insoluble compound with the alumina of the mordant, and this insoluble body further forms a coloured lake with Alizarin. If the fatty acid is absent, the full brilliancy of the red cannot be obtained by any means; and if the alumina is absent, no red at all is obtained. From this it is evident that the presence of both elements is essential to success; and such being the case, it is only reasonable to infer that oil and alumina in combination constitute a *compound* mordant, and that the oil is just as important as the alumina, although the latter is the real base of the colour lake. Cloth mordanted for Turkey-red can also be dyed in basic colours, the oil then acting as mordant, so that with mordant (phenolic) colours (Alizarin, etc.) the metallic base of the fatty compound is the mordant, and with basic colours (Methylene blue, Magenta, etc.), the fatty element is the mordant.

For these reasons oil preparations have been called "oil mordants"; and as their importance as such is universally recognised, it only remains to consider their preparation and application in practice.

The chemistry of the subject is too complex to treat adequately in a brief notice like the present, and therefore the following remarks will be confined to the practical aspect of oil mordants. Further particulars respecting the theory of the subject are easily obtainable from the many works dealing specially with the question of the chemical technology of oils, fats, and soaps; and to such works as these the reader is referred for concise chemical data.

Castor Oil.—The basis of most oil mordants used at the present time is castor oil, the essential constituent of which is the glycerin compound of ricinoleïc acid, the composition of which is represented by the formula $C_3H_5(O.C_{18}H_{33}O_2)_3$. When boiled with caustic soda or sodium carbonate the oil is decomposed, with the formation of the sodium salt of the ricinoleïc acid and the liberation of glycerin.

$$3NaOH + C_3H_5(O.C_{18}H_{33}O_2)_3 = 3NaO.C_{18}H_{33}O_2 + C_3H_5(OH)_3.$$

The ricinoleate of soda is the well-known castor oil soap, and is used as such for the "preparing" of cloth for the steam style of printing. More frequently, however, an ammonio-soda-soap is employed for this purpose, as the ammonia volatilises on drying the padded cloth, leaving the free fatty acid on the fibre. On treating castor oil soap with mineral acids the ricinoleïc acid is set free, and can then be combined with ammonia and soda in any required proportions; or ammonia and soda soaps can be made separately and mixed as desired.

In practice the following method of preparing ricinoleïc acid has been in use for many years:—

RICINOLEÏC ACID.

40 kilos. castor oil.
28 „ caustic soda 70° Tw.
80 „ water.

Boil together (adding water to replace that evaporated) until a few drops of the soap give a perfectly clear solution with cold water; then neutralise with about

15 kilos. sulphuric acid 168° Tw.
100 „ water,

and boil again until the floating mass of fatty acid becomes quite thick. Now allow the solution to stand some time, then draw off the watery portion, and wash the fatty acid two or three times with hot water. Finally, draw off all the water and collect the fatty acid.

From the above ricinoleic acid a "prepare" for steam Alizarin reds and pinks is made as under:—

OIL PREPARE FOR REDS AND PINKS.

500 grms. ricinoleïc acid.
200 ,, titrated ammonia.
200 ,, ,, sodium carbonate solution.
100 ,, water.

1000 grms.

This equals 50 per cent. fatty acid.

For reds and pinks printed together the cloth is passed, before printing, through the above solution reduced to 5 per cent.; for pinks alone, 2½ per cent. fatty acid is sufficient.

TITRATED SODA AND AMMONIA (for above).

For the soda take 133 grms. soda ash per litre.
For the ammonia take 689 grms. ammonia 6 per cent. per litre.

20 c.c. of either solution ought to neutralise 43·4 c.c. $\frac{N}{1} H_2SO_4$.

A slight excess of ammonia is not injurious, but it is unnecessary in any oil prepare.

Although the ricinoleates are of great practical utility, they are not considered to give results equal to those obtained by the use of the *sulphoricinoleates*, and, in consequence, the latter are by far the most commonly employed both for printing and dyeing.

On the large scale the preparation of sulphoricinoleic acid is carried out in doubled-cased lead-lined pans, fitted with lead agitators and "draw-off" taps. A constant stream of cold water circulates between the casings, and serves to keep the temperature of the contents below 30° C., above which a quite different reaction is apt to take place, to the utter destruction of the oil mordant as such. The castor oil is placed in the pan, and concentrated sulphuric acid is allowed to trickle into it slowly through a glass tube. The mixture is stirred the whole time, and when all the acid has been added it is allowed to stand overnight—or longer in winter—to complete the reaction. The product is then well washed with brine, and either neutralised in the pan or drawn off for treatment elsewhere.

In practice, the following proportions have given good results; but the quantity of sulphuric acid is subject to modification according to the time of year at which the "oleine" is made. In winter and cold weather it is frequently necessary to use as much as 40 to 50 per cent. of sulphuric acid calculated on the weight of oil.

SULPHORICINOLEÏC ACID.

To 40 kilos. castor oil, add slowly at not above 30°–35° C.
10 ,, sulphuric acid 168° Tw.

Allow to stand 12–24 hours and then wash by decantation with

{ 120 kilos. water at 35° C.
{ 12 ,, common salt or Glauber salt.

Run the wash water from under the fatty acid and repeat the washing twice, with the same proportions of salt and water. Finally allow all the fatty acid to rise to the surface and then skim it off or run off the water beneath it. Yield = 53 kilos.

Sulphoricinoleate of Soda—Oleine, etc.

250 grms. of the above acid.
500 ,, water.

Add about
150 grms. caustic soda 15° Tw. until the solution is just slightly alkaline, then add water to make up to 1000 grms.

1000 grms.

This equals 25 per cent. fatty acid.

The above may be used for Turkey-red dyeing and for various other purposes including the preparation of compound tin mordants, which are also employed extensively in chintz printing and other steam styles. The ammonia salt may be made in a similar way.

Sulphoricinoleate of Ammonia 25 per cent.

250 grms. sulphoricinoleïc acid.
500 ,, water.
110 ,, ammonia (6 per cent. NH_3).
140 ,, water.

1000 grms.

In addition to the simple alkaline salts of the above fatty acids it is in many instances advantageous to make use of their stannous and stannic compounds, especially where particularly bright colours are desired. The tin sulphoricinoleates are soluble in ammonia and can therefore be applied to the cloth without difficulty. As a rule they form about 2 per cent. of the total fatty bodies present in a "prepare," but they may be increased if occasion demands, although if too great a quantity be used the white ground of the printed cloth is apt to become yellow.

Stannous Sulphoricinoleate.

50 kilos. sulphoricinoleate of soda 25 per cent.

Heat to 40° C. and add slowly, stirring all the time,
3·2 kilos. stannous chloride in
20 ,, cold water.

A slight excess of stannous chloride is advantageous. Filter off to 17·8 kilos. = 35·6 kilos. of paste from 100 kilos. oleine.

The ammonio-stannous salt is made by adding the above to "ammonia oleine," and the stannic compound by precipitating the fatty acid from sulphoricinoleate of soda with oxymuriate of tin.

Ammonio-stannous Sulphoricinoleate.

250 grms. sulphoricinoleïc acid.
250 ,, stannous sulphoricinoleate.
300 ,, cold water.

Add about
120 ,, ammonia 6 per cent. and make up with water to

1000 grms.

Stannic Sulphoricinoleate.

1000 grms. sulphoricinoleate of soda 25 per cent.

Add gradually, stirring all the time,
90 grms. oxymuriate of tin.

Wait a little after each addition, and guard against an excess of tin at any one time, otherwise the product separates out badly.

1000 grms. of the soda "oleine" 25 per cent. = 375·5 of the tin salt.

In using these tin compounds for preparing calico for the steam style they are mixed with the ordinary oleines in the first instance, and then reduced with water to the proper strength, a sufficiency of ammonia being added to dissolve the tin compound, or "Tin Oil," as it is termed. Thus for steam work containing heavy Alizarin reds the following mixture is used for preparing the cloth:—

5 per cent. "TIN OIL" PREPARE.
20 kilos. of 25 per cent. "Tin Oil."
Reduced with water and ammonia to make
100 kilos.
This mixture contains 5 per cent. fatty acids.

25 per cent. "TIN OIL" (for above).

980	grms. 25 per cent.	sulphoricinoleate of soda.
20	,,	stannous sulphoricinoleate.
1000		

The sulphoricinoleate of soda may be replaced by the corresponding ammonia salt, either wholly or in part, and castor-oil soda soap (ricinoleate of soda) may also be employed with satisfactory results.

One of the most important stages in the dyeing of Alizarin reds is the oiling and steaming of the goods after dyeing. The object of this is to brighten the red, and it may be attained by using any of the ordinary "oleines" or "soluble oils," especially if they contain a little oxalic acid. A much better result, however, is obtained by using one or other of the following "oil prepares."

BRIGHTENING OIL FOR MADDER REDS I.

200	grms.	sulphoricinoleate of soda 25 per cent.
15	,,	stannous-ammonia sulphoricinoleate.
125	,,	oxalate of ammonia 3° Tw.
660	,,	water.
1000	grms.	= 5 per cent. fatty acids.

BRIGHTENING OIL FOR MADDER REDS II.

200	grms.	sulphoricinoleate of soda 25 per cent.
3	,,	oxalic acid.
$2\frac{1}{2}$	,,	stannous chloride.
600	,,	water and enough ammonia and water to dissolve the precipitate and make up to—
1000	grms.	= 5 per cent. fatty acids.

The dyed cloth is padded in either of the foregoing solutions, then dried, steamed for an hour at 15 lbs. per sq. in. pressure, and then washed and soaped. The oil enters into combination with the colour lake, which ultimately consists of Alizarin, alumina, tin, and fatty matter.

The presence of oily or fatty compounds on the fibre intensifies the depth and increases the brilliancy of the majority of colouring matters used in calico printing, and for this reason almost all goods are now prepared in oleine before printing, the chief exceptions being those upon which patterns are printed in alumina and iron mordants. These goods have to be dyed after printing, and if the cloth contained any fatty matter this would attract dyestuff to the white parts of the cloth and thus stain them, possibly beyond remedy. Hence the oil is applied after dyeing as described above.

Olive Oil was at one time used exclusively for the preparation of "oleines," "soluble oils," etc., and is still largely employed for dyeing the best Turkey-reds. Its price prevents its general application now that castor oil has been found equally suitable for most classes of work. Many experiments, on an industrial scale, have been made, with the hope of substituting a cheaper oil for olive oil in Turkey-red works, but so far but little success has attended these efforts. Castor oil and cotton-seed oil both yield bright, even brilliant, reds, but they do not possess the extraordinary fastness to light, soap, and acid that is associated with the old-fashioned Turkey-red on an olive oil prepared foundation, neither are they so rich and full in appearance. For high-class Turkey-red, therefore, olive oil is still the fatty matter *par excellence* to use.

In the old processes of Turkey-red dyeing the cloth was repeatedly treated in an emulsion made from olive oil and a weak solution of soda or sheep-dung. After each padding it was hung in a hot stove or chamber to dry and "age." During the successive paddings and "ageings" the oil became transformed into a substance capable of combining with alumina mordants, and the oleate of alumina (?) thus formed was in turn capable of combining with Madder or Alizarin to form Turkey-red. What the nature of the chemical changes undergone by the oil in "ageing" really is cannot be affirmed with certainty, but it is probably transformed into oxyoleïc acid by the combined action of heat and air. That some process of oxidation takes place is generally admitted, and this fact has led to many attempts at hastening the process. Beyond noting that various oxidising agents were added to the oil itself, and that the oil was oxidised before use by treating it with chlorine, etc., it is unnecessary to go into these old methods, since they are now rarely, or never, employed. Steiner impregnated the cloth in hot, pure olive oil, then dried it at 70° C., and afterwards treated it in weak solutions of soda, "stoving" after each treatment for two hours at 75° C.; in this way he shortened the process, but even this short process has had to give way before the "oleine process," which, when properly worked, yields reds equal to anything hitherto produced.

The manufacture of oil mordants of all descriptions from olive oil is identical with that of similar mordants from castor oil; in fact, the only difference between the two series of compounds is that due to the slightly different composition of olive oil.

Olive oil consists essentially of the glycerin compound of oleic acid, which contains three atoms less of oxygen than the corresponding glycerin compound of castor oil. In addition, olive oil contains *tripalmitin*, and it is not unlikely that this may account for the superiority of olive oil over castor oil for Turkey-red work, or at least influence the result in some way, for it is not uncommon for complex bodies to produce the fastest colour lakes.

When shaken up with dilute solutions of alkali, olive oil is not saponified, but forms the emulsion already mentioned, in which it exists in an extremely fine state of division. The quality of oil best adapted for this purpose is that obtained at the second extraction of oil from the fruit; the product obtained at the first extraction by pressing the ripe fruit in the cold is known as "virgin" or "cold drawn" oil, and is the purest and most highly esteemed quality for food and burning. The oil obtained at the second extraction, by the aid of heat and great pressure, and after the husks and crushed fruit have been steeped in boiling water and piled in heaps until a kind of fermentation has occurred, gradually becomes rancid (*rancid Gallipoli*, Fr. *huile tournante*), owing to the liberation of the free fatty acids, and is the quality most suitable for Turkey-red dyeing. The presence of the free stearic, oleïc, and palmitic acids, together with a certain amount of nitrogenous organic matter, promotes the rapid formation of a more or less permanent emulsion, and is found by experience to ensure the fastest and brightest reds.

An emulsion that is in general use for Turkey-red dyeing by the old process is the following:—

Olive Oil Emulsion 6 per cent.
60 kilos. common olive oil.
39 „ soda crystals ($Na_2CO_3.10H_2O$).
100 „ water.

Mix well until thoroughly emulsified, and then add sufficient water at 50° C. to make the whole up to 1000 kilogrammes. If the emulsion tends to separate, add more sodium carbonate, or about 10 kilos. of cow-dung, until it remains permanent some twelve to sixteen hours. The emulsion can be strengthened or diluted according to circumstances.

Boiled with caustic alkalies or alkaline carbonates, olive oil is saponified in the same way as castor oil, but the soap is not used as a mordant, although it possesses a very similar composition. It consists essentially of sodium or potassium oleate, and its close resemblance to castor oil soap is evident on comparing their respective formulæ,—

$C_{18}H_{33}O.ONa.$	$C_{18}H_{33}O_2.ONa.$
Olive oil soap.	Castor oil soap.

Olive oil soda soap, known better as "Marseilles Soap," is largely used for the after-soaping of Turkey-red dyed goods, and, where not too expensive, for ordinary printed goods of all descriptions. Its advantages are, that it is a dependable article, regular in composition, and neutral.

By acting on olive oil with strong sulphuric acid in the cold, analogous compounds to those prepared from castor oil under the same conditions are obtained. These bodies combined and neutralised with soda or ammonia constitute the olive-oil "oleines," sulphated, soluble, and Alizarin oils of commerce. As previously noted, they are suitable for all purposes to which such compounds are applied, but their cost limits their use to Turkey-red dyeing; and although they are occasionally used for preparing "steam" work, they offer no advantages in this direction over the castor oil preparations.

The manufacture of olive oil "oleins" is identical with that already described for the manufacture of the castor oil compounds, and the various tin oleates can be similarly produced.

The practical application of olive oil will be dealt with in connection with the dyeing of Turkey-red.

Most of the oxidised oils, to which a slight allusion has already been made, are of little practical interest, and if used at all, are used to a very limited extent. One compound, which may perhaps be classed amongst them, is, however, largely employed by the calico printer in the production of "steam Alizarin reds." It is generally known as "chlor oil," and consists of a mixture of olive oil with bleaching powder solution.

"Chlor Oil."
100 kilos. of olive oil.
100 litres of bleaching powder solution 7·2° Tw. (= 25 grms. active chlorine per litre).

Stir well together until the emulsion is homogeneous.

In place of olive oil, the cheaper cotton-seed and rape-seed oils may be used with advantage; in fact, these two oils are perhaps as often employed as olive oil at the present time.

The "oleines" prepared from cotton-seed and rape-seed oils possess different properties from those made from olive and castor oils. They do not dissolve in water, but only form a sort of emulsion; neither do they lend themselves to the production of the best qualities of Turkey-red. At the same time they are used for this purpose, a cotton-seed oil prepare, containing a little cow-dung and an excess of sodium carbonate, being frequently employed in the same way almost as the ordinary olive oil emulsions, except that the goods are steamed instead of being "stoved." This prepare may be made up as follows:—

6 per cent. "Cotton-seed Oil Prepare" (for Turkey-red).

To { 60 kilos. cotton-seed oil add gradually—
10 ,, sulphuric acid 168° Tw.

Allow to act (in the cold) 12–24 hours, and then neutralise with caustic soda. Then add

{ 12 kilos. soda ash.
10 ,, cow-dung.
500 ,, water.

Stir well to emulsify properly, and then add sufficient water to bring the whole up to 1000 kilogrammes.

Goods prepared in this solution are steamed after drying, allowed to lie in pile a day or two, and then lightly washed through dilute sodium carbonate ($1\frac{1}{2}$° Tw.) and water, after which they are mordanted and dyed as usual.

The red produced in this way is very bright, but it does not resist the action of mineral acids so well as that resulting from the use of olive oil, neither does it possess the same "fulness" of shade nor fastness to energetic soaping.

The chief use of cotton-seed oil is for soap-making, and for adding to boiled starch thickenings for the purpose of softening them. Most of the cheap "colour oils" consist of either cotton-seed or rape-seed oil, both of which are suitable substitutes for olive oil in boiled thickening pastes.

(12) Tannic Acid.

The use of tannic acid (the astringent principle of myrobalans, sumach, valonia, gall nuts, divi-divi, etc.) as a mordant depends upon its property of forming insoluble coloured precipitates with the colourless or leuco bases of basic aniline dyestuffs. During this reaction the mineral or organic acids combined with the colour base in the dyestuff are liberated, and if not neutralised in some way, they tend to redissolve the coloured precipitate or "lake." Even an excess of tannic acid forms soluble compounds with basic dyestuffs; hence, in order to obtain insoluble compounds, it is essential to neutralise all free acid whatsoever. This may be done by adding sodium carbonate to the mixed solutions, or to one of them, before the precipitation is effected, but in practice it is found better, in every way, to precipitate the tannic acid on the cloth as an insoluble metallic tannate, the metallic base of which combines, more or less, with the liberated acids. These insoluble tannates possess quite as great an affinity for the leuco bases of colouring matters as does the free tannic acid, and the compounds they form possess the additional valuable quality of being much "faster" to soaping than the simple compounds of tannic acid and colour base.

As is well known, tannic acid produces insoluble salts with aluminium, iron, tin, chromium, and other metallic salts; and consequently cloth mordanted with any of these tannates can be dyed either in basic colours or in mordant colours, like Alizarin, Logwood, etc. This dual character of tannic acid as fixing agent and mordant is of the utmost value, and is taken advantage of in many styles of work. The tannate of iron is a blackish precipitate, which is sometimes made to serve as a grey self colour, and thus tannic acid may, in a sense, be considered as a colouring matter in addition to its other uses. In this capacity, however, it is rarely employed (except in the manufacture of inks), its chief use being to "tone" or darken other colouring matters that are dyed upon it, and are fixed upon the fibre as tannic acid or iron lakes, according to the class of colouring matter employed.

The cotton fibre possesses the property of abstracting tannic acid from its solutions; and so great is its power in this respect that it will retain the whole of the tannic acid it has absorbed from a 5 per cent. solution when it is afterwards steeped in weaker solutions. As a matter of fact, J. Koechlin has ascertained that it will even absorb additional tannic acid from a 2 per cent. solution, and will only begin to part with it in a solution reduced to ·02 per cent. of tannic acid.

Although the steeping method of mordanting is used for dyeing yarn and calico, the most expeditious method of applying tannic acid to the fibre of woven cotton fabrics is by padding in a mangle, as practised by the calico printer to the exclusion of all other methods. Padding entails the use of very much stronger solutions than "steeping," but at the same time a correspondingly small volume of liquor can be used, so that while the process is accelerated, no extra expense for material is incurred. After padding, the cloth is immediately dried over copper cylinders or in hot air, and can then be passed into the fixing bath without any risk of the tannic acid dissolving off and forming a useless precipitate in the bath.

The usual fixing agent for tannic acid is tartar emetic (or other salts of antimony), though, as noted above, other metallic salts are capable of forming insoluble tannates, and are utilised for the purpose in special cases. The tannate of antimony is white, and quite insoluble in water, qualities which render it peculiarly adapted to the production of bright shades; it is precipitated easily in the cold, especially in the presence of common salt; and it dissolves in concentrated caustic soda,—a property which allows of white designs being produced on a dyed basic colour ground.

In mordanting cloth for printing and dyeing, the following method may be employed with good results:—

(1) Pad the cloth through a 5 per cent. tannin solution.

5 per cent. TANNIN MORDANT.

50	grms.	tannic acid.
50	,,	common salt.
900	,,	water.

(2) Dry the goods and fix them by running through a 2 per cent. solution of tartar emetic and chalk.

2 per cent. FIXING LIQUOR.

20	grms.	tartar emetic.
20	,,	chalk.
960	,,	water.

At 40° C.

The chalk is added to neutralise the acidity of the acid potassium tartrate [$C_4H_4O_4(OH)(OK)$], which gradually accumulates as the antimony is taken up by the tannic acid.

(3) Well wash the cloth and then dry it. It may then be dyed at once or printed in caustic soda, steamed, washed, and dyed in basic colours.

Another method of fixing tannic acid on the fibre is first to print an iron or aluminium mordant, "age" and "dung" it as usual, and then dye it up in tannic acid or any of the vegetable tannin matters,—say sumach, for instance. The tannin is fixed on the printed parts of the cloth as an insoluble tannate of iron or alumina, and after soaping, to clear the unprinted portions, it can be dyed up in any required basic colour, thus giving a coloured pattern on a white ground. The same effect can be produced by printing a thickened solution of tannic acid, fixing it in tartar emetic, and dyeing afterwards; also by printing a mixture of aluminium sulphate or alum, acetic acid, tannic acid, and ammonium chloride. The latter is not essential, but aids the fixation. Print, steam, and dye.

5 per cent. Tannin Mordant.

50	grms.	tannic acid.
10	,,	ammonium chloride.
100	,,	water.
Dissolve and add		
10	grms.	aluminium sulphate.
75	,,	acetic acid 9° Tw.
50	,,	water.
705	,,	gum tragacanth thickening.

Before steaming, the tannic acid does not unite with alumina in the presence of the acetic acid, but when the latter is volatilised the precipitation takes place in the fibre, and it suffices simply to wash the goods before dyeing. A better result is obtained by a supplementary fixation in a dilute solution of tartar emetic; in which case the alumina exerts a beneficial influence on the brightness of the ultimate colour, which is also faster than if no alumina were present. By replacing the gum tragacanth with water the solution may be used for ordinary mordanting for printing in caustic soda, as above. The ammonium chloride then prevents the caustic soda "scum" on the printing roller from injuring the parts of the cloth which are intended to retain the mordant and form the coloured ground when dyed. After printing, the goods are passed through the "rapid ager" fixed in tartar emetic (if desired), washed and dyed.

The fact that the tannates of basic colours are soluble in excess of acid is taken advantage of in the printing of steam colours. A thickened paste containing acetic acid, a little tartaric acid, tannic acid, and basic colouring matter is printed on white cloth. The cloth is then dried and steamed, when the acetic acid is driven off and the tannic acid combines with the colouring matter to form an insoluble "lake," which is rendered still more insoluble by a passage through tartar emetic and chalk, whereby the still remaining tartaric acid is neutralised and an insoluble double tannate of antimony and colour base is produced.

For dark shades of blue, green, brown, etc., any of the vegetable tannin matters can be used in all cases where their colour does not detract from that required; but for light shades, tannic acid itself is always preferable, since, in the qualities specially prepared for this class of work, it possesses very little colour—at most only a pale yellow tint.

(13) Various Assistants and Preparations.

It is impossible to give even the briefest description of every substance used in calico printing, therefore only the most important have been dealt with; but there exist many others that will be mentioned in the following pages, and of these some are too well known to require any detailed descriptions, and others are only used occasionally or for special processes. Amongst the former may be classed the various salts of soda and potash, chalk, lime, the various acids, bleaching powder, alcohol, ether, glycerin, glucose, malt, turpentine, benzene, carbolic acid, borax, ammonia, wax, etc., all of which are common articles of commerce. While not entering into any discussion of their general properties or modes of manufacture, their special functions will be pointed out in all cases where they play an essential part in any process given in the following pages, and not already explained. This will prevent needless repetition, and will allow of each "style of printing" being treated as a whole, without the necessity of referring to all parts of the volume at every turn.

The most important preparations that have not been given include vanadium chloride, magnesium acetate, the citrates of soda and ammonia, Chrome yellow and orange, Prussian blue, soda chemick, nitrate of ammonia, and ammonium oxalate.

(1) **Vanadium Chloride** (VCl_2) is a blue solution used as an oxygen carrier in Aniline black printing and dyeing. It may be made according to the following recipe:—

Vanadium Chloride Solution, 1 per cent.
10 grms. vanadate of ammonia (NH_4VO_3).
70 „ hydrochloric acid 30 per cent.
40 „ water.
7 „ glycerin.

Heat until a pure blue is obtained; then make up with water to 1000 grammes. A solution one-tenth of this strength (1 : 1000) is usually employed in practice, and can be reduced from stock as required.

(2) **Magnesium Acetate** [$Mg(C_2H_3O_2)_2$] finds its chief use as a resist for Aniline black. It yields brighter colours than sodium acetate, by reason of the fact that magnesium oxide does not injure the colours to the same extent as sodium hydrate during the reaction brought about in steaming.

Magnesium Acetate 32° Tw.
1000 grms. magnesium carbonate.
4000 „ acetic acid 9° Tw.

Add the magnesium salt to the acid gradually and until it is slightly in excess, then heat gently until the filtered liquor contains no trace of iron; decant, filter, and saturate with acetic acid.

(3) **Citrates of Soda.**—These salts, in varying degrees of acidity, are largely used as resists under iron and aluminium mordants, and under steam Alizarin pinks. They act by preventing the precipitation of the insoluble basic salts and oxides during the ageing and steaming processes. They are prepared by dissolving citric acid in caustic soda.

	I.	II.	III.	IV.
Citric acid	120	120	120	120 grms.
Caustic soda 71° Tw. . .	70	140	210	245 „

I. $C_3H_4(OH)(CO_2H)_2(CO_2Na)$	very acid salt.
II. $C_3H_4(OH)(CO_2H)(CO_2Na)_2$	acid „
III. $C_3H_4(OH)(CO_2Na)_3$	neutral „
IV. („ „) + $\frac{1}{2}$ molecule NaOH	alkaline „

Mixed with China clay, sodium chlorate, and yellow prussiate of potash, these citrates are employed in oxidation discharges on a great variety of dyed grounds.

(4) Citrate of Ammonia [$C_3H_4(OH)(COONH_4)_3$] is prepared by dissolving finely ground citric acid in cold ammonia in a covered cask.

Citrate of Ammonia 20° Tw.
200 grms. finely ground citric acid.
500 „ ammonia 20 per cent. NH_3.
300 „ water.

Dissolve, and add a little water to bring the solution down to 20° Tw.

Citrate of ammonia is used like the citrates of soda for all kinds of resists and discharges. On steaming it decomposes, leaving the free acid on the fibre—an essential in some classes of work.

The *tartrate* is made in the same way and is used for the same purposes.

The *oxalate* is a somewhat insoluble salt, made by mixing solutions of oxalic acid and ammonia in proper proportions. It crystallises out at a strength above 3° Tw., and is mainly used as an addition to "brightening oils" for Alizarin-dyed reds.

(5) **Nitrate of Ammonia** (NH_4NO_3) is a well-known salt. In practice it is prepared by neutralising ammonia with nitric acid.

NITRATE OF AMMONIA 32° Tw.
8,500 grms. ammonia 20 per cent.
Add gradually
12,000 ,, nitric acid 66° Tw.
Neutralise, and set at 32° Tw.

A thickened solution of the above when printed on tannin-mordanted cloth resists the action of an over-print of caustic soda, and preserves the tannin under it from being discharged by the caustic soda cover. The same paste printed on white cloth prevents the fixation of albumen colours, though in this connection it is not quite so convenient to use as zinc sulphate, which is both cheap and effective. Mixed with steam Alizarin red, nitrate of ammonia enables it to resist albumen colour "covers," and thus produce a clean-cut red on a fancy ground not specially engraved for it. This latter style is not much used at present.

(6) **Chrome Yellow and Orange Pigments.**—These pigment colours, although usually bought, are made quite as well and much more cheaply by the colour mixer himself.

CHROME YELLOW I. (Maize).
a { 760 grms. acetate of lead.
4000 ,, boiling water.
Add gradually
b { 300 grms. bichromate of potash.
3000 ,, boiling water.
Wash four times by decantation and filter to a stiff paste.

CHROME YELLOW II. (Lemon).
a { 500 grms. lead acetate.
5000 ,, water.
Dissolve, cool, and add, whilst stirring, a cold solution of—
b { 90 grms. bichromate of soda.
115 ,, aluminium sulphate.
2000 ,, water.
35 ,, sulphuric acid 168° Tw.
Both solutions must be cold, otherwise the pigment tends to become reddish, more like the maize shade. Wash and filter as above

CHROME ORANGE.
a { 600 grms. acetate of lead.
4000 ,, water (boiling).
b { 120 ,, bichromate of potash or soda.
1000 ,, water.
1440 ,, caustic soda 15° Tw.
Add *b* to *a* slowly, stirring constantly, then stir half an hour, wash five times by decantation, and filter to 1150 grammes.

The above three pigments are used for coloured discharges on Indigo, Aniline black, basic, and Alizarin colours, and also for ordinary steam work on white grounds. They are thickened with gum tragacanth, and fixed by means of albumen or its substitutes.

(7) **Prussian Blue Pigment.**—Prussian blue is an important element in the discharging of Turkey-red by the oxidation process, and it is also used largely in the chromic acid discharge of dyed Indigo for the production of greens and light blues. A practical recipe for its manufacture is as under:—

PRUSSIAN BLUE PIGMENT I.

a { 1000 grms. copperas.
   5000 ,, water.
b { 1000 ,, yellow prussiate of potash.
   5000 ,, water.

Add *b* to *a*, stir well, and oxidise the white precipitate by adding gradually first

1060 grms. hydrochloric acid 28° Tw., and second—
1800 ,, bleaching powder sol. 12° Tw.

Allow to settle, and then wash well three times by decantation with boiling water. Settle, and filter through a closely-woven woollen cloth until the paste weighs about 2700 grammes = 25 per cent. paste.

A light blue lake is obtained by grinding together in a mill

750 grms. China clay.
350 ,, gum tragacanth thickening.
250 ,, Prussian blue, prepared as above.

The oxidising of the white precipitate ($Fe_2Fe(CN)_6$) is perhaps better performed with "soda chemick," so as to avoid the formation of calcium sulphate. The precipitation of this salt can also be avoided by washing before oxidising, but, except in rare cases, its presence is not objectionable, besides which a great part of it is dissolved by the wash waters.

Another but more expensive method of making a Prussian blue free from calcium sulphate is the following:—

PRUSSIAN BLUE II.

a { 1,310 grms. copperas.
   10,000 ,, water.
b { 1,000 ,, yellow prussiate of potash.
   10,000 ,, water.

Add together *a* and *b*, settle, decant supernatant liquor, and oxidise with—

75 grms. nitric acid 66° Tw.
200 ,, warm water.

Wash well by decantation and filter to 2700 grammes = 25 per cent. Prussian blue.

(8) SODA CHEMICK 8° Tw.—This is simply hypochlorite of soda, prepared by the double decomposition of sodium carbonate and bleaching powder. It is useful in some classes of bleaching, for "clearing" printed fabrics, and as an addition to soap solutions employed for soaping Paranitraniline reds, etc.

Soda Chemick 8° Tw.

1000 c.c. bleaching powder solution 9° Tw. = 30 grms. of available chlorine.

Add

{ 61 grms. soda ash.
  258 ,, water.

Allow the calcium carbonate to settle and use the clear liquor.

(14) Soap.

Soaping is one of the most important of the after-treatments to which nearly all printed goods are subjected. The soap used must be neutral, or at most contain only a trace of free alkali, otherwise the colours are apt to be injuriously affected. Some colours, like Aniline black and the insoluble azo colours, are not harmed by a little free alkali, but by far the greater number of "steam" and dyed colours are more or less soluble in alkaline solutions, and therefore it is always safer for the standard soap used in any works to be as neutral as it is possible to make it. Any extra alkali can be added when required for a special purpose.

Apart from their use as cleansing agents, soaps are sometimes used to facilitate the dyeing of direct colouring matters, as additions to thickenings, prepares, and finishes, to increase their softness, and, less frequently, as fixing agents for a limited class of mordants like oleate of lead, which is used as a mordant for the Phthaleïn family of colouring matters.

The easiest and quickest method of making soap is to boil oleïc acid with a calculated amount of caustic soda. The operation only takes an hour, and the resulting soap is a practically pure oleate of soda, suitable for all purposes.

50 per cent. Soap I.

50	kilos.	oleïc acid.
43	,,	caustic soda 36° Tw.
7	,,	water.
100		

Boil for one hour, then test in the usual way for neutrality, and add more acid or a little more soda according to circumstances: after each correction boil up again. When satisfactory, add water to replace that evaporated, and make the whole up to 100 kilogrammes = 50 per cent. fatty acid.

In England most of the soaps used in calico printing are made from cotton-seed or palm oils. An example of each of these, as made on the large scale, is given below.

Cotton-Seed Oil Soap.

1200 litres *cotton-seed oil* are placed in a large jacketed pan and heated. 1800 ,, *caustic soda* 17½° Tw. are then added in portions of 500 litres, and the whole is then boiled 10–12 hours until the oil is completely saponified. Any excess of oil or soda is corrected by a suitable addition of one or the other, and after re-boiling up, the soap is run out of the pan into forty-gallon casks, in which it sets as a stiff jelly, containing roughly 40 per cent. of soap. The glycerin is allowed to remain in the soap, as it has no effect on the goods; besides which, its separation would only prolong the process without any corresponding advantage accruing. If required for sale, the soap can easily be freed from glycerin by "salting out"; but if required for use in the works, the cost of carriage of a useless ingredient (glycerin) does not enter into the question, and can be ignored.

In palm-oil soap it is usual to eliminate the glycerin, with doubtful gain.

Palm-Oil Soap.

50	kilos.	bleached palm oil.
100	,,	water.

Heat to the boil and add

30 kilos. caustic soda 70° Tw.

Boil 10–15 hrs. Then salt out with 20–25 lbs. of common salt added to the above mixture, stir up well, and allow the soap to set on the surface. Then run off the salt solution which contains the glycerin, add 150 kilos. of water, boil up again, and salt out a second time. When the second salt solution is drawn off, boil the soap again, then run it into flat zinc-lined boxes, and allow it to set hard, after which it is ready for use. The saponification must be complete before any "salting out" is attempted; and it is well, also, to ensure that the soap is more or less neutral, although a good deal of the free alkali is carried off by the saline wash waters. In the last boiling of the soap, after the second "salting out," sufficient water is added to reduce the soap to a strength corresponding to 60 per cent. *fatty acid.*

The strength of the soap solutions used varies with the class of work under treatment. Turkey-reds and other Alizarin-dyed goods, such as chocolates and purples, will stand a prolonged treatment in a boiling 2–3 per cent. soap solution, while some of the more delicate kinds of "steam work" only require a moderately hot solution containing $\frac{1}{10}$ to $\frac{1}{2}$ per cent. of soap. Between these extreme limits all percentages of soap are employed, and the temperature is likewise determined by the known resistance of the colours to hot soap.

(15) Thickening Pastes.

The following thickening pastes are in general use, and, apart from unimportant modifications, represent those employed throughout the whole calico-printing industry. In many cases two or more thickenings may be mixed together, or a mixed thickening may be boiled at one operation: these points, however, are matters of experience, and cannot either be generalised or dealt with apart from the circumstances which govern them.

The following thickenings may be used both for making standard colours and for diluting (technically "reducing") the same.

I. STARCH PASTE 15 per cent.

1,500	grms.	wheat starch.
8,100	,,	water.
400	,,	cotton-seed oil.
10,000		

Boil and cool.

Used for reducing all kinds of colours containing no alkali, and a general thickening for basic colours.

II. ACID STARCH PASTE 20 per cent.

2,000	grms.	wheat starch.
5,500	,,	water.
2,200	,,	acetic acid 9° Tw.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

Very useful for dark basic colours and such as require acetic acid for their solution.

III. STARCH TRAGACANTH PASTE.

$\left\{\begin{array}{l}\text{1000 grms. wheat starch.}\\ \text{3000 ,, water.}\end{array}\right.$

Mix in the cold and add

6000 grms. tragacanth thickening 6 per cent.

Boil and cool.

For thickening diazo solutions, and, when thinned down, a suitable thickening for medium blotches.

IV. Acid Starch Tragacanth Paste.

1,200	grms.	wheat starch.
6,000	,,	water.
2,000	,,	6 per cent. tragacanth thickening.
800	,,	acetic acid 9° Tw.
10,000		

Boil and cool.

Used for reducing basic colours, and for general use where a soft acid paste is required.

V. Flour and Tragacanth Paste.—This paste is used for printing the insoluble azo colours, and for reducing "Madder colours," that is, the thickened solutions of aluminium and iron mordants. It possesses a good deal of body, and at the same time is soft, and penetrates better than most thickenings of the same consistency.

2,000	grms.	flour.
600	,,	acetic acid 9° Tw.
4,000	,,	water.
3,000	,,	tragacanth thickening 6 per cent.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

VI. Alizarin Red Paste.

1,500	grms.	wheat starch.
7,000	,,	water.
700	,,	acetic acid 9° Tw.
500	,,	tragacanth thickening 6 per cent.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

VII. Reducing Paste for Alizarin Pinks.

1,000	grms.	wheat starch.
7,100	,,	water.
500	,,	acetic acid 9° Tw.
1,000	,,	tragacanth thickening 6 per cent.
400	,,	cotton-seed oil.
10,000		

Boil and cool.

VIII. Gum Senegal Thickening 50 per cent.

5,000	grms.	gum Senegal.
5,000	,,	water.
10,000		

Allow to soak in the cold and then boil up.

Take the solution out of the pan, boil, and filter it through calico into the storage casks. There let it settle until all the sand and grit are deposited, when it is ready for use. Gum Senegal is the best thickening to use for light "blotches" when price is no object; it gives beautifully level shades, which possess a soft, delicate quality unapproached by any other kind of thickening, except, of course, the other natural gums—arabic, gedda, etc. The latter are prepared in precisely the same way as gum Senegal.

IX. British Gum Thickening.—The percentage of British gum varies with the degree of calcination. A moderately torrefied starch yields a good paste at 350 grms. per kilo.

350 grms. British gum.
650 ,, water.

1000

Boil and cool.

If the gum is acid it must not be boiled. British gum is used in place of the expensive "Senegal," and for all kinds of discharges, etc.

X. Tragacanth Thickening 6 per cent.

600 grms. gum tragacanth.
9,400 ,, cold water.

10,000

Allow to soak 24–30 hours, and then boil it until it becomes quite smooth.

Used in combination with other thickenings, and also alone, for many colours which are required to penetrate well into the fabric.

XI. Alkaline Thickening.—Used for Indigo, Sulphur colours, most vat colours, and for the discharging of tannin-mordanted goods.

1,500 grms. British gums
8,500 ,, caustic soda 77° Tw.

10,000

Mix in the cold and then heat to 140° F.

XII. Albumen Solution 50 per cent.

1000 grms. egg albumen.
1000 ,, water (cold).

2000

Dissolve in the cold.

Blood albumen is usually made as 40 per cent. solution. Both are employed for fixing pigment colours.

XIII. Paste for reducing Acid Resists.

$\left\{\begin{array}{l}\text{1,000 grms. China clay.}\\ \text{1,000 ,, water.}\end{array}\right.$

Grind to a fine smooth paste and add

2,500 grms. British gum.
5,500 ,, water.

10,000

Boil and cool.

The thirteen preceding pastes or thickenings include all that may be considered as standards. Other mixtures may be made as required, and the various proportions and ingredients modified as occasion dictates.

Choice of Thickenings.—The choice of the particular thickening to employ in a given case is largely a matter of experience, and depends upon many factors. The quality, style, and condition of the engraving must be taken into consideration, the cost of production must be kept in mind, the question as to whether or not the colour is to penetrate to the back of the fabric must be considered, the surface of the cloth must also be allowed for, and the sharpness or otherwise of the impression must be taken into account. No less important than these points is the question of the "finish" which has to be put on the printed goods. If they are required to possess a soft "feel," the thickening of the printing colour must be capable of being entirely removed without subjecting the goods to a treatment of such severity as to injure the colours; in other words, the thickening must be easily soluble in warm solutions, and not require too prolonged a treatment for its elimination. For this purpose gum Senegal, gum tragacanth, and British gum are the best thickenings to use. On the other hand, when the goods are required to possess a stiff, "boardy" feel, starch may be used with advantage if it fulfils the other conditions essential to a good print, namely, evenness and delicacy. Again, coarse engraving requires much thicker colour to produce a similar impression to that obtained from delicate shallow engraving; but, on the contrary, a thicker colour may be used for lightly engraved "blotches" or backgrounds than is demanded by coarse, heavy "blotches." A thick colour used for these latter would in most cases display every line of the engraving, whereas a thin colour would spread out by capillary attraction, and thus produce a more even ground. The colours employed for two "stippled" rollers, falling one over the other, may be thickened with starch or gum Senegal, according as the stipple is required to show distinctly or to gradate imperceptibly. Sometimes the darker colour is thickened with starch and the lighter with gum Senegal, in which case the gradation is distinct, but not too "hard."

The best thickening for yielding even "blotches" is undoubtedly gum Senegal or gum arabic, but it cannot be used for dark colours on account of the fact that colours thickened with it wash out a good deal on soaping, and, if strong, tend to soil the other parts of the pattern and the white ground of the cloth. For dark blotches, therefore, tragacanth, or tragacanth mixed with starch, are the thickenings most commonly employed; and when the blotch is engraved in fine scale, starch alone is often a most suitable thickening agent to use, since it is cheap and economises colouring matter. A colour thickened with gum Senegal, or even British gum, only yields about half the depth of shade of one of the same strength thickened with starch; hence starch should always be used wherever possible. Strongly alkaline and strongly acid colours are, as a rule, thickened with either natural or artificial gums, as they act on starchy or farinaceous bodies, and either thicken them unduly and make them "sticky," or decompose them altogether.

Another point to notice is that the same colour does not give the same shade with different thickenings. For instance, a colour composed of Alizarin orange, Alizarin yellow, Alizarin blue, and acetate of chromium (a fawn colour) produces reddish shades with starch, and much yellower and softer shades with tragacanth thickening; so that, irrespective of depth, the tone of a colour is also influenced by its thickening, and consequently thickenings are not interchangeable without some alteration in the proportions of the constituents of a mixture of two or more colours.

The order in which the colours of a multicolour pattern are worked in the printing machine further influences the choice of thickening in many cases; notably in those of delicate, easily soiled, and sensitive colours like pinks, salmons, and terra-cottas, fawns, drabs, and pale blues. In such cases, if it is absolutely necessary to print these sensitive colours first, it is always advisable to thicken them with gum of some sort, since the "scum" (from the following rollers) on the surface of a "gum colour" washes off much more easily (and produces less soiling) than it would, or does, from the surface of a "starch colour."

Broadly speaking, the thickening agents given below will, in general, be found the most suitable for the following styles of work:—

(*a*) "BLOTCHES" OR BACKGROUNDS.—Pale: gum Senegal or gum arabic, and also British gum. Dark: gum tragacanth alone, or a mixture of tragacanth and starch. When starch alone is used, it mostly requires flattening or distributing evenly by passing under a "starch roller," *i.e.* an unengraved roller, working in water or starch paste, and furnished with doctors as usual.

(*b*) FINE, SHARP IMPRESSIONS.—Thick colour of any thickening chosen. Starch and the gums are the best; gum tragacanth the least desirable.

(*c*) STIPPLED WORK.—For crisp impressions and sharply defined shadow, use thick colour; for obtaining delicate imperceptible gradation, use thin gum Senegal for preference, and in the second place thin tragacanth or British gum.

(*d*) WHERE THE COLOUR IS REQUIRED TO PENETRATE to the back of the cloth, gum tragacanth is one of the best thickenings to use; and after that, tapioca starch, wheat starch, and flour, all used as thin as possible.

(*e*) ACID RESISTS, DISCHARGES, AND COLOURS.—Gum Senegal or British gum, either with or without China clay. Starch may also be used in many instances.

(*f*) ALKALINE COLOURS, RESISTS, AND DISCHARGES.—Gum Senegal, British gum, and sometimes maize starch.

(*g*) "MADDER STYLE."—Flour and starch, singly or mixed together. Flour is especially good for thickening iron and aluminium acetates as a rule, though it is mixed with a little starch for this purpose. British gum is also used for light madder "blotches" and "pads."

(*h*) PIGMENT COLOURS.—Albumen and tragacanth; more rarely albumen and wheat starch.

(*i*) SOFT GOODS, FLANNELETTES, SATEENS, etc.—Gum Senegal or gum tragacanth are the best to use wherever they can be afforded, especially if the pattern contains heavy masses of solid colour. Small masses and outlines are better and more economically printed in a starch-thickened colour. British gum or dextrin is also a good thickening for blotches in these classes of work, and is usually substituted for the high-priced Senegal. British gum yields yellower shades of Alizarin pink than gum Senegal.

These remarks must not be taken as constituting hard and fast rules for the application of particular thickening matters, but rather as indicating, in a slight degree, some of the purposes to which they are peculiarly adapted. It often happens that the printing price of goods is too low to allow of their being executed in the best way, and in such cases the thickening is generally the first item to be cut down, so that, as previously stated, the choice of a thickening is governed by considerations other than its peculiar appropriateness to the work in hand.

OXIDISING AND REDUCING AGENTS.

Both oxidising and reducing agents play such an important part in textile printing that, although they are dealt with to some extent in an elementary course in chemistry, it has been thought advisable to classify them under one heading, and to enumerate and briefly describe those which are specially applied in printing.

Oxidising Agents.

The simplest and most universal oxidising agent is naturally *atmospheric oxygen.* The printer employs this for obtaining various results, such as the oxidation of iron mordant in ageing, the discharge of tannic acid, the development of Indigo and other vat colours on the fibre, etc. The oxidising action of the air is strongly influenced by various conditions, *e.g.* whether the oxidation takes place in a neutral, acid, or alkaline medium, and whether with or without the assistance of such agencies as heat, moisture, and sunlight. In an acid or neutral medium, air oxidation is usually slow or does not take place. An example of slow oxidation in an acid medium is the ageing of calico impregnated with ferrous acetate (black liquor). In presence of alkalies, especially caustic alkalies, air oxidation usually proceeds much more rapidly. Thus in neutral or acid solution, tannic acid does not undergo oxidation when exposed to the air, but in presence of caustic soda it is very rapidly oxidised and destroyed. Similarly, Indigo and other vat colours are all exposed to the air after dyeing or printing and reducing in the alkaline condition, when oxidation takes place rapidly and evenly. If they were acidulated after dyeing or steaming, oxidation would indeed take place, but it would be very slow. As in all chemical changes, heat generally accelerates oxidation. Direct sunlight and ultra-violet light also seem to promote air oxidation, but no use is made of this in textile printing. The presence of moisture is in most cases indispensable to oxidation. Thus indigo white, if perfectly dry, can be exposed to a dry atmosphere without turning blue, and hydrosulphite of soda, one of the most oxidisible bodies, can be kept in dry air indefinitely. As is well known, catalysts often favour air oxidation, but they do not find employment for this purpose in calico printing. A notable exception to this is met with in Green's Aniline black process, in which paraphenylene diamine brings about the oxidation of aniline to Aniline black by atmospheric oxygen alone.

In some cases of air oxidation it has been noticed that the amount of oxygen consumed is considerably in excess (often double) of that required by theory. Thus, Herzog and Manchot found that if the barium compound of indigo white is oxidised in the air, it yields Indigo blue and an equivalent amount of hydrogen peroxide, and the reaction might be expressed by the equation

$$C_{16}H_{12}N_2O_2 + O_2 = C_{16}H_{10}N_2O_2 + H_2O_2.$$

It is assumed that, under such conditions, the oxygen molecule is split into two atoms of nascent oxygen, the reaction resulting in the simultaneous formation of Indigo and hydrogen peroxide. This constitutes one of the best examples of what is called "auto-oxidation." In how far this phenomenon plays a part in textile colouring is not known with any degree of certainty, but it is possible that it may account for some things which have hitherto remained unexplained.

Ozone, which is technically produced by the action of the silent electrical discharge on dry air, has been suggested as a means of bleaching, but has not met with practical success.

Since oxygen is more readily soluble in water than nitrogen, it follows that the air dissolved in water is richer in oxygen than the atmosphere. Ordinary water must therefore be considered in a sense as an oxidising agent: when saturated with air at atmospheric pressure it contains at the ordinary temperature about 6 c.c. of dissolved oxygen per litre.

Hydrogen Peroxide (H_2O_2), which comes into the market as a 3 per cent. solution, and which is sometimes prepared by the user by adding sodium peroxide to cold dilute sulphuric acid, does not lend itself to any of the processes of printing, but is largely used for bleaching delaines previous to their being printed.

Chlorine in the free state was the first artificial bleaching agent employed for cotton. It was soon abandoned in favour of Eau de Javelle, this being subsequently replaced by bleaching powder. Within recent years liquefied chlorine has come into the market, and is sold in steel cylinders, from which the gas can be continuously drawn on opening the tap. Although endeavours have been made to re-introduce gaseous chlorine for the bleaching of calico and to utilise it for the chlorination of delaines, they have not been successful.

Both in bleaching and in the chlorination of wool chlorine acts as an oxidising agent, decomposing water and liberating nascent oxygen.

$$H_2O + Cl_2 = 2HCl + O.$$

In water, chlorine dissolves at the ordinary temperature to the extent of 2·4 vols. to one of water. The aqueous solution, which is best prepared by adding hydrochloric acid to a solution of bleaching powder or of hypochlorite of soda, finds application in the chlorination of wool.

Bleaching Powder, technically the most important of the hypochlorites, is prepared by absorbing chlorine in slaked lime, and is generally assumed to consist of a mixture of calcium hypochlorite and calcium chloride, although it never contains the amount of available chlorine demanded by the formula $Ca(OCl)_2 + CaCl_2 + 2H_2O$. This should be 49 per cent., but a good bleaching powder seldom contains more than 35 per cent. of available chlorine. Bleaching powder always shows an alkaline reaction, this being due either to the presence of free lime or basic hypochlorites. Bleaching liquor, obtained by dissolving chlorine in milk of lime, comes into the market as a clear liquid, generally standing at 28° Tw., and containing, like bleaching powder, calcium hypochlorite as its effective constituent. By hydrochloric acid, calcium hypochlorite, like other hypochlorites, is decomposed with evolution of chlorine. The chief use of bleaching powder is in bleaching, but small quantities are also used for clearing whites, the discharge of Turkey-red and other purposes.

Hypochlorite of Soda is made by dissolving chlorine in caustic soda, or by the action of sodium carbonate on bleaching powder, or, lastly, by the electrolysis of brine. It is used to a limited extent in bleaching and in chlorinating wool.

Chlorate of Soda ($NaClO_3$) now comes into the market in an almost pure condition, and, in consequence of its being cheaper and much more soluble in water, has almost entirely replaced *chlorate of potash* as an oxidising agent in the tinctorial industries.

Chlorate of soda comes into the market in the form of colourless crystals, and dissolves in its own weight of water at the ordinary temperature, and in half its weight at the boil. When used alone in a neutral or slightly alkaline solution, it can scarcely be regarded as an oxidising agent; but in presence of mineral acids, and more especially of catalysts like vanadium chloride, cerium chloride, yellow prussiate, salts of copper, etc., it acts as a powerful oxidising agent, and is extensively employed as such in the production of Aniline black and in discharge work.

Barium Chlorate [$Ba(ClO_3)_2$] forms colourless crystals, which are soluble in water. It is not used as such in printing, but serves for the production of other chlorates, such as chlorate of alumina and aniline chlorate, by double decomposition with the corresponding sulphates.

Chromic Acid (CrO_3), although commercially available, is too drastic an oxidising agent to find employment in textile printing. Its salts, however, the chromates and bichromates, are extensively used.

Bichromate of Potash ($K_2Cr_2O_7$) crystallises in hard, well-defined orange crystals and is not very readily soluble in water, the solution saturated at the ordinary temperature containing about 9 per cent. of the salt. As such it does not usually exert an oxidising action, though this may occur under certain conditions. Thus, if calico is impregnated with a solution of bichromate of potash and is then exposed to sunlight or to ultra-violet light, the fabric is tendered through formation of oxycellulose, and a considerable amount of chromic oxide is precipitated on the fibres. Mineral acids, like sulphuric acid, liberate chromic acid from bichromate of potash.

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$

Chromate of Potash (K_2CrO_4) is easily obtained from the bichromate by neutralising with potash or caustic potash.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Chromate of potash forms yellow crystals, which are much more soluble in water than the bichromate. In itself it is not an oxidising agent, but acts as such in presence of acids, such as sulphuric acid, because they liberate chromic acid from it.

Bichromate of Soda ($Na_2Cr_2O_7 + 2H_2O$) is much more readily soluble in water, and is also cheaper than bichromate of potash, and for these reasons it has almost entirely taken the place of the latter in textile colouring. It forms orange-coloured deliquescent crystals, which dissolve in their own weight of water at the ordinary temperature. In other respects it resembles the potassium salt.

Chromate of Soda ($Na_2CrO_4 + 10H_2O$) is obtained by neutralising the bichromate with soda or caustic soda.

The chromates and bichromates find extensive application in the fixation of Aniline black and in Indigo discharge work.

Red prussiate of Potash [$K_3Fe(CN)_6$] comes into the market in the form of orange-red crystals. It is fairly soluble in water, and acts in presence of caustic alkalies as a powerful oxidising agent.

Permanganate of Potash ($KMnO_4$).—A deep purple salt, possessing powerful oxidising properties in either acid or alkaline solution. It is occasionally used in the bleaching of cotton, in the eradication of printing faults, in the discharging of colour from spoilt goods, and in the production of Manganese brown. It cannot be employed in printing, since its oxidising action is so energetic that it destroys all thickening agents except silicate of soda, and silicate of soda is an impracticable thickening for many reasons.

Permanganate of Potash, $KMnO_4$, is sold in the form of dark violet needle-shaped crystals, which dissolve in water with an intense bluish-red colour. Permanganate of potash is one of the most powerful oxidising agents, and acts as such in neutral, alkaline, and acid solution. When acting in neutral solution it deposits hydrated peroxide of manganese, and simultaneously liberates caustic potash.

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO(OH)_2 + 3O.$$

It is a good bleaching agent for cotton and linen, and finds some application as such. According to H. Kämmerer (Eng. Pat. No. 5612, 1907), it may be used for preparing wool for printing by running the material through a 10 per cent. solution of sulphuric acid containing a small amount of permanganate. The process has several advantages over the usual chlorinating process.

The other well-known oxidising agents are only of very small importance in textile printing. Thus, **sodium nitrate** has been more or less successfully employed for Indigo discharge work according to Freiberger's process.

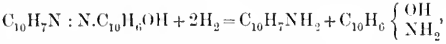
Bromate of Soda has been suggested for the same purpose.

Persulphates and **perborates** have also been suggested as oxidising agents for various purposes, but it is doubtful whether they find any application at all at present in textile printing. The same applies to **peroxide of lead** (PbO_2) and **peroxide of manganese** (MnO_2). **Ferric** and **cupric salts** may be regarded as mild oxidising agents; and although copper compounds find extensive application in textile colouring, they are usually regarded more in the light of carriers of oxygen than of oxidising agents.

Reducing Agents.

Broadly speaking, reducing agents may be defined as substances which more or less readily withdraw combined oxygen from or add hydrogen to other substances. They generally consist either of elementary bodies like zinc and other metals in a fine state of division (also metalloids like red phosphorus), or of lower oxides or compounds of lower oxides of the elements which readily pass into a higher state of oxidation.

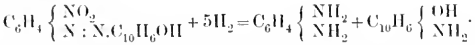
In textile printing, reducing agents find application for several different purposes. Thus they may be used for reducing metallic oxides, such as ferric oxide, to prevent local fixation of the iron, or of chromic acid, as in certain processes of mordanting cotton with chromium, or, again, for the discharge of Manganese bronze. Another use is for reducing Indigo and other vat dyes to their alkali-soluble leuco compounds, and in this capacity they find employment in dyeing, in direct printing, and in discharge work. Their action on azo dyes is of a different character, inasmuch as these are completely destroyed when reduced, and the colour does not consequently return on exposure to the air. The rupture of the molecule invariably takes place in the azo group. Thus, in the case of Alphanaphthylamine claret, the reduction takes place according to the equation



$$C_{10}H_7N : N.C_{10}H_6OH + 2H_2 = C_{10}H_7NH_2 + C_{10}H_6\left\{\begin{matrix}OH\\NH_2\end{matrix}\right.,$$

alphanaphthylamine and amidonaphthol resulting.

In case the azo dye contains two azo groups, it is evident that it will require twice the amount of reducing agent; and if it contains a nitro group, the amount required is still further increased. Thus, in discharging Paranitraniline red, four of hydrogen are required for the azo group and six for the nitro group, according to the equation

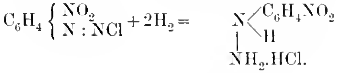


$$C_6H_4\left\{\begin{matrix}NO_2\\N : N.C_{10}H_6OH\end{matrix}\right. + 5H_2 = C_6H_4\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right. + C_{10}H_6\left\{\begin{matrix}OH\\NH_2\end{matrix}\right..$$

Not all azo dyes are reduced with the same facility. Thus, most of the direct cotton colours are easily discharged by reducing agents, while the insoluble azo dyes are much more difficult to discharge. With mixtures of azo dyes, selective action is sometimes noticed. A typical case of this kind may be observed in the green produced by dyeing cotton with a mixture of Chrysophenine and Diamine sky blue. If this is treated with stannous chloride, the blue only is discharged, leaving the yellow intact; but if titanous chloride be applied in limited amount, the yellow only is discharged; with excess of the latter reagent, the whole of the colour is discharged.

In some cases a leuco compound of a colouring matter may serve for the reduction of another colouring matter. Thus, according to Eng. Pat. No. 21746, 1905, the alkaline solution of Indigo white, if allowed to act upon Brom-indigo, reduces the latter to its alkali-soluble leuco compound, Indigo being precipitated. Advantage is taken of this behaviour of the leuco compounds of certain dyestuffs, such as Patent blue, Erioglaucine and Induline scarlet, in order to accentuate the discharging action of hydrosulphite (sulphoxylates). The amount of dyestuff required in the discharge paste is very small in comparison with the hydrosulphite present, so that the former appears to act in a sense as a "carrier of hydrogen." Still better results are obtained by substituting *anthraquinon* for these colouring matters. This substance is readily reduced by the hydrosulphite to the corresponding hydroanthraquinon, and this in turn reduces the dyestuff being reconverted thereby into anthraquinon, the cycle of reactions continuing until the reduction is complete.

Another important function of reducing agents in textile printing is based upon their action on diazo compounds, which are reduced thereby to the corresponding hydrazines, which latter do not react with phenols to form dyestuffs. Thus, when stannous chloride is allowed to act on nitro-diazobenzene chloride (diazotised paranitraniline), reduction takes place in the following sense:



$$C_6H_4\left\{\begin{matrix}NO_2\\N:NCl\end{matrix}\right. + 2H_2 = \begin{matrix}N\left<\begin{matrix}C_6H_4NO_2\\H\end{matrix}\right.\\|\\NH_2.HCl.\end{matrix}$$

This type of reduction is utilised in the production of the resist style in the application of insoluble azo dyes (*q.v.*).

Zinc Dust, or zinc powder, is the product which distils over from the retorts in the extraction of the metal from its ores. It forms a fine, heavy, slate-coloured powder, which consists of a mixture of metallic zinc and oxide of zinc. A good product should contain about 80 per cent. of metallic zinc. Exposed to a damp atmosphere, zinc powder is liable to deteriorate rapidly, oxidation taking place.

Although zinc powder constitutes one of the most powerful reducing agents, it finds practically no direct application in printing, partly on account of its tendency to stick in the engravings of the printing rollers, and partly because of the grit which it contains. On the other hand, it is the chief reducing agent employed in the dyeing of Indigo and certain other vat dyes, and also serves as the reducing agent in the manufacture of hydrosulphites. When acting in its capacity of reducing agent, zinc passes directly to the condition of zinc oxide, ZnO, no intermediate lower oxide being known.

Stannous Chloride ($SnCl_2.2HO_2$), technically known as "Tin crystals," forms well-defined colourless crystals, and usually comes into the market in hermetically sealed iron drums. It is a fairly strong reducing agent, and was formerly used in large quantities in calico and wool printing for discharging azo dyes, and in calico printing as a resist under insoluble azo dyes. At the present time it has been to a large extent replaced by cheaper and more efficient reducing agents. The aqueous solutions of stannous chloride show a tendency to hydrolyse, with formation of free hydrochloric acid, which may bring about the tendering of cotton. To obviate this defect, sodium acetate or ammonium sulphocyanide is usually added to printing pastes containing stannous chloride.

Titanous Chloride ($TiCl_3$) comes into the market in the form of a dark violet 20 per cent. solution. It is one of the most powerful acid reducing agents known, but has not hitherto been successfully applied in calico printing on account of its acidity, which causes tendering on drying or steaming. In dilute aqueous solution this defect does not occur; and in consequence of the rapidity and completeness with which it reduces azo dyes, titanous chloride is the most suitable reagent for stripping these colours, *e.g.* in spoilt work. To prevent the precipitation on the fibre, in such cases, of titanic hydrate, some oxalic acid should be added to the stripping bath. **Titanous sulphate** [$Ti_2(SO_4)$] is also a commercial article in a 20 per cent. solution, and is used, like the chloride, for stripping purposes.

Titanous Sulphocyanide [$Ti(CNS)_3$] obtained by double decomposition of titanous sulphate and barium sulphocyanide, while being as energetic a reducing agent as the chloride, does not tender the cotton fibre, and can subsequently be employed with good results in discharging direct colours, insoluble azo dyes, and Indigo. In acting as a reducing agent in discharge work, it mordants the cotton in the discharged parts with titanic hydrate, so that the goods may be subsequently dyed, if desired, in any mordant colour, a coloured discharge being thus obtained. Thus, if calico dyed a medium shade of Indigo is printed with thickened titanous sulphocyanide, dried, and run through boiling caustic soda at 2° Tw., a white pattern on a blue ground results. If the piece is then dyed in Alizarin orange, a brilliant (and fast) orange pattern on a blue ground is obtained. By printing simultaneously two "colours" on Indigo-dyed calico, one containing hydrosulphite N.F. (free from zinc), and the other titanous sulphocyanide, drying, steaming, running through boiling caustic soda, and then dyeing in Alizarin orange, both white and orange patterns are obtained on a blue ground.

Ferrous Sulphate or Copperas ($FeSO_4.7H_2O$) (see also p. 191) is not a powerful reducing agent in neutral or acid solution. When acted upon by caustic alkalies or milk of lime it is decomposed, yielding ferrous hydrate,

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4,$$

which is a fairly strong reducing agent. Exposed to the air, it rapidly absorbs oxygen, with formation of ferric hydrate,

$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3.$$

Ferrous sulphate was formerly used very largely for the "setting" of Indigo vats, but its use for this purpose is now very restricted, partly owing to the excessive amount of sediment found in the vat, and partly on account of the loss of Indigo (about 20 per cent.) which is experienced in dyeing in the "copperas vat." Small quantities of ferrous sulphate are used in the direct printing of Indanthrene (*q.v.*).

Sodium Hydrosulphite ($Na_2S_2O_4$).—According to Schär a solution of this salt was first prepared by Schönbein, who recognised its reducing properties. Schützenberger first prepared it in a solid state, and ascertained its composition to be $NaHSO_2$. The later researches of Bernthsen and others have shown, however, that its composition is represented by the formula $Na_2S_2O_4$.

Hydrosulphurous acid and its salts may be prepared in many different ways, but only one of these is used in practice, viz. the reduction of bisulphite of soda by means of zinc powder. Under the most favourable conditions the reaction takes place according to the following equation,

$$3Zn + 10NaHSO_3 = Zn_3Na_2S_3O_{10} + Na_2SO_3 + 3Na_2S_2O_4 + 5H_2O,$$

so that 65 parts of zinc should yield 174 parts solid hydrosulphite of soda.

A solution of hydrosulphite of soda is frequently prepared in the works for Indigo dyeing by adding zinc powder to commercial bisulphites of soda, in the proportion of one pound of the former to one gallon of the latter, means being taken (*e.g.* addition of ice) to prevent undue heating. When the reaction is over, milk of lime is added in excess, and the product may then be used directly for dissolving Indigo, or as an addition to the vat. It is preferable, however, to filter the solution, *e.g.* through a filter press, but in doing so every care should be taken to prevent exposure of the liquid to the air, otherwise oxidation of the hydrosulphite may take place so rapidly that in a short time the solution loses its reducing power.

For some years past solid hydrosulphite of soda, containing amounts of $Na_2S_2O_4$ varying from 60 to 95 per cent., has been in the market in the form of a dry, almost white, powder. It is largely used in the dyeing of Indigo and other vat dyes, but, owing to the rapidity with which its solutions oxidise in contact with the air, it is not suitable for textile printing. When oxidised in the air hydrosulphite of soda yields bisulphite of soda,

$$Na_2S_2O_4 + H_2O + O = 2NaHSO_3.$$

Baumann, Thesmar, and Frossard discovered that when hydrosulphite of soda is treated with formaldehyde, it yields a compound which is stable in the air, but is decomposed on steaming, and then exerts a powerful reducing action. By their discovery the use of hydrosulphite in textile printing was rendered practicable, with the result that many new and valuable effects have thereby been introduced which could not previously be obtained.

When concentrated aqueous solutions of hydrosulphite of soda and formaldehyde are mixed, an elevation of temperature takes place and a compound is formed having the composition $Na_2S_2O_4.2CH_2O.4H_2O$, and this product comes into the market under various names, such as **Hydrosulphite N.F.**, **Hyraldite A.**

If the solution of this formaldehyde compound is subjected to fractional crystallisation it separates into two products, viz. the formaldehyde compound of bisulphite of soda and the formaldehyde compound of sulphoxylate of soda ($NaHSO_2$),

$$Na_2S_2O_4.2CH_2O + H_2O = NaHSO_3.CH_2O + NaHSO_2.CH_2O.$$

The pure sulphoxylate of soda has not been isolated. Its formaldehyde compound, when acting as a reducing agent, is converted into the formaldehyde compound of bisulphite of soda, and, as will be seen from the equation

$$NaHSO_2.CH_2O + O = NaHSO_3.CH_2O,$$

has twice the reducing capacity of ordinary hydrosulphite-formaldehyde.

The sodium sulphoxylate hydrosulphite compound ($NaHSO_2.CH_2O.2H_2O$) comes into the market under different names, such as **Rongalite C.**, **Hydrosulphite N.F.** (conc.), **Hyraldite** (conc.), in the form of irregular lumps which are white or colourless and semi-translucent. When kept for some time it gradually deteriorates and gives off a disagreeable smell. It is readily soluble in water, and the aqueous solution may even be boiled in contact with the air without losing its reducing action. When printed on calico or other material, dried and steamed (especially if the steam is superheated), it acts as a powerful reducing agent and does not tender the material.

Reductite is the name given to a compound of hydrosulphite of soda and glucose. It comes into the market in the form of a grey-coloured paste, and is used for the same purposes as the formaldehyde compound.

Alkaline sulphides, especially **sodium sulphide** (Na_2S), though cheap, and in many cases efficient as reducing agents, cannot be used in textile printing on account of their corrosive action on the copper rollers of the printing machine.

Sulphites and Bisulphites.—Of the sulphites, **potassium sulphite** (K_2SO_3) has been used in considerable quantities in resist work under insoluble azo dyes, on account of its great solubility in water. It comes into the market as a concentrated aqueous solution, standing at 90° Tw. Potassium sulphite, while acting as an efficient resist under Paranitraniline red, Alphanaphthylamine claret, etc., does not coagulate albumen, and can consequently be employed in conjunction with pigment colours for obtaining coloured resists. For white resists the cheaper **bisulphite of soda** ($NaHSO_3$) is largely employed at the present time. It comes into the market in solution, generally marking 62° Tw., or in the form of the solid metabisulphite ($Na_2S_2O_5$).

Arsenious Oxide (As_2O_3), generally known as "white arsenic," may be classed as a mild reducing agent. It is sold in the form of a fine white powder, and finds a limited application as a reducing agent in preventing the fixation of iron. **Arsenic trisulphide** (As_2S_3) was formerly used as a reducing agent for Indigo.

Of other inorganic substances, **Hydrazine sulphate** ($N_2H_4.H_2SO_4$) may be mentioned as having been suggested as a means for discharging direct cotton colours; but although it is now technically available, it is doubtful whether it finds any application in textile printing.

Glucose ($C_6H_{12}O_6$) is prepared by hydrolysing starch by heating under pressure with dilute sulphuric acid. The acid is subsequently neutralised and removed by means of milk of lime. Glucose comes into the market in the form of irregular lumps of a brownish colour, or in the form of a colourless transparent thick syrup known as "crystal glucose." In either case the product does not consist of pure glucose, but contains, besides, many other organic compounds. In presence of caustic soda, glucose acts as a fairly powerful reducing agent, and is largely used in the direct printing of Indigo by the so-called "glucose" or "Schlieper and Baum" process. It also finds employment for the fixation of other vat dyes and of sulphide colours.

PART VII.

STYLES OF PRINTING.

STYLES OF PRINTING.

General.—Technically speaking, calico prints are not classified according to their styles of design, but according to their modes of production. What is meant, therefore, when a piece of print is described as belonging to a certain "style," is that it has been executed by a particular process, a process involving a series of chemical and mechanical operations more or less peculiar to itself. Some of these operations may (and sometimes do) individually form parts of other processes, but when certain of them are associated and performed in a definite order, they constitute a definite process and give rise to a definite "style of printing." Hence calico prints are divided into distinct groups or "styles" according to the means whereby their colours are applied to and fixed upon the fibre.

This by no means implies that only one class of colouring matter can be used for a particular style. On the contrary, all colours that are capable of being applied and fixed in the same general way can be printed in combination so long as no one of them injuriously affects the others. Thus the various colours of an elaborate multicolour pattern, whilst perhaps bearing no resemblance to each other in chemical composition, are yet capable of being applied and treated in the same way, simply because each of them possesses certain properties which enable it to withstand the action of the various operations that are essential to the full development and fixation of each of the others. It must not be supposed from this that all colours belonging to a certain style of work can be printed together indiscriminately. Their powers of resistance to acids, alkalies, soap, etc., vary considerably, and must be taken into account when certain colours are used. For instance, pale shades of ultramarine blue printed along with strong Alizarin red and basic aniline colours are liable to be destroyed by the acid fumes given off by the red during "steaming," or by the accidental acidity of the tartar emetic bath used for fixing the latter; and, again, Prussian blue printed in combination with the same colours is decomposed and converted into a buff by the hot, strong soap solution through which they are usually passed after steaming, fixing, and washing. In these and numerous other cases, when an unstable colour cannot be replaced, it is necessary to modify the process, and thus the main divisions or "styles" of calico printing are further subdivided into minor styles. Instances of this necessity for special treatment might be multiplied *ad libitum*, but the above will serve to show that sensitive colours cannot be employed in combination with those containing ingredients which are apt to act upon them detrimentally, even though both classes of colour may belong to the same general "style."

To classify the styles of printing satisfactorily is a somewhat difficult matter, by reason of the fact that some of them will not readily take their place in any list, while others may be classed in several. On the whole, however, the following arrangement will be found convenient.

There are—

(1) Direct printed Styles, in which the colour is applied directly to the fibre by printing, and fixed thereon by "steaming."

(2) Dyed Styles.—A mordant being first fixed upon the fibre, and the colour afterwards applied by dyeing.

(3) Insoluble Azo Colour Styles, depending on the production, by combination of diazo compounds with phenols, of the actual colouring matter on the fibre.

(4) "Discharge" Styles, in which a dyed ground or a mordant is removed locally, leaving a white or coloured pattern on the original ground.

(5) "Resist" or "Reserve" Styles, the object of which is to produce a pattern on a coloured ground by first printing on the white cloth a substance that will prevent the fixation of any colouring matter or mordant afterwards applied over it.

(6) Raised Styles.—Similar in many respects to the "dyed styles," but produced with mineral bodies in place of dyestuffs, which are practically all organic bodies.

(7) Linings.—A mixed style, made up of many others, but distinguished for the most part by the class of its patterns and colour effects.

(8) Metal printing Styles.—The application of metallic powders to the production of designs in gold, silver, etc.

(9) "Crepons" or "Crimps."—A style of work based upon the action of strong caustic soda on cotton, and whereby crinkled stripe effects are obtained by printing on plain cloth.

And lastly, as belonging to no one style, those classes of work which are executed by a combination of parts of two or more styles, and cannot, therefore, be included in any, since they partake of the nature of several. Some combined styles are so generally employed as to constitute distinct classes. These will be dealt with as they occur in the consideration of the processes by which they are produced.

The above distinctions of styles are based upon the means and methods of applying colour to, and fixing it upon, the fibre, and as such they represent the general methods employed in the execution of all kinds of calico prints, be their ultimate use what it may. The textile colourist has nothing to do with the purpose to which a print is put beyond supplying suitable colours, and therefore the above technical arrangement of "styles" has been adopted in preference to that according to which goods are divided into cretonnes, dress goods, shirtings, etc.

Each of the foregoing styles may be subdivided into minor styles according to the class of colouring matter employed, but, in the main, the operations connected with these modifications remain the same, although the chemical reactions they bring about are different; so that all colouring matters that are capable of being applied and fixed in the same general way may be printed together, if they do not react upon one another in process.

(1) DIRECT PRINTED STYLES.

In direct printed styles the colour is applied to the fabric along with various substances which form an insoluble precipitate with it on "steaming" for a longer or shorter period. Amongst the most important colours applied in this way are those known as the Alizarin colours, basic colours, direct colours, Sulphide colours, vegetable colours, Aniline black, and certain mineral colours and pigments.

After printing, the goods are simply dried and then steamed, and, after a fixing process in the case of basic colours, soaped and washed.

The "direct style" might much more appropriately be called the "steam style," since steaming is its most distinctive feature; but the term "steam style" has unfortunately been applied, in some quarters, to a class of work distinguished by its defects—*e.g.* its gaudy colour, inharmonious combinations, general "looseness" to light and washing, and its utter lack of either technical or artistic merit—and consequently "steam work" has come to be looked upon by the public, or at least the untrained, as identical with the worst and cheapest of poor goods. So far from this being the case, however, some of the finest and the fastest colours known are fixed by "steaming," and some of the highest class work produced is steam work.

The fastness of steam colours depends upon the colour lake being formed on the cloth itself; and in order to prevent any combination taking place between the various ingredients of a colour before printing, the mordants employed are only such as have no action on the colouring matter in the cold or in presence of certain substances added to further lessen their affinity for the colour base. In steaming, these restrainers are volatilised or decomposed, and, at the high temperature of the chamber, the mordants and colouring principles combine to produce an insoluble lake, which virtually dyes the cloth in just those parts printed. The colours developed by steam usually require several other operations to fix them thoroughly on the cloth; and the latter is also usually prepared in oleine, or some preparation of oleine and tin, for the purpose of both brightening the colours and rendering them faster to soap, etc.

The usual process followed in the production of the "fast steam style" consists in the following series of operations:—

(*a*) PREPARING.—Pad the cloth in a $2\frac{1}{2}$–5 per cent. solution of castor oil oleine (soda or ammonia ricinoleate, with or without the addition of stannous or stannic salts). Dry.

(*b*) PRINTING.

(*c*) STEAMING in continuous or cottage steamers.

(*d*) FIXING in $\frac{1}{2}$–2 per cent. solution of tartar emetic and chalk.

(*e*) CHROMING (where required) in 1 per cent. solution of bichromate of potash.

(*f*) SOAPING.—Steamed goods are always soaped to clear out all superfluous matters. The strength of the soap solution varies from $\frac{1}{10}$–$\frac{1}{2}$ per cent. of soap, and its temperature between 160° F. and the boil, according to the colours and effects required.

Fixing, chroming, soaping, and washing are all performed in the "continuous open soaper" already described. Where goods contain no basic colours, the fixing is omitted; and where Aniline black or Catechu or steam Prussian blue are absent, the chroming may likewise be dispensed with. Alizarin colours and other mordant colours require no other treatment after steaming than a simple washing and soaping. At the same time they are easily capable of withstanding the other operations, and can therefore be used in combination with practically every colour fixed by "steaming."

Indigo and similar vat colours, Aniline black, and Paramine brown may also be included amongst the colours applied directly to the fibre by printing. They are not really "steam colours" in the ordinary sense of the term, neither can they be introduced into so great a variety of colour schemes as some of the "steam colours" proper; but "steaming" or "rapid ageing" in a rapid ager is essential to their fixation; and in so far as they are applied and fixed by the same mechanical means as ordinary steam colours, they may, for convenience, be classed in one of the subdivisions of "direct printing."

Application of Mordant Colours.—By "mordant colours" are understood those colouring matters which, while possessing no colouring power of any practical use in themselves, are yet capable of combining with metallic oxides to form insoluble coloured precipitates on the cloth. They constitute perhaps the most important series of colours at the disposal of the calico printer; and if they do not yield the most brilliant shades, they at least possess qualities which compensate for this lack, and which render them of the utmost value in the production of the highest class of decorative designs, and not less so in that of dress goods and strictly utilitarian fabrics.

As a class, the mordant colours are easily applied; they furnish a good range of rich, full colours, varying from bright reds, yellows, blues, and greens, to the softest and most delicate tones of grey, fawn, olive, and salmon; in "direct printing" any of them may be associated in almost any colour scheme, thus allowing of the designer's ideas being realised to the fullest extent, and affording the colourist ample scope in the arrangement of his colour combinations; and above all, they are fast to light and soap.

Many of the *lakes* produced by the mordant colours are identical with those used by artists; and of the rest, the greater number are equally rich and permanent, so that an artist designer need have no fear of his work being crippled in reproduction if his design is drawn up, in the first instance, with due regard to the limitations and possibilities of calico printing. Much of the outcry at modern colours is neither more nor less than an expression of ignorance; and if the self-satisfied critics would only condescend to even dabble in the subject they descant upon, they would soon learn to keep silence in the company of expert chemists and calico printers, who at least do know what they are using when they apply certain substances to cotton, linen, wool, or silk, and that is more than most "art critics" know when they attempt to belittle the results obtained by scientific research, and at the cost of much money, many failures, and long experience.

Amongst the most extensively employed "mordant colours" are: Alizarin of all brands; Alizarin yellows, blues, greens, heliotropes, grenates, and Bordeaux; Alizarin orange or Nitro-alizarin; Alizarin viridine; Alizarin cyanines; Anthracene brown, yellow, and blue; Chrome violet and Chrome violet blue; Solid green O; Gallocyanine, Gallopurple, and Cœruleïn olive; Chrome Azurol S, Modern blue, Blue 1900, etc.; the vegetable dyestuffs—Logwood, Quercitron bark, and Persian berries; and, in addition, various brands, preparations, and derivatives of the foregoing and of a vast number of other dyestuffs, mostly artificial, which are applied similarly.

Alizarin is the best type of mordant colours, inasmuch as it yields the brightest, fastest, and most varied range of colours with different mordants. Its alumina lake is red; its iron lake black or purple, according to the strength of the iron; its tin lake is orange; its chromium lake a rich claret shade; and its mixed alumina and iron lake a strong, deep, full chocolate, which can be made to approach black or red by increasing or diminishing the proportion of the iron to the alumina. A fine chocolate is also obtained from a mixed chromium and iron mordant; this is usually the chocolate employed in "steam work," for which it is frequently "toned" by the addition of a little yellow—Quercitron bark. The orange from Alizarin and tin is only utilised in the brightening of the red, to which it imports a brilliant scarlet tone; a better and purer orange is obtained from Nitro-alizarin in combination with alumina and tin. A rich, warm brown is given by Nitro-alizarin and chromium mordants, but the iron lake is of no great interest.

ALIZARIN [$C_{14}H_6O_2(OH)_2$] is the essential colouring principle of the madder root, and is prepared artificially and in large quantities from anthracene—a coal-tar product. It is a yellow powder sent out by the makers, ground up in water, in the form of a 20 per cent. paste; it is insoluble in cold water, but is so finely ground that it combines readily with its mordants on "steaming," and so does not require to be dissolved in any medium before use.

Three other dyestuffs closely resembling Alizarin in their chemical composition and general properties are – (1) Anthrapurpurin, (2) Flavopurpurin, and (3) Purpurin. They all give shades of red with alumina, and behave in the same way as Alizarin towards other mordants. Alizarin itself yields a crimson shade of red; Anthrapurpurin a bright full red; Flavopurpurin a yellow and rather flat red; and Purpurin, a dull bluish red, inclining to a brownish or claret tone. Mixtures of Alizarin with Anthrapurpurin or Flavopurpurin are sold as "*blue and yellow shades of Alizarin*" respectively; and it is such mixtures that form the different commercial brands of Alizarin. Those containing a large proportion of Flavopurpurin are mostly employed for reds and brownish chocolates, while those containing more Anthrapurpurin are the best for pinks and claret shades. Pure Alizarin in combination with alumina yields deep, pure crimson shades, and with chromium, full, rich maroons; it is also the best for purples.

NITRO-ALIZARIN OR ALIZARIN ORANGE [$C_{14}H_5.NO_2.(OH)_2$] is applied in the same way as Alizarin, from which it is prepared by the action of nitrous acid. With alumina or stannic mordants it yields orange shades remarkable for their brilliancy, and with chromium mordants a fine orange brown. Both colours are fast to light and soap.

Most of the other mordant colours, with the exception of the vegetable dyestuffs, yield only slightly different shades of one colour, whatever the mordant used may be. Logwood is only employed with chromium and iron salts for blacks, and Persian berries and Quercitron bark give various tones of yellow with alumina and tin mordants, and in strong colours, browns with chromium mordants. In practice, no other mordants are used for the vegetable colours. Sapan wood finds a limited use in some "steam" chocolates, as a cheap (but loose) substitute for Alizarin.

As a general rule, the mordant colours yield the finest results when printed on oil-prepared cloth. The percentage of fatty matter put into the cloth will vary with the depth of the colours to be printed; and the question as to whether or not tin oleates should be introduced will also be decided by the shades to be produced. Tin compounds should be avoided whenever a bright Alizarin-iron purple is desired, as the shade would be dulled considerably by the addition of orange, due to the combination of part of the Alizarin with the tin in the "prepare." A pure castor oil "oleine" is a good standard "prepare," and can be used for all styles. For reds and pinks and most basic Aniline colours the addition of tin improves the shades, but it is not absolutely essential to the attainment of good results, and can be used or not as desired. For dark steam colours about 5 per cent. of fatty matter is applied to the cloth; for light colours, half that quantity is sufficient. The percentage refers to the strength of the solution of oleine thus:—

5 per cent. OIL PREPARE.
1 part ricinoleate of soda, or an "oleine" 25 per cent.
4 „ water.

As the cloth often absorbs its own weight of liquor, it will approximately take up the amount of fatty matter represented by the percentage of the "prepare," all the water being driven off on drying.

With the exception of Alizarin reds, pinks, scarlets, and oranges, the composition of most "steam printing colours" is extremely simple, requiring little beyond a suitable thickening, a little acetic acid, and a single mordant. But reds, pinks, etc., are somewhat more complicated, since bright shades with Alizarin can only be obtained by a combination of alumina, tin, lime, and oil, together with tartaric, citric, or oxalic acids, either free or as salts of the mordanting bases. As a matter of fact, lime is apparently necessary to the full development of all shades obtained from Alizarin, and consequently it enters into all that are employed as self colours; it may be left out of colours used solely for the making of compound shades, though its inclusion is by no means detrimental in most cases where Alizarin blue is absent. On the whole, however, lime salts are better avoided when their presence is unnecessary, since they precipitate a large number of colouring matters, and it is not always possible to foresee what colouring matters will have to be added to a compound shade to bring it up to the required standard.

In passing, it may be noted that the mordant colours when applied by direct printing are as often called "extract colours," from the fact that originally the first steam colours were prepared from extracts of Madder, Logwood, Quercitron bark, and other vegetable colouring matters.

In the following examples of printing colours, care has been taken to select only such typical examples as have, under proper conditions, yielded consistently good results on the large scale. Beyond giving these necessary types, it would be useless to enlarge the text with a mass of "practical receipts," consisting of mere modifications of those given, for although the principles involved always remain the same, their working details differ according to the varying conditions under which they are applied; and success depends upon so many factors, that each firm in adopting a process has generally to modify it to some extent in order to ensure the best results being obtained from its existing plant, system, and methods of work.

No two firms make up their colours in exactly the same way; and consequently the recipes given below must not be taken as representing the only proportions, or even ingredients, possible to use, but must rather be regarded as a selection from the immense number of printing colours employed in actual practice.

(1) **Alizarin.**—Alizarin red is prepared in two distinct ways: (*a*) by adding the Alizarin to a thickening containing all the essential mordants; and (*b*) by adding the mordants to a paste containing the Alizarin. In both cases the final additions must only be made immediately before printing, as a reaction takes place between the colouring matter and mordants if they are allowed to stand in contact for any lengthened period.

ALIZARIN RED A. (Alumina).

27	kilos.	water.
9·5	,,	starch.
9·5	,,	6 per cent. tragacanth thickening.

Boil, cool, and add

9·5	kilos.	chlor oil. (See Oil Mordants.)
10·5	,,	acetate of lime 23° Tw.
8·5	,,	acetate of alumina 22° Tw.
11·5	,,	sulphocyanide of aluminium 27° Tw.
14	,,	tartrate (or oxalate) of tin.
100		

When required for printing, four parts of the above paste are mixed with one part of Alizarin and (for ordinary reds) two parts of "paste for reds" (see Pastes):—

4	kilos.	mordant paste.
2	,,	red paste or "reduction."
1	,,	Alizarin 20 per cent. (yellow shade).

For very dark reds the reducing paste may be omitted. Print on oiled cloth; steam 1¼ hours, with or without pressure; wash, soap, wash.

As the result of many experiments, it has been found that by boiling the Alizarin with the thickening and adding the oil mordants hot a brighter red can be obtained with a smaller quantity of oil and tin compounds than when the latter and the Alizarin are added cold. Thus—

Alizarin Red B. (boiled).
47 kilos. water.
13 „ starch.
13 „ Alizarin 20 per cent. (yellow shade).
3 „ acetic acid 9° Tw.
Boil, turn off steam, and at once add—
2·5 kilos. chlor oil (see Mordants).
2·5 „ stannic hydrate 20 per cent. paste.
2·5 „ oxalate of tin.
Cool, and immediately before use add *cold*—
3·5 kilos acetate of lime 23° Tw.
4 „ nitrate of alumina 23° Tw.
10 „ sulphocyanide of alumina 20° Tw.
100 kilos. (after boiling the thickening).
Print as above on oiled cloth, etc.

A steam Alizarin red, suitable for printing on *unoiled* cloth, has been described by P. Wilhelm (*Bull. Soc. Ind. Mulhouse*, p. 69, 1908).[1] For this purpose he adds the required amount of fatty matter to the printing colour in addition to the usual oil mordants, and overcomes its liability to precipitate the metallic mordants by employing a modified form of sulphoricinoleic acid, together with a suitable amount of formic or lactic acids, or a mixture of the two, and a small quantity of acetate of soda.

The lactic acid is only adapted for strong reds, since it retards the development of the colour on steaming. On the other hand, formic acid can be used safely for both reds and pinks; it offers no obstacle to the formation of the colour lake on steaming, and it effectually prevents the precipitation of insoluble aluminium and calcium sulphoricinoleates.

The special sulphoricinoleic acid mixture is prepared as follows:—

Emulsion.
450 grms. freshly made sulphoricinoleic acid,
450 „ 16 per cent. gum-tragacanth thickening,
100 „ acetic acid 9° Tw.,
are beaten together and allowed to stand for six days at the ordinary temperature; then add
8650 grms. tragacanth thickening 5 per cent.
350 „ formic acid 92 per cent.
The whole then forms 10 kilos. of an extremely stable white emulsion, in which the fatty acid exists in a very fine state of division. Being practically insoluble and mixed with organic acids, it has no action on the other mordants until the printed goods are steamed. During the steaming it combines gradually with the mordants in presence of the cloth, and the metallic sulpholeates thus formed are fixed thoroughly on the fibre, and then behave as ordinarily towards the colouring matter (Alizarin).

The advantages claimed for the following red are—(1) that it renders unnecessary the preliminary preparation of the cloth; (2) that it is easy to work

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[1] *Journal of Soc. of Dyers and Colourists*, 1908, page 199.

and very stable; (3) that a good Aniline black can be obtained in combination with it, since the cloth is free from all traces of alkali; (4) that the whites are less yellowish than when the cloth has been prepared in "oleine"; and (5) that it is as bright and fast to soaping and light as is the ordinary "steam Alizarin red" For the preparation of the fastest red on unoiled cloth Wilhelm gives the following instructions, and insists upon the necessity of adding the ingredients in the order indicated:—

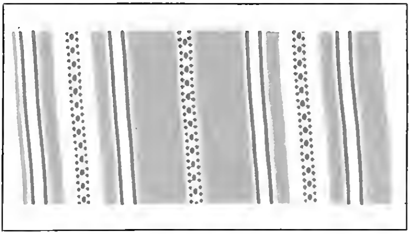
Alizarin Red (on unoiled cloth).

160	grms.	starch.
150	,,	water.
100	,,	tragacanth thickening.
50	,,	acetic acid 9° Tw.
150	,,	Alizarin 20 per cent. (yellow shade).
{ 25	,,	oleine.
{ 25	,,	stannic sulpholeate.
Boil, cool, and add		
130	,,	nitrate of alumina 23° Tw.
40	,,	stannic oxalate.
75	,,	acetate of lime 23° Tw.
22	,,	formic acid 92 per cent.
100	,,	emulsion.
18	,,	acetate of soda.

Print on unprepared cloth; steam 1½ hours, and wash and soap as usual.

Alizarin pinks may be made in the same way, employing a "blue shade" of Alizarin, and reducing the standard colour to any desired extent by the addition of starch paste.

In another method, employed largely for the production of Alizarin reds on *unoiled* cloth, use is made of Lizarol D., a formaldehyde compound of ricinoleic acid, put on the market by Messrs Meister, Lucius & Brüning.[1] Lizarol is insoluble in water, does not form any lake in the printing colour, and comes into action with the mordants and Alizarin in the steaming process only, forming during this process the bright red colour lake.



Alizarin Red and Pink (with Lizarol).

According to Fehling, both the mono- and polyricinoleic acids are suitable for adding to steam Alizarin reds.[2]

Battegay has also worked on the same subject, and has obtained the best results by adding an acetic acid solution of ricinoleic acid to the printing paste.

Alizarin Pink may be made exactly as any of the above reds by simply employing a suitable brand of "blue shade" Alizarin instead of the yellow shade. Used at full strength, such "pinks" yield dark rich reds inclining to crimson; it is only when they are reduced considerably that true *rose pinks* are obtained. As a rule, however, Alizarin pinks differ slightly from the reds both in composition and in the proportions of their ingredients.

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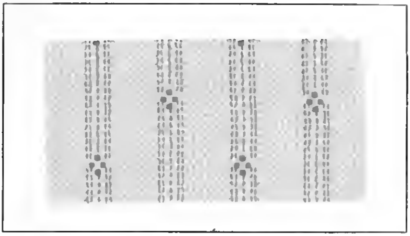
[1] Eng. Patent, 13790 (1908).

[2] *Rev. Gen. des Mat. Col.*, p. 74, 1909.

An Alizarin pink extensively used on the large scale in an important works is compounded as follows:—

ALIZARIN PINK I.
630 grms. starch paste for reds (see Thickenings).
100 ,, Alizarin (blue shade).
140 ,, aluminium sulphocyanide 23° Tw.
40 ,, acetate of lime 23° Tw.
30 ,, oxalate of tin (stannic).
60 ,, citrate of alumina 40° Tw.
———
1000

Print on oiled cloth, steam, wash, and soap. If the pink is printed as a shirting or other single colour, it is usually soaped strongly in the rope form; in other cases it passes through the "open soaper" at full width, as is usual with most steam work.



Alizarin Red and Pink (on Oiled Cloth).

CITRATE OF ALUMINA 40° Tw.
500 grms. hydrate of alumina 15½ per cent. paste.
220 ,, citric acid.
28 ,, soda ash.
200 ,, water.
Stir till dissolved.

A much brighter pink is obtained by adding a small quantity of the basic colour Rhodamine to the above. The brand of Rhodamine sent out by the Badische Anilin und Soda Fabrik is the best to use for this purpose: it is a pure product, and, unlike many other Rhodamines, it is not precipitated by the alumina in the printing paste, and thus it gives an even shade, free from "specks." The proportions taken are—

1000 grms. Alizarin pink I. (above).
3 ,, Rhodamine 6 G. 100 per cent. (B.A.S.F.) in—
50 ,, acetic acid 6° Tw.

"Blotch" pinks, or pinks used for the printing of grounds, and stipple engraving, are made up with either starch, starch and gum tragacanth, British gum, or Senegal gum. The last always gives the best results, and is invariably used when its price is no obstacle. Starch is apt to give a "mealy" surface, and even when mixed with tragacanth it almost always requires to be "crushed," *i.e.* the printed cloth must be passed under a plain unengraved roller working in starch paste—a "crush roller"—in order to obtain a perfectly smooth, even blotch. Tragacanth alone is an excellent thickening to use for many qualities of cloth, but gum Senegal produces the finest results in all cases, and is a reliable thickening on all kinds of cloth.

As a rule, the quantity of mordant to a given weight of Alizarin is proportionally greater in pinks than in reds, the reason being that as they are reduced or diluted they require extra mordant to bring about their full development in "steaming." The extra mordant may be added to either the standard colour or to the reducing paste: the former is the more usual and more convenient method.

GUM ALIZARIN PINK II. (for blotches).

{ 630 grms. gum Senegal solution 50 per cent.
{ 100 „ Alizarin (blue shade) 20 per cent.

Mix well and add

30 grms. stannic oxalate.
40 „ acetate of lime.
60 „ citrate of alumina 40° Tw.
140 „ sulphocyanide of aluminium 23° Tw.

1000

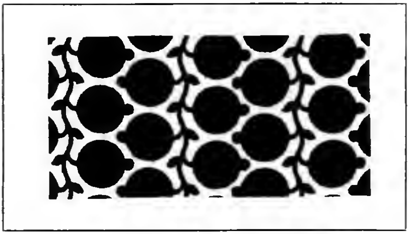
Print on oiled cloth; steam, etc., as usual.

For light shades the above pink is merely reduced by the addition of gum Senegal. Thus—

	Medium Pink.	*Pale Pink.*
Standard Pink	1	1
Gum Senegal 30 per cent. . . .	9	40 or more.

Acetate, nitrate-acetate, or nitrate of alumina may be used instead of the sulphocyanide, but, for the most part, the latter is preferred because it does not attack the doctors, and thus prevents the dulling of the shade from dissolved iron. The nitrate and nitrate-acetates tend to impart a yellowish tone to the pink, and are sometimes employed expressly for that purpose. A similar effect may be obtained by using a yellower brand of Alizarin, but in general the shade of pink is not so bright as when nitrate of alumina is employed, since, apart from the shading and brightening properties of the latter, the yellow brands of Alizarin yield colours somewhat dull in character.

"Cover" reds and pinks, and their resists, will form part of a separate division.



Alizarin Claret.

Alizarin Claret (Chrome).—The Alizarin chrome lake is employed largely as a "blotch" in cretonne printing, and as a constituent of an enormous number of "extract" browns, greys, olives, etc. For blotch work it may be made as follows, the lake, of course, being produced by steaming:—

STEAM ALIZARIN CLARET A.

140 grms. starch.
300 „ water.
50 „ acetic acid 9° Tw.
240 „ gum-tragacanth thickening 5 per cent.
180 „ Alizarin X. 20 per cent. (British Alizarin Co., Ltd.).
30 „ cotton-seed oil.

Boil, cool, and add

70 grms. acetate of lime 23° Tw.
90 „ acetate of chrome 25° Tw.

1100 = 1000 after boiling.

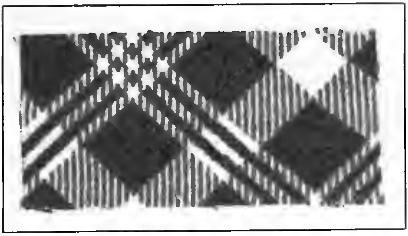
Print on oiled cloth, and steam, etc., as for reds. Steam Alizarin claret enters largely into a great many compound tertiary shades; and as many of the colours associated with it in this connection are precipitated by acetate of lime, this latter must be omitted in all clarets used for mixtures.

STEAM ALIZARIN CLARET B. (for mixtures).

745	grms.	acid starch paste.
150	,,	Alizarin X. 20 per cent. (British Alizarin Co., Ltd.).
75	,,	acetate of chrome 24° Tw.
30	,,	cotton-seed oil.
1000		

The shades of claret may be varied by using different brands of Alizarin, or by adding other mordant colours, or by mixing aluminium and chromium mordants together.

The Alizarin Bordeaux of the Bayer Co., Ltd., also yield fine shades of claret, and, as they are fixed with alumina, they may be used to modify the shade of steam Alizarin reds, without unduly dulling the colour.



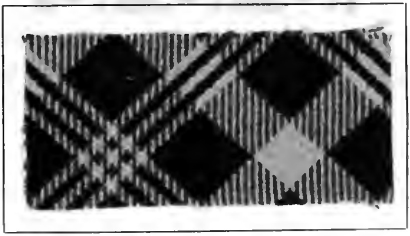
Brilliant Alizarin Bordeaux R.

STEAM ALIZARIN BORDEAUX (red shade).

105	grms.	brilliant Alizarin Bordeaux R. paste.
100	,,	water.
641	,,	starch-tragacanth thickening.
70	,,	sulphocyanide of aluminium 18° Tw.
53	,,	acetate of lime 23° Tw.
21	,,	castor oil.
10	,,	oxalate of tin 25° Tw.
1000		

Print, steam, etc., as for reds.

Steam Alizarin Bordeaux (blue shade) is made as above, but with Alizarin Bordeaux B.P. paste.



Brilliant Alizarin Bordeaux B.P.

Steam Alizarin Purple (Iron). — Steam Alizarin purples or violets have lost much of their importance since the introduction of Chrome violet-blue (Geigy), Chromoglaucine (Meister, Lucius & Brüning), and other chrome violets too numerous to mention. They are, however, still largely used for some purposes for which their fastness renders them difficult of replacement. Steam Alizarin purples are frequently brightened by the addition of Methyl violet.

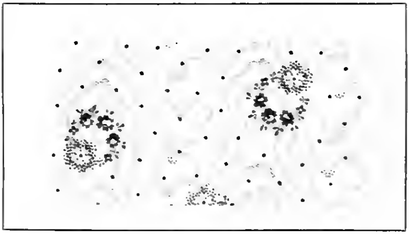
Alizarin Purple A.

565 grms. acid starch paste.
170 ,, Alizarin (blue shade) 20 per cent.
110 ,, acetate of lime 23 per cent.
85 ,, pyrolignite of iron 32° Tw.
10 ,, Methyl violet B. extra.
60 ,, acetic acid 1½° Tw.

1000

Print on oiled cloth, steam, wash, and soap.

For light purples or lavenders, the pyrolignite of iron is often replaced by potassium ferrocyanide.



Steam Alizarin Purple.

Light Steam Alizarin Purple B.

696 grms. acid starch paste.
15 grms. Alizarin (blue shade) 20 per cent.
200 grms. gum tragacanth 5 per cent.
15 grms. acetate of lime 23° Tw.
4 grms. potassium ferrocyanide, in—
70 grms. water.

1000

Print, etc., as for reds.

A brighter shade results from the addition of 0·75 grm. of Methyl violet to the above.

Steam Alizarin Chocolate.—Used alone with any single mordant, Alizarin does not give a good shade of chocolate, but when toned with a little Quercitron bark extract, and fixed with chrome and iron, it produces a very fine, fast shade, useful alike for blotches, fine outlines, objects of any size, and mixtures.

Chocolate A.

300 grms. water.
175 ,, tragacanth thickening 4 per cent.
75 ,, starch.
50 ,, acetic acid.
40 ,, cotton-seed oil.
160 ,, Alizarin X. 20 per cent.
60 ,, Quercitron bark extract 48° Tw.

Boil, turn off steam, and add

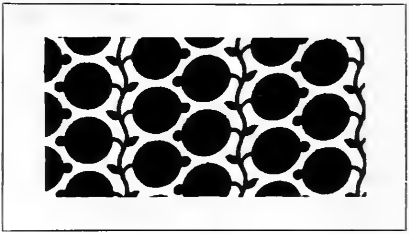
15 grms. yellow prussiate of potash (ground).

Allow time to dissolve; then cool and add—

75 grms. acetate of lime 23° Tw.
150 ,, acetate of chrome 18° Tw.

1100 = 1000 after boiling.

Print on oiled cloth, steam, wash, and soap.



Alizarin Chocolate.

The foregoing chocolate is for blotches and large objects for which a soft, thinnish colour is required. For finer engraving and general work it may be thickened with starch, with or without the addition of a little British gum. The gum helps to improve its working qualities, which, in common with all strong Alizarin colours, are not too good when it is used at full strength.

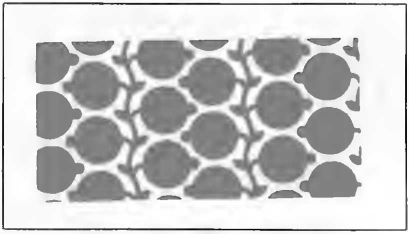
In conjunction with Persian berry or Quercitron bark extracts, the above chocolate gives a fine range of useful browns, and affords a convenient means of darkening many colours without the actual addition of black, which always has the effect of deadening even dark shades.

(2) **Other Alizarin Colours.**—Among these are the Nitro-alizarin or Alizarin orange, Alizarin yellows, blues, greens, browns, and a great number of other colours, such as Alizarin Bordeaux, Grenate, and colours fixed in a similar way.

ORANGE (NITRO-ALIZARIN).—This colour is a beautiful pure orange, and forms the point of departure of a large variety of salmons, terra-cottas, and other mixed shades. For printing as an orange it is made as under:—

ALIZARIN ORANGE (bright).

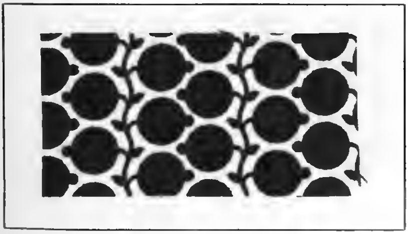
420	grms.	acid starch paste.
200	,,	gum tragacanth 2 per cent.
100	,,	Alizarin orange 20 per cent.
200	,,	nitrate of alumina 20° Tw.
50	,,	acetate of lime 23° Tw.
30	,,	oxalate of tin.
1000		



Alizarin Orange (Alumina).

For salmon shades the above orange is mixed in various proportions with steam Alizarin pink.

A browner shade of orange is obtained by reducing a colour made up with a chromium mordant—a colour which in strong shades is a warm chestnut brown.



Alizarin Orange (Chrome).

ALIZARIN ORANGE (with Chrome).

700	grms.	acid starch paste.
150	,,	Alizarin orange 20 per cent.
75	,,	acetate of chrome 25° Tw.
45	,,	acetate of lime 23° Tw.
30	,,	olive or cotton-seed oil.
1000		

For mixtures with Alizarin blues and yellows, the acetate of lime is left out of the above.

The Alizarin oranges are printed on oiled cloth, and treated exactly as the reds.

Alizarin Blue S. (Bayer).

Alizarin Blue.—Alizarin blue comes into the market in different forms, some of which are soluble and others insoluble in water. The bisulphite compounds—Alizarin blue S., and S.B., and S.R.X., in powder, and S. 2 R. in paste—are those most usually employed. They are extremely soluble in cold water, and can be added directly to the thickening paste without previous solution. The Anthracene blues are similar in properties to the Alizarin blues, and are applied in precisely the same way. The following recipes for Alizarin blue S. will serve for all the others belonging to the same class.

Alizarin Blue I. (Chrome).

50	grms.	Alizarin blue S. powder.
650	,,	starch paste.
150	,,	4 per cent. gum tragacanth.
150	,,	acetate of chrome 25° Tw.
1000		

Alizarin Blue II. (zinc).

60	grms.	Alizarin blue S.
820	,,	starch paste.
120	,,	zinc sulphate ($ZnSO_4.7H_2O$).
1000		

Dissolve in the cold.

Alizarin Blue III. (with Nickel).

60	grms.	Alizarin blue S.
820	,,	starch paste.
120	,,	acetate of nickel 15° Tw.
1000		

Alizarin Blue IV. (with Copper).

60	grms.	Alizarin blue S.
820	,,	starch paste.
120	,,	acetate of copper 15° Tw.
1000		

Print on oiled cloth, steam, wash, and soap.

The chromium and copper lakes of Alizarin blue are by far the fastest in every respect; in light shades the copper lake is the faster of the two, especially to light. The zinc and nickel lakes are much more pleasing in tone than the preceding, but they lack resistance to the action of light, fading to bluish and reddish greys after an exposure of twelve days to moderate sunlight. Along with mordant yellows and Alizarin claret, Alizarin blue is largely used for the production of all shades of olive, brown, grey, and other "mode" or tertiary shades.

Chromoglaucine, Pilochromine (M., L. & B.), Phenocyanine, Corein, the Alizarin cyanines, Gallophenine, Alizarin black, Gallo navy blue, etc., are all applied in a similar way to Alizarin blue S. The percentage of colouring matter may vary according to the concentration and depth of shade required, and the proportions of mordant will have to be adjusted so as to supply the requisite amount of metallic oxide to fix fully the whole of the colouring matter, but in most other respects nearly all the mordant blues may be made up on the lines of Alizarin blue S. Chromium acetate is the group mordant.


Gallophenine (Bayer).

Insoluble mordant blues, like Gallamine blue and its class, are rendered soluble by steeping in bisulphite of soda for a certain length of time. For instance—

Gallamine Blue.

40	grms.	Gallamine blue.
50	,,	water.
40	,,	bisulphite of soda 66° Tw.

Allow to stand 2–3 days and then add

770	grms.	starch paste.
100	,,	acetate of chrome 25° Tw.
1000		

Print on oiled cloth, steam 1 hour, wash, and soap.

"Modern violet" and "Modern blue," Blue 1900, and derivatives of Gallocyanine, which form leuco compounds, or are put on the market as such, give excellent colours for "blotch work." They are fixed almost as well by tannic acid as by chromium mordants, and may therefore be shaded or toned with any of the basic colours. Usually both mordants are used in combination, especially in the case of the Chrome violet blues (of Geigy). The addition of "hydrosulphite" is also beneficial. Tannic acid has the effect of "bluing" the shade of the chromium compounds, which is somewhat reddish in tone. As an example of this class of colour the following will serve:—

Dark Blue (blotch).

3,500	grms.	Chrome violet blue (Geigy).
1,500	,,	Setoglaucine blue (Geigy).
8,000	,,	acetic acid 9° Tw.
2,000	,,	acetin.
5,500	,,	water.
10,000	,,	starch.
4,500	,,	tragacanth thickening 5 per cent.
300	,,	cotton-seed oil.
3,500	,,	50 per cent. solution of hydrosulphite N.F. (M., L. & B.).

Boil, cool, and add

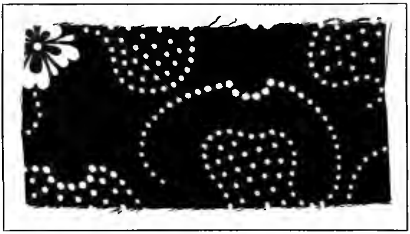
3,000	,,	Alizarin oil 25 per cent.
10,000	,,	tannic acid sol. 1 : 1 (= 50 per cent.).
12,000	,,	acetate of chrome 15° Tw.

104,300 = 100,000 grms. after boiling.

Print on oiled cloth, steam, allow to lie a short time, and then wash and soap.

The Phenocyanines are also leuco bodies, and are best allowed to lie, after steaming, for some time before they are washed; or they may be very lightly "chromed" if the other colours in the pattern will allow of it. Phenocyanine blues mixed with Alizarin yellows yield very bright shades of olive, which may be modified by the addition of any of the mordant colours.

Amongst the many other blues and violets that are applied in the same way as Alizarin blue, the following are largely employed both as self shades and in mixtures:—Chrome azurol S., Chrome violet, Gallazol blue, and Gallo navy blue.



Chrome Azurol S. (Geigy).

Chrome Azurol S.

40	grms.	Chrome azurol S. (Geigy).
120	,,	water.
80	,,	acetic acid 6° Tw.
600	,,	starch-tragacanth thickening.
160	,,	acetate of Chrome 18° Tw.
1000		

Print, steam, and wash.

Chrome Violet.

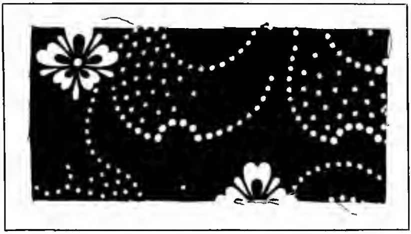
40	grms.	Chrome violet (Geigy).
150	,,	water.
60	,,	acetic acid 6° Tw.
600	,,	starch-tragacanth thickening.
30	,,	acetin.
120	,,	acetate of Chrome 18° Tw.
1000		

Print, steam, and wash.

Chrome Violet (Geigy).

Chrome azurol may be mixed with either Chrome violet or with Calico yellow for the production of various shades of purple or olive.

Gallazol blue is made up in a similar way.

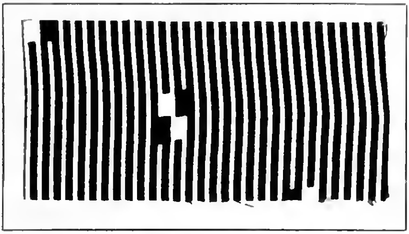


Gallazol Blue (Geigy).

GALLO NAVY BLUE.

50	grms.	Gallo navy blue R.D. conc. paste (Bayer).
170	,,	water.
650	,,	starch-tragacanth thickening.
30	,,	acetic acid 6° Tw.
100	,,	acetate of Chrome 32° Tw.
1000		

Print, steam, and wash.



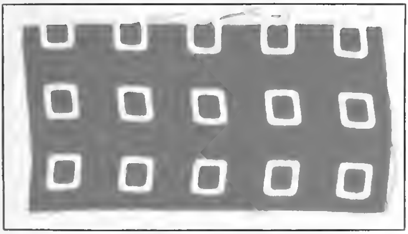
Gallo Navy Blue (Bayer).

Gallo navy blue, either alone or toned with other colours, is useful for both "blotch" and "peg" work in the "steam styles."

Alizarin Yellows.—The Alizarin, Anthracene, or Calico yellows range in shade from a greenish sulphur to a deep red orange. They form suitable lakes with chromium, tin, and aluminium mordants. The chromium lakes are the fastest in all respects, though not the brightest. To a great extent the Alizarin yellows have displaced the vegetable yellows, especially in the making of mixed shades like olives and "mode" colours.

ALIZARIN YELLOW I.

630	grms.	starch paste.
200	,,	Alizarin yellow G.G. paste or R. paste (M., L. & B.).
100	,,	nitrate-acetate of chrome 38° Tw.
50	,,	acetate of lime 23° Tw. (optional).
20	,,	cotton-seed oil.
1000		



Calico Yellow (Geigy).

ALIZARIN YELLOW II.

200	grms.	Calico yellow F.F.E. 20 per cent. paste (Geigy).
40	,,	water.
660	,,	thick starch paste.

Boil till the yellow is dissolved, then cool and add

100	grms.	acetate of chrome 18° Tw.
1000		

ALIZARIN YELLOW III. (very brilliant).

40	grms.	Anthracene yellow 100 per cent. (Geigy).
40	,,	acetic acid 9° Tw.
80	,,	water.
700	,,	starch-tragacanth paste.
100	,,	acetate of alumina 15° Tw.
40	,,	oxalate of tin.
1000		

Alizarin Greens.—These colours include Cœruleïn, Alizarin green, and Alizarin viridine, all of which produce fast lakes with chromium oxide, and are used both as self colours and as constituents of a great number of compound shades.

CŒRULEÏN OLIVE I.

200	grms.	Cœrulein S. paste (bisulphite compound).
150	,,	water.
500	,,	thick starch-tragacanth paste.
150	,,	acetate of chrome 32° Tw.
1000		

CŒRULEÏN OLIVE II.

50	grms.	Cœrulein conc. powder.
150	,,	water.
100	,,	bisulphite of soda 66° Tw.

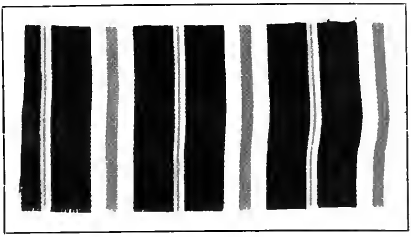
Allow to act two to three days, then add

550	grms.	thick starch-tragacanth paste
150	,,	acetate of chrome 32° Tw.
1000		

ALIZARIN GREEN S.

150	grms.	Alizarin green S. (paste).
660	,,	starch-tragacanth paste.
150	,,	acetate of chrome 20° Tw.
40	,,	cotton-seed oil.
1000		

Bisulphites of chrome and nickel may also be used as mordants.



Alizarin Viridine.

ALIZARIN VIRIDINE.

40	grms.	Alizarin viridine (powder) (Bayer).
200	,,	water.
100	,,	acetic acid 9° Tw.
120	,,	starch.
400	,,	water.
20	,,	cotton-seed oil.

Boil, cool, and add—

120	grms.	acetate of chrome 30° Tw.
1000		

Alizarin viridine is the brightest and purest green of its class, Cœruleïn being a deep olive, and Alizarin green inclining to a dull blue, especially in light shades. All are printed on oiled cloth, and then steamed, etc., as for reds.

Dinitroso-Resorcin is a colouring matter yielding green and brown shades, very fast to light and soap. It is sold as Solid green O., as Resorcin green, and as "fast myrtle," but it is easily prepared as follows:—

DINITROSO-RESORCIN 25 per cent.

500	grms.	finely ground resorcin $C_6H_4(OH)_2$.
650	,,	sodium nitrite 94 per cent. $NaNO_2$.
3000	,,	water.

Dissolve and add

3000	,,	ice; then run in gradually—
700	,,	sulphuric acid 123° Tw.

Stir all the time, and keep the temperature down by adding fresh ice if necessary. The dinitroso product will precipitate out. Wash well by decantation, and filter to 3050 grammes = 25 per cent. paste.

With iron mordants the above yields dark myrtle greens; with chrome and alkaline copper mordants, dark browns. The iron and chromium lakes are the most generally employed, and the latter forms a useful dark brown blotch in ordinary "steam work," and a pleasing series of lighter browns and fawns when reduced in strength. It may be printed on oiled or unoiled cloth, the former giving a slightly better result. On the whole, however, there is not a great deal of difference between the two shades, and it is practically immaterial upon which cloth the colours are printed.

GREEN D.R.

100	grms.	dinitroso-resorcin 25 per cent.
100	,,	water.
100	,,	25 per cent. ammonia.

Dissolve and add in the cold

25	grms.	glycerin.
580	,,	starch-tragacanth paste.
95	,,	potassium ferrocyanide (finely ground).

Stir till the ferrocyanide is dissolved, then strain and print.

BROWN D.R. (with chrome).

150	grms.	dinitroso-resorcin 25 per cent.
100	,,	potassium sulphite 70° Tw.
250	,,	5 per cent. gum-tragacanth thickening.
350	,,	starch paste (acid).
150	,,	acetate of chrome 25° Tw.
1000		

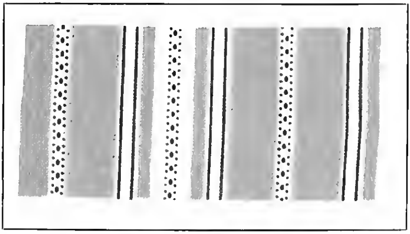
Print, steam, and open-soap at 80–90° C.

The brown D.R. at full strength gives a fast dark "cutch brown"; when reduced 1 : 10 or more, pleasing shades of a warm fawn, very fast to light and soap.

Two other nitroso compounds—Chrome bistre N.O. and Viridone F.E.—are put on the market by Messrs Meister, Lucius & Bruning. Chrome bistre gives fine deep brown shades with chrome mordants, while Viridone with iron salts yields a far brighter green than dinitroso-resorcin, and with a chrome mordant gives useful and fast shades of khaki.

Chrome Bistre N.O.

60	grms.	Chrome bistre N.O.
340	,,	water.
500	,,	starch-tragacanth thickening.
100	,,	acetate of chrome 32° Tw.
1000		



Chrome Bistre and Viridone F.E.

Viridone F.E.

60	grms.	Viridone F.E.
245	,,	water.
50	,,	acetic acid 9° Tw.
470	,,	starch-tragacanth thickening.
30	,,	glycerin.
15	,,	olive oil.
80	,,	pyrolignite of iron 15° Tw.
40	,,	sulphocyanide of iron 15° Tw.
10	,,	bisulphite of soda 72° Tw.
1000		

Print, steam, wash, and soap.

Anthracene Brown gives a useful shade of dull dark brown, employed sometimes as a self colour, but more frequently to tone down compound shades.

Anthracene brown produces very fast lakes with both aluminium and chromium mordants. The aluminium compound is reddish; that with chromium is somewhat yellower and much duller, but at the same time faster to washing and much more generally useful.

Anthracene Browns.

I.

70	grms.	Anthracene brown G. 20 per cent. (B.A.S.F.).
20	,,	acetic acid 9° Tw.
760	,,	starch paste.
150	,,	acetate of chrome 15° Tw.
1000		

II.

70	grms.	Anthracene brown G. 20 per cent.
20		acetic acid 9° Tw.
720	,,	starch paste.
150	,,	acetate of alumina 15° Tw.
40	,,	oxalate of tin.
1000		

The oxalate of tin helps to brighten the shade, but it may be omitted if required.

In combination with Persian berry extract, or Quercitron bark extract, Anthracene brown yields a range of fine quiet "mode" shades, varying from the deepest dull brown to pale buffs.

Brown A.P.B. (dark).

150	grms.	Anthracene brown G. 20 per cent.
15	„	Persian berry extract 48° Tw.
560	„	starch-tragacanth paste.
250	„	acetate of chrome 15° Tw.
25	„	acetate of lime 23° Tw.
1000		

Print, steam, wash, and soap.

Other Alizarin colours may also be mixed with Anthracene brown in any proportion for the production of a great variety of subdued tints fast to light and soap. In fact nearly all greys, olives, fawns, and other "mode" shades are obtained by mixing a few standard colours in various proportions; and one of the most important is Anthracene brown, by reason of its fastness and the facility which it affords for "flattening" a tint without altering its character to the extent that black or blue would do.

In addition to the few dyestuffs of the Alizarin class here mentioned, there is a vast number of others which are applied in the same way and for the same purposes.

Application of the Natural or Vegetable Dyestuffs.

The use of these colouring matters has gradually diminished, until at the present time only about five of them find any extensive application in calico printing. These five are—Logwood, Persian berries, Quercitron bark, Catechu, and Peachwood. Others are occasionally employed in some styles of work, but, with the exception of Indigo, which is a thing apart, they belong to the past rather than to the present; and as they cannot compare in any way with their artificial competitors, they will not be dealt with here.

Logwood.—Logwood still retains its place as an important colouring matter, for the simple reason that none of the artificial blacks have so far been capable of application to all the purposes to which Logwood is adapted. Although, in many cases, Aniline black has entirely replaced Logwood, yet it cannot be printed satisfactorily with certain colouring matters, and consequently Logwood still plays an important part in the production of black-ground steam styles. Apart from its use as a black, it is a most unreliable colouring matter: in mixtures it rapidly fades, with the result that any compound shades containing it are completely transformed after a short exposure to light; and for greys, blues, and violets, with iron, chromium, tin, copper, and aluminium mordants, it is altogether out-of-date, not to say useless, so far as permanency is concerned.

For ordinary steam styles the black obtained with chromium mordants is the one generally preferred in practice. It is, if anything, better than a Logwood-iron black, and is not so liable to affect injuriously the colours along with which it is printed, though it requires carefully working to avoid this mishap. But iron blacks are altogether unsuited to printing with either Alizarin reds and pinks or basic colours; and as these enter into practically all steam styles, the Logwood iron blacks have fallen into disuse, except for a few special purposes to be noted later.

The tendency of chrome-Logwood blacks to "green" is overcome by the addition of a little Alizarin, which forms a claret with chrome mordant, and their blue tone is corrected by a similar addition of the yellow colouring matter, Quercitron bark.

A good black for printing is made as under :—

Black L.

150 grms. starch.
100 ,, British gum.
400 ,, water.
60 ,, acetic acid.
25 ,, Alizarin X. 20 per cent. (British Alizarin Co., Ltd.).
30 ,, Quercitron bark extract 48° Tw.
135 ,, Logwood extract 48° Tw.

Boil and add

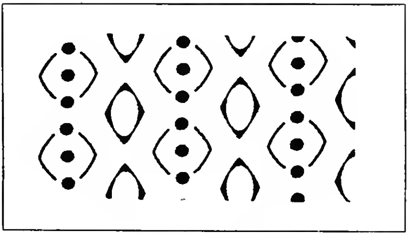
16 ,, chlorate of soda.

Cool and add

6 ,, finely ground potassium ferrocyanide.
130 ,, nitrate-acetate of chrome 38° Tw.
40 ,, acetate of lime 23° Tw.

1092 = 1000 when finished.

Print and steam as usual, then wash and open soap. The chlorate of soda and yellow prussiate of potash aid in developing the black by oxidising the Logwood during the steaming process.



Steam Logwood Black.

Hematein (West Indies Chemical Co.), a dry preparation of Logwood extract and Hemolin, a similar body, may both be used in place of Logwood. They are from two to three times stronger than Logwood extract, and must be employed accordingly.

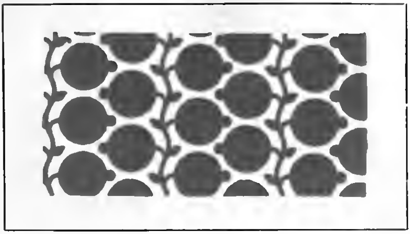
What is known as "Fast steam black," "Carmine black," etc., is simply a reduced Logwood containing the necessary mordant. It is made by precipitating Logwood with bichromate of potash, and then treating the black lake thus-obtained with bisulphite of soda. A printing colour is made from the resulting solution by merely adding the necessary quantity of thickening paste. Thus—

4 kilos. starch paste or tragacanth thickening.
1 ,, "fast steam black."

Fast black works very well for blotches; it does not "scum" so much as the ordinary Logwood black, neither does it "stick in" so badly as a rule.

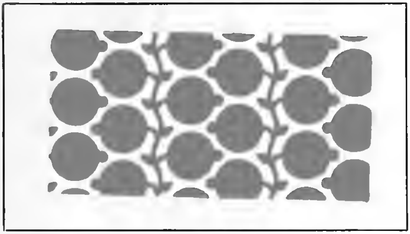
Persian Berry Extract.—This colouring matter is an extract from the dried unripe berries of various species of *Rhamnus*; it is used largely in printing for the production of steam yellow, orange, brown, and olive. The shade of yellow varies according to the mordant used.

Berry Yellow I. (chrome).
120 grms. starch.
60 ,, acetic acid 9° Tw.
570 ,, water (or 530 water and 40 oil).
150 ,, Persian berry extract 48° Tw.
Boil, cool, and add—
100 grms. acetate of chrome 25° Tw.
——
1000



Persian Berry Yellow (Chrome).

Berry Yellow II. (chrome and tin) a quiet lemon shade.



Persian Berry Yellow (Tin).

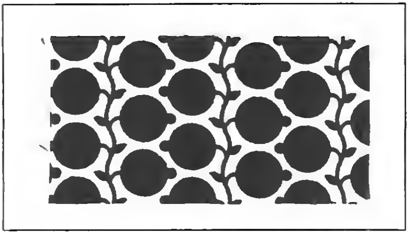
150 grms. Persian berry extract 48° Tw.
500 ,, water.
60 ,, acetic acid.
120 ,, starch.
50 ,, cotton-seed oil.
Boil, cool, and add—
90 grms. citrate of tin.
30 ,, acetate of chrome 25° Tw.
——
1000

Steam Orange (Berry, Alumina, and Tin).
200 grms. Persian berry extract 48° Tw.
455 ,, water.
75 ,, acetic acid 9° Tw.
120 ,, starch.
50 ,, oil.
Boil, turn off steam, and add whilst hot—
25 grms. alum (finely ground).
Cool and add
25 grms. acetate of soda.
50 ,, tin crystals.
——
1000

Shaded with a little Alizarin blue, Persian berry gives an old gold colour:—

Old Gold.
100 grms. Persian berry extract 48° Tw.
1½ ,, Alizarin blue S.
825 ,, starch tragacanth paste.
75 ,, acetate of chrome 25° Tw.
——
1000 (about). Print and steam all the above colours as usual.

Various shades of fast olives, browns, and greys are produced by mixing Persian berry yellow with Alizarin blue and Alizarin red, also fixed with chrome mordants Similarly, a brighter range of greens and oranges, etc. are obtained by adding suitable basic colours to Persian berry yellow, which, up to a certain point, acts as a mordant for them, so that, in many cases, no addition of tannic acid is necessary.



Steam Brown (Persian Berries, Alizarin and Chrome).

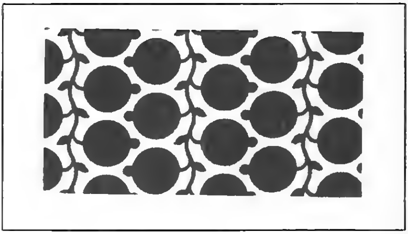
STEAM BROWN.

4 parts Berry Yellow I.
1 part Claret (for mixtures).

Quercitron Bark Extract.—This colouring matter, usually known as "bark," is an extract from the inner bark of the *Quercus tinctoria*. Its properties, so far as calico printing is concerned, are identical with those of Persian berry extract, and it is applied in exactly the same way as the latter.

The various shades of yellow and brown obtained from "bark" by means of chromium, aluminium, and tin mordants are yellower and duller in tone than the corresponding shades derived from Persian berries, but they are equally fast, and are quite as important.

The chief use of bark is in the making of olives and browns, for which purpose it may be mixed with any of the steam Alizarin or the basic aniline colours.



Quercitron Bark Yellow (Chrome).

Peachwood.—Peachwood is a red colouring matter obtained from a species of *Cæsalpinia*. With tin mordants it gives fairly bright reds; with aluminium mordants, dull bluish reds; and with mixed aluminium and iron mordants, a dull purple. None of these colours are very fast to soap; and, with the exception of the last, none of them are of any practical value at the present time. A purple printing colour made up as follows is occasionally still employed in mixtures:—

PEACHWOOD PASTE.

450	grms.	Peachwood extract 9° Tw.
325	,,	water.
80	,,	starch.
40	,,	light British gum.
25	,,	cotton-seed oil.
Boil and add		
5	,,	potassium ferrocyanide (finely ground).
Cool and add		
75	,,	nitrate of alumina 25° Tw.
1000		

The above mixed with Alizarin chrome reds and a little Logwood black is used for steam chocolates and other cheap reddish shades such as maroons and clarets. It takes the place of part of the Alizarin, and, being much cheaper, it is more economical to use in cases where a certain amount of fastness can be dispensed with.

Catechu.—Although Catechu, obtained from species of *Acacia*, *Uncaria*, and *Areca*, has been displaced to a great extent by modern artificial dyestuffs, it is still used in calico printing for steam browns and drabs, very fast to soap, light acids, and alkalies, and in the "madder dyed style" for obtaining browns in combination with red, chocolate, and purple.

Acetate of chrome is the mordant chiefly used for Catechu browns, but the colour can be modified by the addition of other mordants. For example, iron salts produce a greening effect; aluminium salts give a yellowish brown; and lime salts dull the red shade of brown, given with chromium mordants, to a fine dark warm drab or fawn. In all cases the further addition of an oxidising agent —*e.g.* sodium chlorate or a copper salt—is essential to the full development of steam Catechu colours.

Catechu solutions are best thickened with gum Senegal or British gum; starch gives a stronger shade, but it is apt to gelatinise on standing, with the result that, when printed, it produces an uneven, "blebby" impression. The addition of tragacanth and oil tends to overcome this disadvantage, but it is always safer to use the above gums when blotches or large objects are to be printed in Catechu browns.

The following catechu colours have been used on the large scale with success:—

CATECHU BROWN I. (warm chestnut shade).

750 grms.	10 per cent. Catechu solution (see below).
100 ,,	starch.
70 ,,	6 per cent. gum tragacanth.
20 ,,	cotton-seed oil.
20 ,,	sodium chlorate.

Boil, cool, and add

40 grms.	acetate of chrome 32° Tw.
1000	

10 per cent. CATECHU SOLUTION.

100 grms.	Catechu in cubes.
450 ,,	acetic acid 9° Tw.
450 ,,	water.

Boil till the catechu is dissolved, and then make up to 1000 grms. with acetic acid at 9° Tw.

CATECHU BROWN II. (warm drab shade).

600 grms.	10 per cent. Catechu solution.
240 ,,	British gum.
100 ,,	water.

Boil and add

20 ,,	sodium chlorate.

Cool and add

30 ,,	acetate of chrome 30° Tw.
20 ,,	acetate of lime 23° Tw.
1010—boil to 1000.	

Catechu Drab.

600	grms.	10 per cent. Catechu solution.
230	,,	British gum.
100	,,	water.
Boil and add		
20	,,	sodium chlorate.
Cool and add		
25	,,	acetate of chrome 30° Tw.
15	,,	acetate of lime 23° Tw.
10	,,	potassium ferrocyanide (powdered).
1000		

Catechu Brown III.

600	grms.	Catechu 10 per cent. solution.
240	,,	British gum.
90	,,	water.
Boil, cool, and add		
30	grms.	nitrate of copper 80° Tw.
30	,,	acetate of chrome 30° Tw.
20	,,	acetate of lime 23° Tw.
1010		

The above colours are printed on oiled or unoiled cloth, steamed one hour without pressure, and soaped. In the last recipe, acetate of copper may replace the nitrate: and, if desired, any of the colours may be treated in a boiling ½ per cent. solution of bichromate of potash for their further fixation, or for the development of any lead yellow that may have been printed at the same time.

Catechu possesses the property of becoming fixed upon the fibre by a process of oxidation; and although the shades so obtained are not very dark (unless the oxidation is completed by running through bichromate of potash), they are sufficiently fast to resist the operations of "dunging" and dyeing in Alizarin (madder style), and consequently they frequently appear in combination with dyed reds, etc. This particular application of Catechu will be dealt with in connection with the "dyed styles."

Of the other natural dyestuffs, only a few find an occasional use at the present time. The extracts of Divi-divi, Gall Nuts, and a preparation called "Cutcheline" all possess a certain amount of colour which can be fixed with chrome or iron mordants. They give various shades of drab, stone, fawn, and buff, and, used with some of the Alizarin colours, quite a series of soft tones of olive, sage, and other quiet "mode" shades. The same effects, however, are for the most part obtained nowadays by the use of the faster and more reliable Anthracene brown, in conjunction with Alizarin colours suited to the purpose.

Application of Basic Colours.

The basic colours consist of salts of various (mostly colourless) organic bases. The solutions of these salts, though highly coloured, are incapable of dyeing the vegetable fibres permanently, hence the base requires to be precipitated thereon in an insoluble form. For this purpose tannic acid (or such tannins as, for instance, sumach, gall nuts, myrobalans, etc.) has been found the most generally useful, since it forms insoluble salts with the colour bases, and thus fulfils the conditions of their fixation on the cloth as coloured lakes. The tannates of the colour bases are, however, soluble to some extent in water, especially if precipitated in presence of excess of tannic acid or other acids, and therefore they are not entirely fast colours. But free tannic acid is not essential to the formation of insoluble colour lakes. The insoluble metallic tannates of antimony, tin, aluminium, and iron are equally capable of combining with the organic colour bases, and not only yield highly coloured compounds, but compounds quite insoluble in water, and practically so in soap solutions.

Upon this valuable property of metallic tannates is based the application of the basic aniline colours in calico printing.

A mixture of thickening, colouring matter, tannic acid, and organic acid (to prevent the precipitation of the dyestuff) is printed on the cloth, which is then dried and steamed. During the steaming the dyestuff and tannic acid combine to form the somewhat soluble lake, which is then rendered quite insoluble by being passed through a solution of tartar emetic and chalk. The chalk simply serves to neutralise the acidity of the bath due to the production of the acid tartrate of potash by the abstraction of the antimony by the tannic acid. In this way an insoluble double tannate of antimony and colouring matter is obtained, which is attached permanently to the fibre.

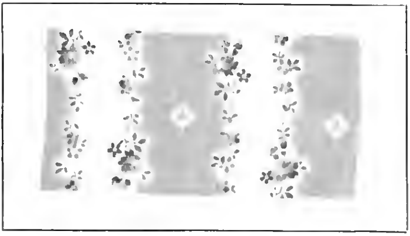
The chemical constitution of the basic dyestuffs is too complicated to be touched upon here, but particulars of their composition and properties are easily accessible in such works as *A Manual of Dyeing* by Knecht, Rawson and Loewenthal, and other similar works on the subject. All that can be dealt with at this stage is their practical application as "steam colours."

The usual method of making up a basic colour printing paste is to add a solution of the dyestuff to a previously prepared thickening, then add the necessary amount of acetic or tartaric acid, and finally the tannic acid solution. The amount of tannic acid, of course, varies with the dyestuff employed; and where any doubt exists as to the quantity required, it can be readily removed by making a few printing trials with different proportions of tannic acid to dyestuff. As a rule, it will be found that the proportion is about three of tannic acid to one of dyestuff, but this is by no means a general rule, and must be only taken as a basis for experiment.

In the following receipes taken from actual practice, the best proportions have been determined by experiments on a works scale, and may be regarded as correct:—

METHYLENE BLUE.

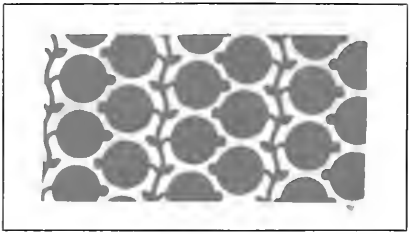
200 grms.	10 per cent. solution of Methylene blue N.
600 ,,	thick acid starch paste (see thickening).
100 ,,	5 per cent. tragacanth paste.
100 ,,	50 per cent. tannic acid solution.
1000	



Methylene Blue.

10 per cent. SOLUTION METHYLENE BLUE.

100 grms.	new Methylene blue N.
250 ,,	acetic acid 9° Tw.
50 ,,	tartaric acid.
600 ,,	water.
1000	



Auramine.

AURAMINE YELLOW.

140	grms.	of starch.
50	,,	British gum.
452	,,	water.
10	,,	tartaric acid.

Boil, cool a little, and add

20	grms.	Auramine (concentrated) (M., L. & B.).
50	,,	acetic acid 9° Tw.
30	,,	cotton-seed oil.

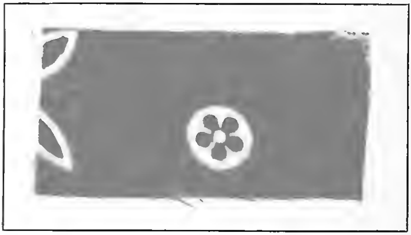
Cool and add —

250	grms.	50 per cent. tannic acid solution.
1000		

Some brands of Auramine yellow are reduced to 20 per cent. pure colour by the addition of dextrin, and these require only a little more than their own weight of tannin to fix them.

RHODAMINE PINK.

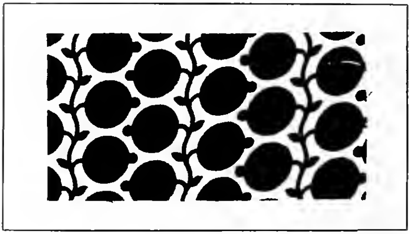
10	grms.	Rhodamine 6 G. (100 per cent.).
50	,,	acetic acid 9° Tw.
10	,,	tartaric acid.
100	,,	water.
600	,,	starch paste.
200	,,	50 per cent. tannin solution.
1000		



Rhodamine.

METHYL VIOLET (blue shade).

25	grms.	Methyl violet B. extra (B.A.S.F.).
60	,,	acetic acid 9° Tw.
60	,,	water.
10	,,	tartaric acid.
715	,,	starch paste.
130	,,	50 per cent. tannin solution.
1000		

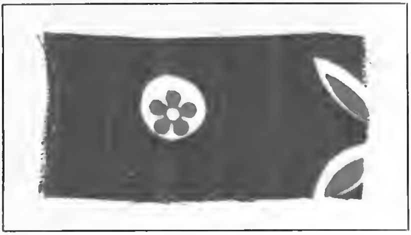


Methyl Violet.

The red shades are prepared in exactly the same manner. Sometimes 3–4 per cent. of glycerin is added to aid the solution of the dyestuff.

BRILLIANT GREEN.

20	grms.	Brilliant green.
130	grms.	acetic acid 9° Tw.
70	,,	water.
660	,,	starch paste.
120	,,	50 per cent. tannin solution.
1000		



Brilliant Green, with addition of $\frac{1}{8}$th of its weight of Thioflavine T.

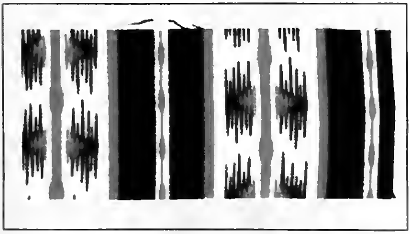
The Induline blues, which are largely used for dark navy blotches, require special treatment, as they do not dissolve easily in the ordinary solvents, and are apt to produce uneven effects if not properly prepared. For example, the colours Induline for printing R. B. brands in powder are best made up according to the following directions :—

INDULINE R. FOR PRINTING.

20	grms.	Induline R. powder.
60	,,	ethyltartaric acid 20° Tw.
40	,,	acetin.
50	,,	water.
Dissolve and add		
80	,,	acetic acid 9° Tw.
600	,,	acid starch paste.
150	,,	50 per cent. tannin solution.
1000		

After printing and steaming, all basic colours are fixed in the following bath :—

20	grms.	tartar emetic.
10	,,	chalk.
970	,,	water.
1000		



Turquoise Blue G.G.

A fine bright greenish-blue is obtained from Turquoise Blue G.G. (Bayer), which is applied in the same way as Methylene blue.

It is almost needless to say that any of the basic colours can be mixed together in any proportion to form compound shades. Such shades are, in practice, restricted to very bright colours—greens, violets, oranges—as the strength and brilliancy of the standard colours render it extremely difficult to make delicate greys, fawns, etc., twice alike. The slightest excess of pure colour alters the whole tone of the compound; and therefore, as the mode shades are very sensitive and delicately balanced, they are generally prepared from less pure primary tints.

One or other of the foregoing recipes will serve for all basic colours used as such. When they are combined with mordant dyestuffs a rather different method is adopted. Thus a very dark myrtle green is boiled as under:—

MYRTLE GREEN.

100	grms.	starch.
290	,,	water.
200	,,	5 per cent. tragacanth.
120	,,	Persian berry extract 48° Tw.
40	,,	Logwood extract 48° Tw.

Boil and add

20	,,	Diamond green (B.A.S.F.).
100	,,	acetic acid 9° Tw.

Cool and add

90	,,	acetate of chrome 25° Tw.
40	,,	50 per cent. tannin solution.
1000		

The small amount of tannin used in this case is compensated for by the fact that the Persian berry acts as a mordant for basic colours, as do also most of the Alizarin colours to a certain extent.

Another method of fixing basic colours is based upon their property of forming insoluble compounds with arsenite of alumina. It was the only method available before the discovery of the tannic acid lakes of basic colours; and although prohibited in most countries on account of the poisonous nature of its ingredients, it is still used to a slight extent in this country and America. As a matter of fact, the arsenic contained by the colour is in an insoluble form, and is not followed by the injurious consequences that are attributed to it by non-technical legislators.

The following formula will serve as an example of the general method of preparing basic colours for printing.

RHODAMINE PINK.

10	grms.	Rhodamine 6 G. extra.
50	,,	acetic acid 9° Tw.
100	,,	water.
750	,,	alumina paste.
90	,,	arsenic standard.
1000		

ALUMINA PASTE.

60	grms.	flour.
60	,,	starch.
850	,,	"Red Liquor" (acetate of alumina) 8° Tw.
30	,,	cotton-seed oil.
1000		

Boil and cool.

ARSENIC STANDARD.

150	grms.	arsenious acid (As_2O_3).
850	,,	glycerin.
1000		

Heat till dissolved ; or—

150 grms. arsenious acid.
150 ,, borax.
700 ,, water.
——
1000

Print on oiled or unoiled cloth, steam, wash, and lightly soap. The brightest and fastest colours are produced on oiled cloth : the oil acts both as a mordant for the colouring matter and as a fixing agent for the alumina. In steaming the alumina, oil and arsenious acid combine to form an insoluble precipitate of aluminium arsenite and oleate, and this, in turn, combines with the colour base, producing an insoluble lake.

The alumina lakes of the basic colours are more brilliant than the corresponding tannin antimony lakes, but their fastness to soap is inferior, and they are only used in those classes of work where brightness is more important commercially than fastness.

Basic colours may also be fixed mechanically with albumen, but this method is rarely employed except when they are used to modify the shade of pigment colours, and in the zinc oxide process of resisting aniline black. The mordant dyes when fixed on the fibre may also act as mordants for basic colours. Consequently basic colours are sometimes added to "extract" printing colours with the object of brightening or otherwise modifying the shade.

Amongst the "fast steam colours," the basic colours fixed with tannic acid are, as a class, by far the most brilliant at the disposal of the calico printer. As regards fastness, they cannot compare with the "mordant colours," although individual members of the group leave little to be desired in this respect. But they afford facilities for the production of colours that cannot be obtained in any other way, and they allow of an enormous range of shades being introduced into styles that were formerly restricted to a few colours only. They comprise all tones of red, blue, yellow, green, violet, and grey, and, as they are all applied in the same manner, they can be mixed together to form an infinite variety of secondary and tertiary tints ; so that, with their ease of application, their great tinctorial strength, their vast variety, and their adaptability to many diverse styles, the basic colours constitute one of the most important classes of substances used in calico printing.

Of the numerous basic colours now on the market the following few are perhaps the most generally useful, though it is difficult to single out the best from among so great a number of equally good products :—

Reds :—Rhodamine, Irisamine, Induline Scarlet, Magenta.

Yellows :—Auramine, Thioflavine T., Tannin Orange, Acridine Yellow, and Rhoduline Yellow.

Blues :—Methylene, Thionine, Marine, Victoria, Indoine, Indulines, and Acetinduline.

Greens :—Malachite, Brilliant, Diamond, Methylene.

Violets :—Methyl, Ethyl, Rhoduline.

Browns :—Bismarck, and similar products.

Greys :—Nigrosine, Methylene.

Many of the above colours are sold under different names by different makers, and most of them are made in several shades, so that almost any tone can be obtained easily without mixing.

Application of Pigment or "Albumen" Colours.

These colours include the highly coloured, insoluble substances, whether mineral or vegetable, that are applied to the fibre in an insoluble state. Their fixation is effected by means of a solution of albumen with which they are mixed, and which, on drying and steaming, coagulates and encloses the pigments in an insoluble envelope—fixes them on the fibre mechanically in the same way that paint is fixed on canvas by drying oils. The most important 'pigments' are:—Chrome yellow and orange; Guignet's Green (an oxide of chromium); Ultramarine blue, and its derivatives Ultramarine pink, green, and violet; Vermilion and numerous imitations and substitutes, which consist for the most part of aniline colour lakes, and even of red lead tinted with basic colours, lampblack, and the various earths—*e.g.* siennas, umbers, ochres, etc.—and mixtures of oxide of iron, with other precipitates for special shades of buff and fawn.

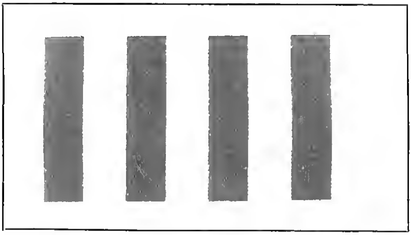
With varying proportions, according as to whether they are in paste or powder form, the method of making up and of applying each of the above colours is practically identical.

PIGMENT RED.

250	grms.	Vermilion.
500	,,	40 per cent. blood albumen solution.
250	,,	8 per cent. gum tragacanth.
1000		

PIGMENT YELLOW OR ORANGE.

300	grms.	Chrome yellow or orange.
300	,,	40 per cent. blood albumen solution.
30	,,	cotton-seed oil.
20	,,	glycerin.
30	,,	turpentine.
320	,,	6 per cent. tragacanth thickening.
1000		



Ultramarine Blue (Lancashire Ultramarine Co., Ltd.).

PIGMENT BLUE (pink, green, or violet).

300	grms.	Ultramarine blue or pink, etc.
300	,,	40 per cent. albumen solution.
30	,,	glycerin.
20	,,	turpentine.
30	,,	oil.
10	,,	ammonia.
310	,,	6 per cent. gum-tragacanth thickening.
1000		

PIGMENT GREEN.

240	grms.	Guignet's Green.
280	,,	40 per cent. albumen solution.
410	,,	6 per cent. tragacanth thickening.
10	,,	ammonia.
30	,,	turpentine.
30	,,	oil.
1000		

PIGMENT GREY.

400 grms. lampblack.
300 ,, albumen 40 per cent. solution.
300 ,, 6 per cent. gum tragacanth.
———
1000

In making all pigment colours, the pigment is first thoroughly incorporated with the albumen, which is added gradually; the thickening is then added and the whole well mixed. In works where grinding mills are installed, the process can be carried out much more rapidly and perfectly than when the ingredients have to be beaten together by hand or in a colour pan. The whole of the mass can be ground until it is perfectly smooth and homogeneous.

The great disadvantage of pigment colours is that they are excessively liable to froth in printing, owing to the churning action they are subjected to in the colour box. So far, nothing has been successful in entirely overcoming this difficulty, but its effect has been reduced to a minimum by the addition of various substances which do not retain air, such as benzine, turpentine, and ammonia. Oil exercises a beneficial effect in this direction, and at the samo time it helps to prevent "sticking in."

In the process patented by W. E. Kay and The Calico Printers' Association, Ltd., glue or casein is made to take the place of albumen as the fixing agent. To this end the printing colour is made up of glue or of a solution of casein in borax and the pigment colour. This is printed on, and the pieces are subsequently passed through a chamber containing formaldehyde vapour, which renders the glue (or casein) insoluble in water.

After printing, pigment-coloured goods are steamed for an hour; the albumen is completely coagulated during this process, and adheres firmly to the cloth enclosing the pigments, with which it is mixed, in an insoluble envelope, and thus fixing them on the fibre.

Pigment colours fixed in this way are very fast to soaping, but being more or less attached to the surface of the cloth, they are apt to be removed by rubbing, and for this reason they are always soaped in the "open soaper" at full width—never in the rope state.

The chief use of pigment colours is for the printing of shirtings, linings, and pale blotches on all sorts of cloth. Being fast to light, pale pigment blotches do not fade; but they cannot be used in cases where a lustrous finish is required all over the surface of the cloth, because they produce a dull matt surface which remains even after the most severe calendering.

In addition to direct printing, pigment colours are largely used for coloured resists under Aniline black, and for discharges on Indigo-dyed grounds.

Application of Direct Dyeing Colours.

The direct cotton colours do not find any very extended employment in "steam styles," except for obtaining tinted grounds on previously printed goods. The shades they give are neither very fast nor very bright in most cases, at least not so bright as those obtained with basic colours, though brighter than all but a few of the mordant colours. They are usually printed with the addition of phosphate of soda, the slight alkalinity of which aids their penetration into the body of the cloth. If required to resist soaping, a further additicn of albumen may be made, in which case they yield colours fairly fast to soap. They possess the property of becoming fixed upon the cotton fibre without the aid of any mordant, and for styles that are not required to withstand washing they are a useful class of colour to use.

The range includes all colours, and all may be applied in the same way. Some variation in the proportions is of course necessary according to the depth of shade required, but, that apart, the following formula will answer for all.

DIRECT COLOUR PRINTING PASTE.

50 grms. of direct colour (Erika, etc.).
400 „ boiling water.
520 „ 6 per cent. tragacanth thickening.
30 „ phosphate of soda.
———
1000

Heat together and cool when solution is effected. Print, steam one hour, and wash.

THE SAME WITH ALBUMEN.

50 grms. Erika pink, Diamine sky blue, etc.
200 „ boiling water.

Dissolve and add

30 grms. phosphate of soda.
450 „ 6 per cent. gum-tragacanth thickening.

Boil, cool, and add

270 grms. 40 per cent. blood albumen solution.
———
1000

Print, steam, wash, and soap.

The addition of a small proportion of glycerin to the printing colour greatly facilitates (according to Justin Müller) its fixation.

The direct colours play an important part in two styles to be dealt with later — "discharges" and "crepons" — but for ordinary steam work their employment is very limited, not to say unimportant. Some very beautiful effects may be realised by their means, but unfortunately they are not fast; and as they possess no compensating advantages, they cannot compete with or replace the faster mordant and basic colours.

Aniline Black.

Unlike other coal-tar colouring matters, Aniline black does not exist as a dyestuff ready for application, but must be produced upon the fibre itself. Neither is it wholly a "steam colour," for its development, under proper conditions, can be brought about quite as easily by a mere exposure to the warm, moist atmosphere of an "ageing room" as by a run through a steam ager, or by a prolonged steaming in a continuous steaming-apparatus.

Aniline black is in reality an oxidation product of aniline, and it is formed on the fibre by printing a thickened mixture of a soluble aniline salt, an oxidising agent, and one of several oxygen carriers, which always consist of a salt of some metal capable of existing in two states of oxidation. After printing, the cloth is dried and exposed to the action of air or steam, under the influence of which the printed parts assume, in a very short time, a dark green appearance, due to the formation of a body known as "Emeraldine," an oxidation product intermediate between aniline and Aniline black proper. To convert the Emeraldine into black it is subjected to further oxidation by a run through a hot solution of bichromate of potash, which transforms it into "Nigraniline," or into a still more highly oxidised body known as "Ungreenable Black."

The salts of Emeraldine are green, but when treated in alkaline or soap solutions they are converted into the base which is of a deep blue colour so intense as to be virtually a black. An insufficiently oxidised black rapidly regains its original green colour when exposed to the action of the acid reducing agents so often present in the air of manufacturing districts, and for this reason it is necessary to push the oxidation of the aniline beyond the stage represented by Nigraniline. This may be done in several ways, but a run through bichromate of potash is the most generally convenient in practice, and quite satisfactory. The "Nigraniline" obtained by treating Emeraldine in a *cold* solution of bichromate is a very deep violet black base, the salts of which are also of the same deep hue. It turns green much less readily than Emeraldine, but it is none the less very susceptible to the action of mineral acids and reducing agents, both of which re-convert it into salts of Emeraldine. Hence a *hot* solution of bichromate is always used where possible, since it exercises a more energetic oxidising action, and produces a black very fast to acids, alkalies, air, soap, and light. In all probability the aniline is oxidised beyond the state of Nigraniline. It is a fact well known to most practical men, that the presence of free aniline is essential to the formation of an absolutely fast ungreenable black, but whether this means that the Nigraniline combines with a further quantity of aniline in the final reactions, or whether the aniline simply neutralises the acidity of the lower products of oxidation, is still unknown. Neutrality certainly does promote the formation of an ungreenable black, and in conjunction with energetic oxidation at a comparatively high temperature (102° C.) it allows of a good, fast black being obtained without the necessity for a subsequent treatment in bichromate of potash.

This fact is taken advantage of in styles of printing which do not permit of *after-chroming*. A little free aniline is introduced into the printing mixture, together with an excess of some neutral oxygen carrier [$K_4Fe(CN_6)$], and these, by neutralising the acids liberated in "ageing" or steaming, not merely tend to the production of an ungreenable black, but also prevent, to a great extent, the tendering of the printed fabric during the process of oxidation. If these *unchromed* blacks are not quite so satisfactory, as regards their absolute resistance to "greening" agencies, as the *chromed* blacks, they are at least sufficiently good to outlast any of the colours with which they are associated, and which have necessitated the omission of the final "chroming."

An Aniline black printing colour consists of three distinct parts:—(1) a soluble salt of aniline, (2) an oxidising agent, and (3) an oxygen carrier. The aniline salt employed is generally the hydrochloride, though the tartrate, chlorate, nitrate, and other salts are occasionally used for special purposes. The only oxidising agent used in practice is chlorate of soda. It comes into the market in a state of great purity, and is generally preferred on account of its cheapness and solubility—two qualities which render it more economical and efficient than chlorate of potash. The oxygen carriers, on the other hand, are more numerous, but, as a rule, only about four find any extended application, namely, copper sulphide, copper sulphocyanide, vanadium chloride, and yellow prussiate of potash. The blacks produced by means of the latter salts are designated respectively Copper sulphide black, Copper sulphocyanide black, Vanadium black, and Prussiate black. These four, together with a fifth known as "Chromate black" from the quantity of chromate of lead it contains, are the only blacks, out of the scores of oxidation blacks that have been proposed from time to time, that have attained to any degree of permanent success. All the others are obsolete, and, with the exception of Green's recently patented process and the Diphenyl black of Meister, Lucius & Brüning, the above compounds hold undisputed sway in practice.

(1) COPPER SULPHIDE BLACK.—The introduction of copper sulphide as an oxygen carrier was due to Charles Lauth in 1864.

The Copper sulphide black is by no means an easily worked colour; it is always liable to attack the doctors if the latter are not varnished, and even then their edges are more or less rapidly affected, so that they require constant attention and re-sharpening to keep them in working condition. But, all things considered, it is a valuable colour, and if carefully prepared and worked as cold as possible the oxidation of the sulphide to sulphate in the printing paste may be reduced to a minimum, and the quality of the "doctor edge" be preserved accordingly. The great disadvantage of sulphide of copper is that it is extremely apt to stick in the engraving, no matter how carefully the colour may have been prepared, and therefore it is always replaced by the Prussiate or Vanadium blacks (which contain no insoluble matter) whenever the style of work permits.

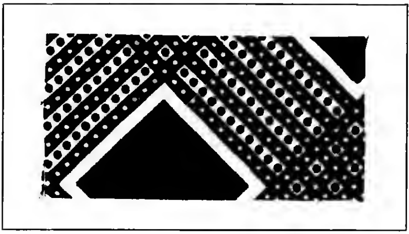
An excess of free aniline is always allowed in Copper sulphide blacks to overcome the tendering of the fibre, and to promote the formation of ungreenable black in the "chroming" process. A little ammonium chloride is also frequently added to aid in the reactions. The following is a black in actual use:—

Copper Sulphide Black.

150	grms.	starch.
80	,,	British gum.
528	,,	water.
40	,,	chlorate of soda.
35	,,	oil (cotton-seed).
5	,,	Methyl violet (to sighten the colour).
Boil, cool, and add		
95	grms.	aniline salt (hydrochloride).
17	,,	aniline oil.
50	,,	sulphide of copper (30 per cent. paste).
1000		

Print on white cloth, dry, and pass for three minutes through the "rapid ager" at not above 65° C. If desired, the development of the black may be more slowly but quite as well effected by hanging the printed goods in an "ageing room" for 10–24 hours. This method is adopted when the black is printed along with aluminium or iron mordants, and it develops very well at the temperature of a cool chamber 55°–60° C.

Ordinary goods, after ageing or steaming for three minutes, are afterwards "chromed" in a hot solution of bichromate of potash (1 per cent.).



Aniline Black (Copper Sulphide).

(2) Copper Sulphocyanide Black.—The use of cuprous sulphocyanide as an oxygen carrier was patented by Higgin in 1868. Blacks made according to Higgin's process oxidise more slowly than sulphide of copper blacks, and they withstand a longer steaming, besides which they work a good deal better in printing. It is surprising, therefore, that they are not used more, but for some reason they appear to have fallen into disfavour.

CUPROUS SULPHOCYANIDE BLACK.

150	grms.	starch.
90	,,	British gum.
530	,,	water.
20	,,	oil.
40	,,	chlorate of soda. Boil, cool, and add—
25	grms.	ammonium chloride.
20	,,	water.
80	,,	aniline salt.
20	,,	aniline oil.
25	,,	cuprous sulphocyanide paste ("white paste").
1000		

Print, dry, and either age, pass through the rapid ager, or steam fifteen minutes, chrome and soap.

If printed with colours that require an hour's steaming, the cloth, after the development of the black, must be passed through an atmosphere of ammonia before being subjected to the prolonged action of hot steam. This applies to all aniline blacks printed with steam colours.

Higgin's black is frequently combined with the "Chromate black" of Schmidlin.

(3) VANADIUM BLACK.—The researches of Lightfoot and of G. Witz and A. Guyard resulted in the introduction of vanadium salts as oxygen carriers. In presence of the requisite quantity of chlorate of soda, one part of vanadium is sufficient to convert two thousand parts of aniline into black. Metavanadate of ammonia was at first used, but H. Schmid showed that the chloride is better, and in practice the latter salt is always used. A recipe for its preparation has already been given.

The amount of vanadium used varies according to the class of work in hand; 3 grammes of 1 per cent. solution of the chloride per kilogramme of printing colour is about the average, but for fine patterns which allow of oxidation at a higher temperature 5 grammes is a usual quantity to employ.

As Vanadium blacks contain no solid matter, they print much better than either of the preceding or the chromate of lead blacks; but, on the other hand, they oxidise more rapidly; and as the black already formed in the colour before printing would only adhere mechanically to the cloth and would be washed off in soaping, it is of the utmost importance only to add the vanadium chloride to the colour immediately before use.

Apart from its good working qualities, Vanadium black is exceptionally well adapted for printing along with steam Alizarin reds and pinks. The mere trace of metallic vanadium which it contains has no effect on the Alizarin colours, and if it is printed in lightly engraved patterns it may be steamed with safety after a run through ammonia vapour subsequent to its development by ageing in the rapid ager. The following recipe has given good results on the large scale:—

VANADIUM BLACK.

100	grms.	starch.
80	,,	British gum.
570	,,	water.
40	,,	chlorate of soda.
20	,,	cotton-seed oil. Boil, cool, and add cold—
90	,,	aniline salt.
20	,,	aniline oil.
5	,,	1 per cent. vanadium chloride solution.
95	,,	water.
1000 after boiling.		

After printing and drying, the above black is developed by running through the rapid ager—2 minutes at 80°–90° C.—or it may be hung in an "ageing room" at 32°–36° C. until it has become quite black, after which it may be chromed. If developed by a short passage through the ager at a high temperature (95° C.) it is not necessary to "chrome" it; but, of course, all aniline blacks are improved by "chroming," and therefore it is not to be omitted unless it destroys the other colours printed along with the black.

Vanadium and copper sulphide or ferrocyanide of potash are sometimes used together to form mixed blacks, but it is doubtful whether any advantage is derived from this procedure unless it be that in the case of the ferrocyanide a certain amount of Prussian blue is formed which modifies the shade. If the blue is intended to act in this way the printed goods must not be soaped after chroming, but passed through a chalk bath at 60° C. and then well washed in hot water.

(4) Prussiate Black.—Prussiate black was invented by Lightfoot in 1863, and was patented by him in July of that year, five months before Cordillot applied for a patent for a similar black. For ordinary printing the following black yields excellent results:—

100	grms.	starch.
20	,,	British gum.
61	,,	potassium ferrocyanide.
707	,,	water.

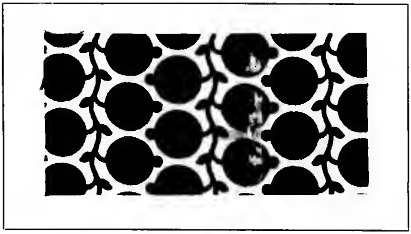
Boil, turn off steam, and add

28	grms.	chlorate of soda.

Cool and add

84	,,	aniline salt (which dissolves in the cold).

After printing, this black is developed by a run of four minutes through the rapid ager at, at least, for the best results, 95° C. If it be now passed through the vapour of ammonia it may be steamed with perfect safety for about an hour in the continuous steamer—an advantage which allows of it being used in conjunction with a large number of "steam" colours. Although it contains a large amount of iron, it can be employed successfully with steam Alizarin reds and pinks if printed with care, and by interposing a "starch roller" between the black and pink or red rollers.



Aniline Black (Prussiate).

For black and white effects Prussiate black is merely developed by running the goods through the rapid ager followed by a chroming and soaping. The prolonged steaming is only employed when it is required for the ordinary steam colours printed in combination with the black; it is not by any means necessary to the development of the black, although it improves its shades in some respects, and certainly makes it more resistant to the "greening" action of acids and reducing agents.

If ferrocyanide of ammonia be used in place of the potash salt, and a sufficient quantity is employed to neutralise the mineral acids liberated in steaming, it is quite possible to obtain a black that is practically "ungreenable" without any after-treatment with bichromate of potash. The printing colour, however, does not keep very long, and must be used at once. Curiously enough, too, sodium ferrocyanide has a similar effect in accelerating the decomposition of the printing colour. Why this should be is not satisfactorily explained, but it is a well-known fact in practice, and has prevented the use of the sodium salt for printing, though it is occasionally used in the dyeing of plain blacks.

The chief advantages of the Prussiate (potash) blacks are that they have practically no "tendering" action on the fibre, that they work as well as any other colour in printing, and that they keep well for two or three days if stored in a cool place. They are more expensive to produce than the preceding blacks, and do not yield quite the same shades, but these are minor points in comparison with their facility of application, etc., and, at the present time, it is safe to say that Prussiate blacks are more largely used in printing than any other.

(5) Chromate Black.—This black was invented by J. Schmidlin, and can be used as a steam colour in the ordinary way, since, under proper conditions, it has no action on the cotton fibre. It consists of aniline salt, chlorate of soda, and chromate of lead, with occasionally an addition of amonium chloride. The lead chromate plays the double rôle of an oxidising agent and a neutralising agent. As a rule a copper salt is added when the rate of development requires to be accelerated.

Chromate Black I.

80 grms. starch.
595 ,, water.
100 ,, Chrome yellow 40 per cent. paste.
Boil and add
100 ,, ammonium chloride.
Cool a little and add
25 grms. chlorate of soda.
Cool completely and add
95 grms. aniline salt.
5 ,, aniline oil.
——
1000

The printed goods are steamed for fifteen to twenty minutes without pressure, and then washed and soaped. No chroming is necessary.

Chromate Black II.

60 grms. starch.
590 ,, water.
100 ,, lead chromate 40 per cent. paste.
Cool a little and add
25 grms. chlorate of soda.
Cool completely, and add
100 grms. aniline salt.
25 ,, copper sulphide 30 per cent. paste.

Print, steam fifteen minutes, wash and soap. If the black is in combination with "steam colours," pass the goods through ammonia vapour after the first steaming, and then further steam for an hour. Chromate and sulphocyanide of copper blacks are frequently mixed together for "steam work," and give a more brilliant black than the chromate alone, which at best only produces a black of a dull bronzy tone.

The large quantity of solid matter in Chromate blacks tends to make them work badly, but when carefully prepared they are especially suited to the printing of fine designs in which a crisp definition is essential, and, as they require no subsequent chroming, they lend themselves to a greater variety of styles than the other aniline blacks.

An addition of a small proportion of para phenylene-diamine to all Aniline black colours has the effect of rendering them less liable to "green."

A black made up with chlorate of aniline and sulphide of copper is at times used for certain styles; and a modification of Koechlin's tartrate of aniline black is also employed occasionally in steam work, though rarely at present.

CHLORATE OF ANILINE.

450	grms.	chlorate of barium.
300	,,	aluminium sulphate.
1500	,,	water.

Heat to boil, and, after complete precipitation, cool to 40° C. and add—

470 grms. aniline oil.

Stir well and use the filtrate, which is a solution of aniline chlorate.

The printing paste is made as under:—

850	grms.	chlorate of aniline solution.
100	,,	starch.

Boil, cool, and add

50 grms. 25 per cent. copper sulphide paste.

Print, and develop as for sulphide of copper black.

KOECHLIN'S BLACK.—In this black, invented by Camille Koechlin, the hydrochloride of aniline is replaced by the tartrate; in other respects it is a copper sulphide black, and is used in the same way. In practice the tartrate is made directly during the preparation of the printing colour:—

60	grms.	starch.
90	,,	British gum.
520	,,	water.
60	,,	ammonium chloride.
90	,,	aniline oil.
Boil and add		
40	,,	chlorate of soda.
Cool, and when cold add		
90	grms.	tartaric acid (finely powdered).
And when quite dissolved add		
50	grms.	sulphide of copper 30 per cent.
1000		

Print, age, and chrome. This black does not develop very rapidly, and after passing through the rapid ager it is advisable to hang the goods in an ageing chamber for twenty-four hours. The tartrate of aniline is not capable of yielding a black, but under the influence of heat and moisture a double decomposition takes place between the ammonium chloride and the tartrate, and aniline hydrochloride is produced on the fibre, and is gradually oxidised to black. The best results are obtained by a slow, gentle oxidation in an ageing chamber at a temperature of 70°–80° F.

Koechlin's black may be regarded as obsolete. It is rarely or never used nowadays, and must always be chromed to produce anything like a passable black. The conditions of Aniline-black printing are now generally understood, and there is no longer any necessity to employ expensive salts like the tartrate of aniline to avoid "tendering" the fibre. At the time of its introduction it was the only black that did not attack the fibre to an injurious extent, but at the present time the value of the cheaper aged blacks is sufficiently proved by the fact that they are still used every day in enormous quantities, while the tartrate black is now of scientific interest only.

In all cases where any Aniline black is printed on oiled cloth the proportion of aniline salt and chlorate of soda should be increased, and no aniline oil should be used. If these precautions are neglected it is impossible to obtain a good black, as the oil acts as a resist.

In many styles Aniline black has completely displaced Logwood, but the latter still maintains its importance as a steam colour by reason of its mode of fixation, which is identical with that of other steam colours. Moreover, a great number of steam colours are destroyed by the fumes of acid and aniline that are evolved during the steaming process; so that, although the Prussiate and Chromate blacks may be steamed for at least half an hour, they cannot be substituted indiscriminately for Logwood. Olives containing Methylene blue come out a dirty yellow, due to the destruction of the blue element; pale Alizarin pinks are turned yellow, owing to the acid vapours preventing the Alizarin from combining with the alumina; and even strong reds are not infrequently affected in the same way to a less degree. These defects may be remedied to some extent by passing the goods through ammonia vapour, after the black has been developed in the rapid ager,—indeed, this should always be done. If they are acted upon after this "gassing," as it is termed, they may be improved somewhat by "gassing" again and re-steaming, but, as a rule, it is only the strongest colours that are improved by this extra treatment, the paler ones being irretrievably spoiled. These remarks apply more especially to cases where heavy masses or blotches of black are printed; where only small objects or outlines are printed the black suffers more frequently than the colours, which, nine times out of ten, are as good as when Logwood is used.

Other applications of Aniline black will be given in treating of other styles of printing.

Diphenyl Black.—This black, patented in 1901 by the Farbwerke, Meister, Lucius, & Brüning, is in some respects similar to Aniline black. It consists of the oxidation products of various amines, but, unlike Aniline black, it neither tenders the fibre nor does it turn green, and it can be steamed for an hour with perfect safety, and without in any way impoverishing the surrounding colours.

Diphenyl black comes into the market as "Diphenyl black base" and "Diphenyl black oil D.O.," both of which are used for printing,—the former for steam styles of the most delicate description, and the latter for the more ordinary black and white effects.

The oxidising agent used in most cases is chlorate of soda; aluminium chlorate may also be used, but it is not so convenient. As oxygen carriers the salts of copper are the best. Ferrocyanide of potassium throws the base out of solution, and vanadium salts act too rapidly. Cerium chloride is also a good oxygen carrier, and is employed along with sulphide of copper. Other additions are lactic acid, aluminium chloride, and the necessary thickening materials.

After printing, the goods are aged in the "steam ager" for 1–3 minutes, then steamed for an hour or more, if printed in Alizarin or basic colours, and finally washed and soaped in a slightly alkaline bath. Chroming is to be avoided, as it imparts an unpleasing brown tone to the black, which is, moreover, ungreenable without any such extra oxidation.

Diphenyl base and oil are soluble in acetic acid or acetin. The oil D.O. is in reality a solution of p-amidodiphenylamine in aniline; the base is p-amidodiphenylamine alone. The solution of these bodies in the ordinary acids is possible, but the salts formed are too insoluble to be employed in printing

A good many recipes are available for the production of Diphenyl black, but the following, given by the patentees, will serve as types of those used in the majority of cases:—

Diphenyl Black I.

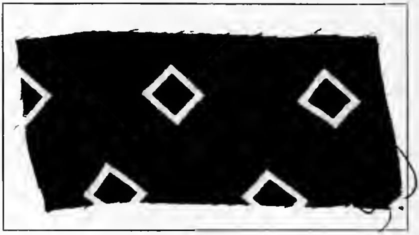
1100 grms. starch.
4500 ,, water.
1080 ,, acetic acid 9° Tw.
200 ,, olive oil.

Boil, off steam, and add—
300 grms. chlorate of soda.

Cool and add a solution of
350 grms. Diphenyl black base I.
1300 ,, acetic acid 9° Tw.
450 ,, lactic acid 50 per cent.

For use, further add—
100 grms. copper sulphide 30 per cent. paste.
300 ,, water.
180 ,, aluminium chloride 52° Tw.
140 ,, cerium chloride 84° Tw.

10,000



Diphenyl Black.

This black may be used with Alizarin and basic aniline colours. After printing it is a light grey and must not be overdried. It is fully developed by a two or three minutes' passage through the rapid ager at as high a temperature as possible. Then, if the patterns contain "steam colours," the goods are further steamed for 1–1½ hours, with or without pressure, fixed in tartar emetic for the basic colours, and finally soaped.

For ordinary work (single blacks and styles commonly associated with Aniline black) the following recipe containing aniline may be recommended.

Diphenyl Black II.

1100 grms. starch.
5315 ,, water.
1125 ,, acetic acid 9° Tw.
200 ,, olive oil.

Boil, cool a little, and add
300 grms. chlorate of soda.

Cool and add
225 ,, lactic acid 50 per cent.
123 ,, hydrochloric acid 28° Tw.
67 ,, water.
500 ,, Diphenyl black oil D.O.

For use add
200 ,, copper sulphide 30 per cent.
630 ,, water.
215 ,, aluminium chloride 52° Tw.

10,000

Print on unoiled cloth, dry gently, age 2–3 minutes at 95° C., and then pass at once into an alkaline soap solution at 60°–80° C.; or if printed with Iron buff, through a hot solution of caustic soda.

As compared with Aniline blacks, the blacks obtained from *Diphenyl Black Base I.* are more expensive, but, at the same time, they are absolutely "ungreenable"; and as they neither give off any injurious acid vapours or gases during "steaming" nor require any after-treatment with bichromate of potash for their proper development, they do not either tender the fibre or destroy any of the colours with which they may be associated.

On the other hand, *Diphenyl Black Oil D.O.* can be used in place of aniline with advantage, for although its initial cost is greater, a good black can be obtained with as little as 4 per cent. (on the weight of printing colour), whereas at least 8 per cent. of aniline salt is required to produce an equally full shade, and, as a rule, not less than 9 per cent. is used.

Diphenyl Black Oil D.O., containing as it does a certain amount of aniline, possesses properties intermediate between those of pure aniline and pure Diphenyl Black Base I.; so that, as regards resistance to "greening" influences, it is superior to aniline. Its effect on sensitive "steam colours" is also much less pronounced, since, in a black prepared from Diphenyl oil D.O., the content of mineral acid is greatly reduced, and no metallic salts, capable of forming dull compounds with the other colours, are used in sufficient quantity to act injuriously. Aniline blacks are certainly simpler in composition, and are more easily and rapidly prepared. If anything, too, they are more regular in action, and are always preferred for finely engraved patterns, when it is possible to use them, not only on account of their cheapness, but because, hitherto, they appear to be more reliable in action, and to yield fuller and deeper blacks. For fine patterns, the strength of the Diphenyl blacks almost invariably requires to be increased, and this makes them more expensive for many of the cheaper "black-cover" styles.

Taken altogether, the Diphenyl blacks are superior to the Aniline blacks for general "steam work," and they certainly give the finest all-round *fast* black on cloth prepared in naphtholate of soda for the dyeing of the azo colours like paranitraniline, etc. For this purpose Aniline black, pure and simple, is useless. It is probable, therefore, that Diphenyl blacks will replace both Logwood and aniline for most "steam styles"; but, owing to the fact that they are turned brown by bichromate of potash, it is not likely that aniline will lose any of its importance in the production of those styles which depend upon "chroming" for the development of their colours—*e.g.* Chrome yellow, steam Prussian blue, Endler's manganese brown, Catechu, etc., all of which are at present used in combination with Aniline black.

A. G. GREEN'S ANILINE BLACK.—In 1907 A. G. Green patented a process for the production of Aniline black, in which the use of an oxidising agent in the black mixture is entirely dispensed with. His process is based upon the fact, first observed by him, that aniline, in presence of an oxygen carrier and a small percentage of a para-diamine or a para-amido-phenol, is easily oxidised to Emeraldine by mere exposure to air. Moreover, by this new process it is possible to effect the oxidation of aniline in the basic state; so that the chief cause of "tendering"—*i.e.* the action of the mineral acids liberated during the "ageing"—is entirely overcome, with the result that the original strength of the fabric remains unimpaired. It is not even necessary to use a mineral acid at all, as the formation of the black is effected quite as well, if perhaps a little more slowly, in the presence of organic acids alone. Mineral acids are cheaper, however: and as it is not essential that they should be present in excess, as is necessary in ordinary Aniline blacks, they can be used with advantage, either alone or in combination with an organic acid. Formic acid is recommended by the inventor.

The most efficient oxygen carrier has been found to be cuprous chloride. Being a lower oxidised salt than the cupric chloride, it does not act upon the aniline so readily, and consequently the decomposition of the black mixture is retarded to such an extent that it remains clear and serviceable for a considerable time. In practice, the cupric salt ($CuCl_2$) is first added to the mixture, and is then reduced to cuprous chloride (Cu_2Cl_2) by the further addition of the requisite quantity of sodium meta-bisulphite, together with an amount of ammonium chloride sufficient to keep the copper salt in solution.

The application of A. G. Green's process is identical with that of the older processes, and the cloth, after printing or padding, is treated in the usual way. The black may be developed either by hanging in a warm, moist atmosphere, or by a passage through the "rapid ager," or by a more prolonged steaming. It is then "chromed" or not as required, and finally washed and soaped

For the dyeing of plain blacks, the new process is already in use; but it has not yet found any extended application in printing, though there does not appear to be any reason for its neglect in this direction, unless it be that the published proportions of ingredients are not suited to printing. Certainly a printing colour containing less than 2½ per cent. of aniline is not likely to yield a black, but on the small scale a fairly good result was obtained with the following colour:—

700 grms.	thick starch-tragacanth paste.
130 ,,	ammonium chloride.

Warm together, and, after cooling a little, add—

50 grms.	copper chloride ($CuCl_2.2H_2O$).
15 ,,	meta-bisulphite of soda.

Cool and add

60 ,,	aniline oil.
4 ,,	paraphenylenediamine.
20 ,,	hydrochloric acid 30 per cent.
21 ,,	formic acid 90 per cent.
1000	

The above was printed on white cloth, aged three minutes at 95° C. The black was not quite satisfactory on emerging from the "ager," but after an exposure of twelve hours to a moist atmosphere, followed by a hot chroming, it improved considerably, and would doubtless have been better for a more prolonged exposure to the air. Probably, too, a slightly larger quantity of mineral acid would accelerate the oxidation without attacking the fibre. Working on the above lines, good results ought to be possible of attainment; it ought to require a few experiments only to arrive at the correct proportions.

The following advantages are claimed for the new process of air oxidation blacks:—(1) that they are more economical than the older blacks, owing to a more complete utilisation of the aniline; (2) that they do not attack the fibre; (3) that they are more stable than any other Aniline black mixtures, owing to the absence of energetic oxidising agents; (4) that the rate of production is increased; and (5) that the absence of noxious vapours removes all risk of injury to the health of the workmen.

One very valuable property of all Aniline blacks is that previous to oxidation they are very susceptible to the action of alkalies and neutralising and reducing agents. The presence of any one of these three classes of bodies is sufficient to prevent entirely the development of the black; so that, on washing the goods after "ageing," the cloth remains perfectly white in those places where such reagents have been applied. The practical application of this property to the production of white and coloured designs on a black ground constitutes an important special style, which will be dealt with under the heading of "Resists and Discharges."

Indigo Printing.

Indigo is a natural colouring matter obtained by a special treatment of the leaves of various species of *Indigofera* which are largely cultivated in India and the East Indies generally. Like the essential colouring principle of Madder—Alizarin—Indigo is now manufactured artificially. The synthetic Indigo comes into the market as a 100 per cent. powder or a 20 per cent. paste, and its purity, regularity of composition, fine state of division, and the ease with which it can be applied without a prolonged grinding, are such that it is rapidly replacing the natural product in calico printing, and to a great extent also in dyeing. It possesses exactly the same properties as the natural dyestuff, and is applied by exactly the same methods. Its chief recommendation to the calico printer is that it is remarkably free from gritty and sandy substances, and that, in dyeing, it can be used at once without any preliminary grinding, and, in printing, it only requires grinding for a short time—often not at all—and can be strained very easily. On the other hand, natural Indigo always contains hard, sandy particles, which are most difficult to remove, even by the most careful straining through fine cloths; and as it comes into commerce in the form of hard, dry cakes, or cubes of variable composition, it always requires to be analysed before it can be used, and then ground for a week or so before it is fit to be employed for printing.

One of the greatest difficulties encountered in printing natural Indigo is due to the presence of gritty matter, which plays havoc with engraved rollers, and it is largely owing to its absence in the synthetic product that the latter has had so favourable a reception.

Artificial Indigo, however, has the defect of its quality. It is not quite so fast to washing as the natural dyestuff, and this has been put down by some chemists to its purity,—that is, to its being pure indigotine, unmixed with indirubin, indigo-brown, and other organic bodies, which are asserted to exercise a beneficial effect on the fastness of natural Indigo. Be that as it may, the difference between the fastness of the natural and artificial Indigoes is too slight to cavil about, and has certainly had no effect in checking the employment of the latter.

The methods of applying Indigo to the cotton fibre, either by dyeing or printing, are all based on its property of being converted by reducing agents into a body known as "indigo-white" which is soluble in alkalies, and, in that form, capable of penetrating into the body of the fabric to which it has been applied, and of being re-oxidised therein to a permanent blue dye. The methods of dyeing and printing vary in detail rather than principle. In the former case the cloth is merely steeped in an alkaline solution of indigo-white and then exposed to the air in the wet state. The yellow-coloured solution absorbed from the dye vat becomes first green and then gradually bluer and bluer, until finally the whole of the indigo-white is re-oxidised to insoluble blue Indigo, and the cloth is found on washing to be permanently dyed. In printing, the reduction of the Indigo, its solution in alkali, and its subsequent re-oxidation all take place on the cloth itself. There are some processes of printing reduced indigo-white as such, but they are now out of date, and never were very successful in the modern sense of the word.

Practically speaking there are only two methods of printing Indigo with any degree of success: (1) the Glucose or Schlieper & Baum process; (2) the hydrosulphite process. They are both in common use, and there is nothing to choose between the results obtained: they are equally good. The glucose process is the older and cheaper of the two, and will be taken first.

The Glucose Process.—This elegant process was perfected at the works of Messrs Schlieper, Baum & Co., and was for a long time the only method of completely utilising the Indigo employed. It depends upon the powerful reducing action of grape sugar in alkaline solutions; and as the reaction takes place either in the cold or at a slightly elevated temperature, it is essential that the grape sugar or "glucose" and the alkali should not be mixed together before the Indigo is printed, as otherwise reduction and partial re-oxidation of the latter would occur in the colour tub instead of on the cloth. To avoid this, which would result in unevenness, the cloth is first prepared in a 20–30 per cent. solution of glucose; it is then dried and printed with a mixture of Indigo and caustic soda.

The preparation of the white cloth is effected in a padding mangle through the following solution :—

Glucose Prepare 30 per cent.

300	grms.	grape sugar.
700	,,	water.
1000		

Dry the goods thoroughly (but not too hard), and then print them in the colour below.

Dark Indigo Blue 3 per cent.

150	grms.	Indigo L. 20 per cent. paste (B.A.S.F.).
850	,,	alkaline thickening.
1000		

Alkaline thickening :—

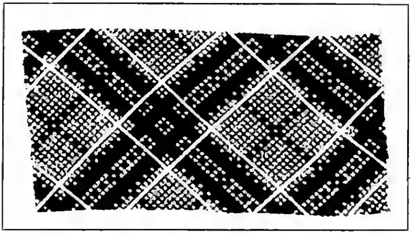
30	grms.	maize starch.
100	,,	dark British gum.
870	,,	caustic soda 77° Tw.
1000		

Mix carefully; heat to 140° F., and then cool before use.

The 20 per cent. Indigo paste above is made by grinding together 200 grms. of Indigo L. in powder (B.A.S F.) and 800 grms. of 4 per cent. gum Senegal solution. If the colour is too thick, it may be thinned by replacing part of the thickening by caustic soda 77° Tw. thus :—

Indigo Blue (thin).

150	grms.	20 per cent. Indigo L. paste.
700	,,	alkaline thickening.
150	,,	caustic soda 77° Tw.
1000		



Indigo (Glucose Process).

For lighter shades of Indigo it is only necessary to reduce the quantity of Indigo paste, making up the kilogramme with caustic soda at 30° Tw.; or the following reducing paste may be used :—

Reducing Paste.

600	grms.	alkaline thickening.
385	,,	40 per cent. gum Senegal solution.
15	,,	glycerin.
1000		

	Medium.	*Light.*	*Pale.*
Dark Indigo blue 3 per cent.	1 part.	1 part.	1 part.
Reducing paste . . .	3 ,,	5 ,,	10 ,, or more.

If these reductions of the strong blue printing colour are used alone the strength of the glucose preparation may be also reduced to as low as 15 per cent., but it is not advisable to go beyond this point lest the colour should suffer.

After printing, the goods ought to be steamed as soon as possible; if they are allowed to lie, the caustic soda absorbs carbonic acid from the air, and its power of reacting with the glucose to reduce the Indigo diminishes in proportion as it becomes carbonated. The reduction may be effected by running the goods through the rapid ager at a temperature as near 100° C. as possible, taking care at the same time to see that the steam is moist and that no air enters the apparatus. A run of ½ minute is, as a rule, quite sufficient completely to reduce the Indigo to indigo white. The best results are, however, obtained by steaming the goods for ½ minute in the special "Indigo ager" already described (see fig. 56), in which the steam enters the chamber through boiling water, and thus becomes thoroughly saturated with moisture, with the result that all the conditions essential to the perfect reduction of the Indigo, and to the solution in the caustic soda of the thickening, are obtained, namely, humidity, a high temperature, and the absence of air. In the ordinary rapid ager these conditions are not easy to maintain; and although, with care and constant attention, it is possible to obtain satisfactory results in this type of ager, the colour is more often than not reduced irregularly, and, on re-oxidising, is found to be uneven. The presence of air prevents the complete conversion of the Indigo into indigo white and, if the steam is at all deficient in moisture, the solution of the indigo white is partial only, and its penetration into the fibres of the cloth more or less irregular. A good deal of colour remains on the surface, and is washed off in the subsequent processes; so that not only is the work spoilt, but a considerable amount of a valuable colouring matter is lost, not to speak of the labour and delay that may be involved in the production of spoilt work.

The colour of the Indigo, as the goods emerge from the ager, ought to be a *brownish olive*; if it is *yellow*, the reduction has been pushed too far, and the colour will never re-oxidise fully; if it is *green*, the reduction is incomplete, and only a portion of the Indigo will be fixed, the rest washing off in the subsequent operations of souring, washing, and soaping.

After ageing, the printed pieces are suspended on rails in a cool hanging room, through which fresh air is allowed to circulate freely between each fold of the hanging cloth, and the floor of which is covered with damp sawdust. In this chamber the pieces remain until the indigo white is re-oxidised to Indigo which is insoluble and becomes permanently fixed on the fibre. The last traces of indigo white are converted back into Indigo by washing the goods in a copious supply of fresh running water, and this is followed by a treatment in dilute sulphuric acid (1°–2° Tw.), and a second thorough wash in water. These operations are conducted in the open width in order to prevent the Indigo from marking off before it is properly fixed. Finally, the goods are washed and soaped and washed again in the ordinary spiral or continuous rope machines, after which they are hydro-extracted to remove the excess of water, and then dried upon cylinder drying machines.

Light shades of Indigo can be re-oxidised completely by washing in running water immediately after ageing, and without the necessity of the intermediate hanging. The goods should be cooled first and the wash waters should be as cold as possible, otherwise the large quantity of alkali present is liable to be dissolved out of the cloth too rapidly, and thus cause the indigo white in solution to "run" before it is oxidised. The above operations of soaping, etc., can then be proceeded with as soon as the colour is fully developed.

The well-known "red and blue style" can be produced perfectly by the glucose process of Indigo printing. Turkey-red dyed cloth is prepared in a solution of glucose, printed with Indigo blue 3 per cent., then aged, hung, washed, and soaped as above. The Alizarin alumina lake of the Turkey-red is dissolved out (or "discharged") by the caustic soda of the Indigo printing colour, and thus leaves a comparatively white foundation under the blue. The unprinted parts of the cloth remain unaffected by the alkali; so that, according as a "blotch" or an object is printed, a red design on a blue ground or a blue design on a red ground is obtained.

By printing other strongly alkaline colours—*e.g.* plumbite of soda—along with the Indigo or mixed with it, it is possible to produce coloured patterns in white, blue, green, or yellow on a red ground. After ageing, such goods are passed through a bath of silicate of soda, then well washed and treated in an acid solution of bichromate of potash which precipitates the lead as Chrome yellow. Green is obtained from the mixture of Indigo and plumbite of soda, and white from a thickened solution of caustic soda containing tin and zinc, etc. This style of work will be described in detail in its proper place under "The Discharge Style."

By combining the glucose preparation with the naphthol prepares used for the development, on the fibre, of the insoluble azo colours, it is possible to print Indigo, by the glucose process, in conjunction with Paranitraniline red and similar colours. The naphthol part of the prepare must not contain any more soda than is required for keeping the β naphthol in solution, otherwise the glucose will be decomposed to an extent which will render the proper reduction of the Indigo impossible. The following is an example of a "prepare" formerly used in practice.

GLUCOSE-NAPHTHOL PREPARE.

a	30	grms.	β naphthol.
	75	„	caustic soda 52½° Tw.
	200	„	water.
b	300	„	glucose (chips).
	395	„	water.

Dissolve *a* and *b* separately, and when they are quite cold mix them together and make the whole up to one litre with cold water. Pad the cloth in this solution, and dry in warm air at as low a temperature as is convenient. Then print on Indigo blue 3 per cent. and any suitable diazo-compound, such as that of Paranitraniline or α Naphthylamine; age as usual to reduce the Indigo, and then, after allowing the goods to remain exposed to the air for a few hours, wash them in a plentiful supply of fresh running water. Finally, soap them in the rope form and dry.

This process was formerly used for the printing of two- and three-colour patterns, *e.g.* Indigo blue, "Para" red, and α Naphthylamine claret, but since the introduction of the hydrosulphite process of Indigo printing, which dispenses with the glucose preparation, it has fallen into disuse. A certain amount of the glucose was always wasted, and the prepared cloth, in any case, had to be dried and treated with extra care before printing.

The glucose process is still in use for the printing of single colour patterns in Indigo and also for "resist" styles, but it has been replaced, in a great measure, by the more convenient and rapid hydrosulphite process, which is adaptable to all styles of Indigo work.

THE HYDROSULPHITE-INDIGO PROCESS.—The distinguishing feature of the "hydrosulphite" process of Indigo printing is the simultaneous application of the colouring matter, its reducing agent, and its alkaline solvent. The printing colours are very stable, as the reducing agent (hydrosulphite-formaldehyde) has no action on Indigo in the cold. The hydrosulphite process is not cheaper than the "glucose process,"—in fact the printing colour itself is dearer,—but it has the advantage that no preparation of the cloth is required before printing, and therefore the rate of production is increased, and some economy effected in labour, time, and steam, by dispensing with the use of the "padding" and drying machines. Moreover, as all the essential elements of the colour are mixed together in a stable paste, which only decomposes when subjected to a high temperature, the goods can be printed at any time without the necessity for making special arrangements. Neither is the hydrosulphite process so dependent for success upon certain conditions of moisture and duration of steaming as is the glucose process. In fact, so long as the temperature of the steam is sufficiently high to bring about the decomposition of the hydrosulphite, the amount of moisture it contains and the length of time it is allowed to act may vary within comparatively wide limits without detrimentally affecting the final result. The steaming is carried out in specially constructed "hydrosulphite agers," which allow of a temperature of 102°–104° C. being obtained. For light patterns the ordinary steam at 102° C., and free from air, answers perfectly well; but heavy patterns require more moisture, and to supply this the apparatus is provided with a water trough inside, at the bottom. From the surface of the water aqueous vapour rises and renders the steam sufficiently humid. A printing colour made up with hydrosulphite and the alkaline paste used for the glucose process is given below. It has been used in practice for several years with excellent results.

DARK INDIGO BLUE 3 per cent.

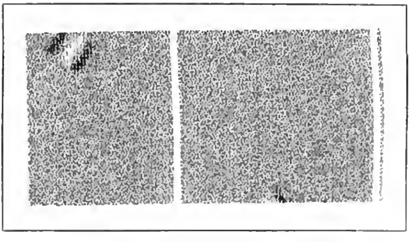
$\left\{\begin{array}{l}\text{80 grms. hydrosulphite conc. N.F. (M., L. \& B.)}\\ \text{420 ,, alkaline thickening. (See page 288.)}\end{array}\right.$

Dissolve by heat, cool, and add

150 grms. 20 per cent. Indigo L. (B.A.S.F.).
350 ,, alkaline thickening.

1000

After printing, steam two to three minutes at 102° C. in air-free and moist steam. Then allow to cool and pass directly, in the full open width, into a continuous washing machine supplied with plenty of fresh, cold running water. Wash until all the alkali is eliminated, then sour, wash again, and finally soap, wash, and dry. The printed goods may be allowed to re-oxidise in the air, but this is not necessary except for some heavy patterns printed in very deep colours.



Indigo (Hydrosulphite Process).

The above colour gives a full navy blue when printed on white unprepared cloth. Lighter shades may be obtained by reducing it with various proportions of a reducing paste containing a little glycerin and about ½ per cent. of hydrosulphite (concentrated) (M., L. & B.).

Reducing Paste (for light shades).

600	grms.	British gum alkaline thickening.
300	,,	40 per cent. gum Senegal sol.
20	,,	glycerin.
5	,,	hydrosulphite conc. N.F.
75	,,	water.
1000		

Both Turkey-red and Paranitraniline red are easily discharged by the alkaline hydrosulphite colour. For Paranitraniline red discharges, the quantity of hydrosulphite must be increased from 12–20 per cent. according to the depth of the engraving and the intensity of the red ground. For ordinary engraving and an average red (corresponding to a "prepare" containing 25 grms. β naphthol per litre) the following Indigo printing paste gives satisfactory results.

Indigo Blue 3 per cent. (for Para red).

120	grms.	hydrosulphite conc. (or Hyraldite conc. Cassella).
100	,,	water.
280	,,	alkaline thickening.
150	,,	20 per cent. Indigo L. (B.A.S.F.).
350	,,	alkaline thickening.
1000		

Print on Para red dyed cloth, and, after ageing, wash and soap as usual.

Turkey-red is discharged by the alkali of the printing colour and therefore does not require any extra addition of hydrosulphite. Better results in every way are obtained when the cloth to be discharged is well soaped in an alkaline soap bath before printing; or a solution of 10–15 grms. of silicate of soda (without any soap) will answer equally well. The only object is to remove surface colour and fatty matters, both of which interfere with the proper action of the discharging agent on the actual ground colour of the dyed fabric.

On naphthol-prepared cloth the brilliant Insoluble azo colours can be printed along with Indigo and any other colours fixed in the same way, such as Sulphide colours and the large class of colouring matters known as the "vat dyes": Indanthrene, Flavanthrene, Ciba colours, Thio-indigo, Brom-indigo, etc.

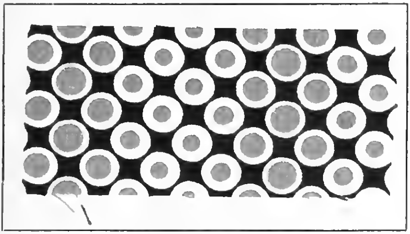
Another artificial preparation of Indigo, not much used at the present time, is Kalle's "Indigo salt" (a bisulphite compound of ortho-nitrophenyl-lacto-keton). It is simply thickened and printed on white cloth. The cloth is well dried and padded, either through a mangle or on the printing machine, with caustic soda, which immediately reacts with the pale yellow salt to form a true Indigo blue.

Application of Vat Dyestuffs other than Indigo.

Brom-indigo (Bayer), a bromine substitution product, yields much redder shades than any of the ordinary artificial Indigoes (Indigo pure, Indigo L., or Indigo M.L.B.), and may be mixed with them in any proportion to modify the shade. When used alone the Halogen-indigoes — Indigo M.L.B./R. and M.L.B./R.R.—can be effectually reduced with much less hydrosulphite than Indigo itself; 50 grms. of hydrosulphite (conc.) being sufficient to reduce fully 200 grms. of a Brom-indigo 20 per cent. paste (or 40 grms. of the dry powder).

Amongst the most important derivatives of Indigo is the Thio-indigo red of Kalle & Co. It comes into the market as "Thio-indigo red paste B.," and yields shades ranging from a deep bluish crimson to the palest of rose pinks. As its name implies, it is a sulphur compound, and it can be used as a direct Sulphide dyestuff for light colours, and as a "vat dyestuff," like Indigo, with hydrosulphite and caustic soda, for dark colours. Mixed with Indigo it allows of exceedingly fast violet shades being produced, which are especially valuable in the printing of shirtings and similar goods.

For a pale pink it is only necessary to use an alkaline thickening and the colouring matter. For red, or rather dark crimson, the addition of a small quantity of hydrosulphite is essential to the production of a full and fast shade. Hydrosulphite may also be added to the weaker colours, but it is not at all necessary.



Brom-Indigo (Bayer).

Thio-Indigo Pink.

a { 15 grms. Thio-indigo red paste B. (Kalle).
  { 50 ,, water.
b { 100 ,, British gum.
  { 835 ,, caustic soda 60° Tw.

1000

Thio-Indigo Red.

{ 150 grms. Thio-indigo red paste B.
{ 100 ,, water.
{ 20 ,, hydrosulphite conc. (Höchst).
{ 730 ,, alkaline thickening (for Indigo).

1000

Violet (Indigo and Thio-indigo)—a reddish shade.

80 grms. Thio-indigo red paste B. (Kalle).
20 ,, 20 per cent. paste indigo L. (B.A.S.F.).
100 ,, water.
25 ,, hydrosulphite N.F. conc. (Höchst).
775 ,, alkaline thickening.

1000

Print on unprepared cloth; age and wash, etc., as for Indigoes.

Thio-indigo scarlet is a similar product to Thio-indigo red, and is applied in practically the same way. Since the introduction of the latter, Kalle & Co. have extended their series by the addition of Brom-indigoes and Thio-indigo orange, yellow and brown.

In combination with other dyestuffs, Indigo is capable of yielding a good many different colours and effects. With Flavanthrene (B.A.S.F.), a yellow vat dyestuff, it forms an olive green, very fast to light and soap. Flavanthrene is not destroyed by oxidising agents, so that if the mixed green is over-printed, with another pattern, in bichromate of potash, and then passed through a "cutting bath" of sulphuric and oxalic acids, the blue part is destroyed where the bichromate is printed, leaving a bright yellow, and thus producing a green and yellow "conversion" effect. If the green is printed on cloth dyed a light Indigo shade, and then treated as above, the result is a four-colour effect from two rollers and two colours, viz. green, yellow, light blue (the ground), and white (the ground colour discharged). This style of Indigo work and other analogous styles have been rendered possible by the discovery of the stable hydrosulphite-formaldehyde compounds, which have completely revolutionised certain branches of the industry, and introduced new ones.

Of late years a considerable number of colouring matters which form leuco-compounds similar to indigo white, or which are applied in a similar way to Indigo, by means of reducing agents and caustic soda, have been placed upon the market by various firms. Amongst the best known of this class of dyestuffs are the Ciba colours (*Soc. Chem. Ind. Basle*), the Indanthrene series (B.A.S.F.), the Sulphide colours, the Helindone colours (M., L. & B.), the Algol colours (Bayer), and others by other makers, whose products possess equally good qualities in many respects. Most of the vat dyes and Sulphide colours by makers other than those mentioned are applied in the same way, and satisfactory results will be obtained from them by following the methods given for those of the above colours to which they approximate most nearly in their general properties.

Ciba Colours.—These colours, which are mostly Indigo derivatives, constitute a class of vat dyestuffs, which is characterised by a fastness to light, acids, alkalies, and chlorine equal to or exceeding that of such admittedly fast colours as Indigo, and the dyed Alizarin purples, reds, and blues, and by a brightness of shade approaching those given by the basic aniline dyes. They may be either dyed like Indigo or printed; they are adaptable to several styles of resist and discharge work; and they can be fixed by either short steaming alone, or by the usual prolonged steaming necessary for the ordinary steam colours.

The application of the Ciba colours, whether by printing or dyeing, depends upon the reduction of the colouring matters, by hydrosulphite, tin, or other suitable reducing agents, to their leuco-compounds, which are soluble in alkalies. The alkalinity of the printing pastes is much less than that of Indigo colours, and consequently the Ciba colours are more or less free from the disadvantages that attend the use of Indigo, which, *when used alone*, requires to be applied in the form of a strongly alkaline mixture. It is a remarkable fact, however, that Ciba blue promotes the reduction of Indigo to such an extent that when the two are used in combination for the production of a certain intermediate shade, the Indigo is completely reduced in the presence of *potassium carbonate only*, whereas, under ordinary circumstances, a large amount of caustic soda is absolutely essential to properly reduce it and fix it upon the fibre; in fact its fixation is prevented in proportion as the caustic soda becomes converted into carbonate by absorption of carbonic acid from the air. The percentage of Indigo (20 per cent. paste) on the weight of Ciba blue paste ought not to exceed 30 per cent., otherwise a portion of it remains unreduced, and will be washed out in subsequent processes.

Mixtures of Ciba blue and Indigo—and indeed all Ciba colours—can be effectually fixed in any rapid ager capable of being worked at a temperature of 102° C. No particular precautions are necessary for excluding air, or for maintaining a regular degree of moisture, though, of course, the regularity of the conditions under which the steaming is performed is conducive to regularity of results.

Another great advantage of Ciba colours is that they may be printed along with colours so diverse in properties as Aniline black, the Insoluble azo colours, and almost any of the ordinary "steam colours" like Alizarin red, basic dyestuffs, and the vegetable colours. They withstand the various operations to which these styles are subjected, and it has been proved by experience that they are practically unaffected by either bichromate of potash, mineral acid baths, tartar emetic, or prolonged steaming.

After steaming, the printed goods are allowed to hang for a short time to re-oxidise. They are then washed in cold water and finally soaped at the boil. This last process is very important: it increases the purity and brightness of the shades, and at the same time increases the fastness of the colours to light and chlorine. A run through a solution of bichromate may be substituted for the hanging of the goods before washing and soaping, but the resulting colours are somewhat duller in appearance.

The printing pastes are exceedingly stable for vat dyestuffs and work well in the machine, as they neither act on the engraved rollers or "take" the doctor edge.

Taken altogether, the Ciba colours as a class are widely applicable in calico printing. They may be dyed, printed, resisted, discharged; they are well adapted to act as discharge colours on Para red, Para brown, Naphthylamine claret, and as resist colours under Aniline black; they may be printed in conjunction with either oxidation, reduction, or ordinary steam colours; and they may be mixed together in any proportion, or with Indigo and Sulphur colours. In short, for all styles in which fastness is of the first importance—*e.g.* shirtings, dress goods generally, and especially delicately coloured muslin curtains—the Ciba colours are well adapted; and if their range of shades were extended to include a strong yellow, they might displace many of the fastest and most valuable mordant dyestuffs at present in use.

The application of the Ciba colours to resist and discharge styles will be touched upon later. The following are a few of the colour pastes used in direct printing.

CIBA BLUE.

250 grms. Ciba blue 2 B.D. paste are gradually added to—
60 ,, 30 per cent. gum Senegal solution whilst stirring with a small brush. When mixed, add—
190 ,, 50 per cent. dextrin solution.

Brush through a fine hair sieve and add—

140 grms. soda ash.
30 ,, glycerin.
130 ,, 30 per cent. gum Senegal.
140 ,, 50 per cent. dextrin paste.

Dissolve at 120° F. and then add—

60 grms. hydrosulphite N.F. conc. (Höchst).

1000

REDUCING PASTE (for lighter shades).

400 grms. 30 per cent. gum Senegal solution.
590 ,, 30 per cent. dextrin paste.
10 ,, hydrosulphite N.F. conc.

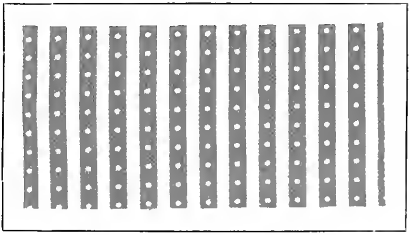
Print on unprepared cloth; steam 2–3 minutes at 102° C. Then hang or allow to lie an hour or so, and then, after washing in cold water, soap at the boil in

2–4 kilos. Marseilles or other suitable soap.
1–2 ,, soda ash.
1000 ,, water.

The strength of the soap is reduced in accordance with the intensity of the shade printed, lighter colours requiring weaker soap.

A run through a hot ½ per cent. solution of bichromate of potash may be substituted for soaping if desired, but the colour becomes greener in tone and loses some of its brightness.

Although no *special* precautions need be taken to avoid the presence of air in the steaming apparatus, it must be understood that the less air present the more perfect the result; consequently the regular "hydrosulphite" agers are the most efficient so long as the temperature is not allowed to exceed 102° C. (217° F.). At a higher temperature the colours are apt to be over-reduced, with a corresponding loss in brilliancy.



Ciba Blue 2 B.D. (S.C.I.B.).

Ciba blue may be combined with sulphur dyestuffs to yield all sorts of compound shades. When mixed with a small quantity of Pyrogene deep black D., for instance, it gives a fine imitation Indigo shade.

Ciba Blue and Pyrogene Black.

A	70 grms.	standard blue A. 50 per cent.	Heat to 120° F. (50° C.), and then add and dissolve whilst stirring—
	448 ,,	gum Senegal 30 per cent.	
	320 ,,	dextrin paste 50 per cent.	
	100 ,,	potash or soda ash.	
	30 ,,	glycerin.	
	20 ,,	hydrosulphite N.F. conc. and then—	
B	2·5 ,,	Pyrogene deep black D.	Dissolve separately.
	6 ,,	caustic soda 66° Tw.	
	3·5 ,,	sodium hydrosulphite powder.	
	1000		

The solution of part B would probably be effected more easily by the addition of 100 grms. of water, which could be allowed for by using 348 grms. of a 40 per cent. gum Senegal in place of the quantity of 30 per cent. gum solution given in part A. The standard blue is made as under.

Standard Blue A 50 per cent.

500 grms. Ciba blue 2 B.D. paste.

Add gradually to

120 ,, 30 per cent. gum Senegal.
380 ,, 50 per cent. dextrin paste.
1000

Strain through a hair sieve before use. After printing, proceed exactly as for the previous blue.

By mixing Indigo and Ciba blue in various proportions, intermediate shades are obtained which are characterised by their excellent fastness to light, acids, alkalies, soap, and chlorine. Considering their comparatively small Indigo content, the fastness to chlorine is remarkable, and seems to point to the conclusion that the Ciba blue not only facilitates the reduction of the Indigo in solutions of alkaline carbonates, but also has some further action upon it in the direction of fixing it more permanently upon the fibre; in fact it seems to play the part of a mordant. Be that as it may, it is indisputable that the Indigo is considerably faster in combination with Ciba blue than when printed by itself. The Alizarins and the direct dyeing colours are well known to combine with the basic aniline colours, and it is not improbable that the

Ciba colours possess a similar affinity for synthetic Indigo. The following recipe will illustrate the preparation of a combined Indigo and Ciba blue printing paste. It contains only 3 per cent. by weight of Indigo pure 20 per cent. paste (=0·6 per cent. indigotine), a quantity that under the ordinary conditions would give a light blue very susceptible to the action of dilute solutions of bleaching powder such as are used for the clearing of printed goods. Yet it resists this operation without any appreciable alteration in shade.

CIBA BLUE AND INDIGO.

90	grms.	Ciba blue 2 B.D. paste.
30	,,	Indigo pure 20 per cent. paste.
620	,,	gum Senegal.
60	,,	glycerin.
140	,,	potash.

Heat to 120° F. and add

60	grms.	hydrosulphite N.F. conc.

Dissolve and cool. Print, steam, hang, wash, and soap as usual.

Ciba blue is sent out both as a powder and in a paste form. The latter is most convenient, but is rather more expensive for carriage. The other colours, violets B. and R., red, scarlet, and bordeaux are also made in paste and powder. With the exception of the reds, all the Ciba colours can be printed by the stannous-oxide caustic process, but the "hydrosulphite process" is to be preferred in most cases.

CIBA BLUE (with stannous oxide).

120	grms.	Ciba blue 2 B.D. paste.
30	,,	stannous oxide 50 per cent. paste.
60	,,	glycerin.
150	,,	British gum (dry).
190	,,	water.
450	,,	caustic soda 90° Tw.
1000		

Allow to stand, and then strain well.

This colour is strongly alkaline, and open to all the objections connected with such colours; but it yields rather darker shades than those resulting from the use of the various "hydrosulphites."

The Ciba violets and heliotrope produce very beautiful shades, ranging from full purples to the most delicate lilacs and heliotropes, according to the strength and brand of colour used. Their preparation does not differ materially from that of the blues.

CIBA VIOLETS OR CIBA HELIOTROPE.

Standard.

750	grms.	Ciba violet B. or R. paste or Ciba heliotrope B.
250	,,	30 per cent. British gum paste.
1000		

Strain before use.

Printing Colour.

335	grms.	standard B. or R.
435	,,	30 per cent. British gum paste.
120	,,	potash or soda ash.
40	,,	glycerin.

Dissolve and add at 120° F.

70	grms.	hydrosulphite N.F. conc.
1000		

When orange in colour, cool down.

Ciba Heliotrope B. (S.C.I.B.).

Print, dry, steam 2–4 minutes at 102° C., hang, or allow to lie a short time, then chrome and wash; or, better still, soap for half an hour at the boil with 4/1000 soap solution, containing 2/1000 of soda ash, which yields the finest, fastest, and most regular shades.

Ciba Red.—A bright and very fast red, made up generally like the preceding colours.

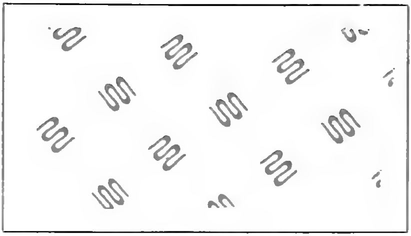
Standard Paste R.

730 grms. Ciba red R. paste.
270 „ British gum paste 30 per cent.
1000

Printing Colour.

550 grms. standard paste R.
115 „ British gum paste 30 per cent.
200 „ caustic soda 66° Tw.
60 „ glycerin.
Heat to 120° F. and add—
75 grms. hydrosulphite conc. N.F.
1000

The printing colour ought to be a deep brownish yellow, and care must be exercised not to exceed the temperature indicated, lest over-reduction ensues.



Ciba Red R (S.C.I.B.).

After printing, the goods are steamed for 4–5 minutes at a rather higher temperature than the other colours, namely, 104°–107° C., then washed and soaped for 5 minutes at 104° F. (60° C.) in a solution containing 4/1000 Marseilles soap and 2/1000 soda ash.

If bluer shades are desired, a run through bleaching powder solution $\frac{3}{4}$° Tw. may replace the soaping.

To obtain the best results from Ciba red it is essential to steam the goods at the above high temperature.

Ciba colours, when printed with—

(1) Alizarin, basic, and other "steam colours," are first aged at 102° C., allowed to lie a short time, and steamed again for an hour in order to fix the other colours. The goods are then passed through tartar emetic, washed, and soaped as usual.

(2) Aniline black: steamed for two minutes at 102° C. and then passed at once into hot bichromate; washed well and soaped.

(3) Insoluble azo dyes on β naphthol containing oxide of antimony: steamed 2–4 minutes at 102° C., allowed to lie a little while, and then well washed, soured, washed, and soaped.

If the Ciba printing pastes have become re-oxidised by long standing, they can be restored to a fit condition for further use by adding 1–2 per cent. of hydrosulphite N.F. conc., and heating gently until the yellowish colour of the leuco-compound appears again.

The best Aniline black to use is the Copper sulphide black, containing a little (very little) free hydrochloric acid. The "steam colours," too, are better for the addition of a small quantity of extra acetic or formic acids, if they are not sufficiently acid in the first instance to resist the slight alkaline "scum" from the Ciba colours.

The Sulphide Colours.—The class of colouring matters known as Sulphide colours form leuco-compounds like Indigo, and can be applied in practically the same way, but with different proportions of alkali and reducing agent. As reducing agents, either glucose or the "hydrosulphites" may be used. The latter are the best and most convenient.

The greatest drawback of the Sulphide colours is that they blacken the printing rollers. This blackening is due to the presence of polysulphides which injuriously attack the rollers, with the formation of copper sulphide. To some extent this defect can be overcome by the addition of sodium sulphite or bisulphite to the alkaline printing pastes, but in this case the use of the "hydrosulphites" is inadmissible, since the final result of the reactions between the sulphite or bisulphite, the "hydrosulphite," and the polysulphides or free sulphur in the colouring matter would be that the polysulphides would remain practically unaffected.

Within recent years many of the sulphide dyestuffs have been more or less freed from free sulphur and polysulphides, and consequently they do not affect the printing rollers injuriously. Of these improved products, the Immedial colours "soluble" and the D. brands of the Thiogene series are typical examples. Some of these pure colours yield the best results with pure hydrosulphite of soda in powder, while others are preferably printed with sulphoxylate formaldehyde compounds like "Hyraldite," "Rongalite," or "Hydrosulphite N.F." The latter compounds yield the most stable colours, but the stability of those prepared with the "hydrosulphite in powder" ($Na_2S_2O_4$) is sufficiently good for most purposes.

If large quantities of colour are required, it is advisable in all cases to prepare it in small separate lots as required, so as to ensure that the colour is in good condition, and not partially decomposed by long standing.

The printing of Sulphide colours must be carefully carried out. Their fixation depends to a great extent on the presence of plenty of moisture; and in printing, therefore, it is essential to guard against overdrying the goods. In a great measure this is prevented by the addition of glycerin to the printing pastes, but it is well not to depend too much on the action of glycerin. The safest plan is to dry the goods in moderately hot air, and not over cylinders, if it can be avoided. A little China clay is often added to the printing colours to lessen their liability to "run" during the subsequent steaming in damp steam.

The preparation of the printing pastes is as follows:—

The colouring matter is beaten up with water, caustic soda, glycerin, China clay, and either glucose or one of the "hydrosulphites" already mentioned. The mixture is heated until the colouring matter is completely reduced and dissolved, and then added to the necessary quantity of alkaline thickening; finally, the whole is warmed again until a perfectly homogeneous paste is obtained, which after cooling is ready for use. For very light shades it is possible to reduce the quantity of alkali down to what is just necessary for the solution of the colouring matter, but, as a rule, it is better to keep the colours strongly alkaline.

The following recipes will serve as types of the methods of preparing sulphide printing colours.

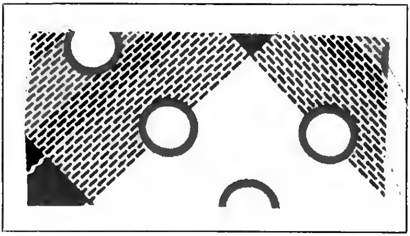
BLACK.

80	grms.	Thiogene black M.D. conc.
50	,,	glycerin.
150	,,	caustic soda 25° Tw.
80	,,	50 per cent. China clay paste.
40	,,	hydrosulphite N.F. conc.
600	,,	alkaline thickening (for Indigo).
1000		

LIGHT BLUE.

10	grms.	Thiogene cyanine C.D. extra.
30	,,	glycerin.
30	,,	caustic soda 25° Tw.
150	,,	water.
150	,,	China clay paste 50 per cent
20	,,	hydrosulphite N.F. conc.
610	,,	alkaline thickening 2 : 1.
1000		

GREEN :—as blue, but Thiogene green C.L.D. extra conc.
YELLOW :— ,, ,, ,, yellow.
GREY :— ,, ,, ,, grey B.D. extra conc.



Thiogene Brown, Thiogene Cyanine, Thiogene Green, Thiogene Black, } (M., L. & B.).

DARK BLUE.

25	grms.	Thiogene cyanine O.D. extra.
50	,,	glycerin.
150	,,	caustic soda 25° Tw.
100	,,	50 per cent. China clay paste.
20	,,	hydrosulphite N.F. conc.
600	,,	alkaline thickening for Indigo.
55	,,	30 per cent. gum Senegal mucilage.
1000		

DARK NAVY BLUE.

50	grms.	Kyrogene pure blue R.
75	,,	glycerin.
100	,,	boiling water.
175	,,	alkaline thickening.
480	,,	British gum starch paste.
60	,,	glucose.

Heat twenty minutes at 150° F.; cool, allow to stand twelve hours, and then add 60 grms. glucose.

1000

The Immedial, Pyrogene, and other Sulphide colours are applied by similar methods. The recipes given below will, in general, be found to yield satisfactory results.

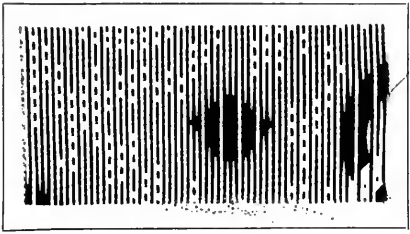
Printing Colour A.

40 grms. Immedial indone B. (free from sulphur).
30 ,, glycerin.
30 ,, caustic soda 70° Tw.
100 ,, boiling water.
630 ,, alkaline thickening (for Indigo) 2 : 1.
100 ,, 50 per cent. China clay paste.

Heat at 140° F. until the dyestuff is dissolved, then cool and add—

35 grms. Hyraldite C. extra.
35 ,, water.

1000



Immedial Indone B. (Cassella).

Printing Colour B.

40 grms. Immedial colour "soluble."
40 ,, caustic soda 70° Tw.
25 grms. glycerin.
100 ,, boiling water.
645 ,, alkaline thickening 2 : 1.
100 ,, China clay paste 50 per cent.

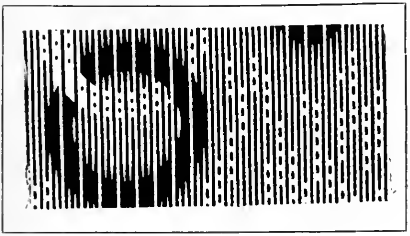
Heat to 140° F., then add—

25 grms. glucose.

Stir for a time, cool, and add further

25 grms. glucose.

1000



Immedial Carbon B. (Cassella).

Other series of Sulphide colours are applied according to one or other of the foregoing formulæ.

After drying, all goods printed with Sulphide colours are passed once or twice through moist steam at 102° C. The steaming takes place in the rapid ager, and lasts from 3–5 minutes according to circumstances. The goods may then be passed through one of the solutions given below :—

	1.	2.	3.	
Water	1000	1000	1000	grms.
Sulphuric acid 168° Tw. .	10	10	10	,,
Copper sulphate . . .	...	2	..	,,
Bichromate of potash .	...	...	5	,,

Finally, they are well washed and soaped.

On the Continent, the Sulphide colours have been employed for several years in the direct printing of shirtings and other goods that are required to stand the action of light and frequent washing. In England, however, their use in this connection is only just developing, probably because the earlier Sulphide dyestuffs were both impure and somewhat insoluble, and gave unsatisfactory results both as regards shade and the working quality of the printing pastes. Now, however, that a great variety of interesting, fast, and fairly bright colours are procurable, there is technically no reason why the printing of the new and pure soluble Sulphide colours should not develop into an important branch of manufacture. The colours purified specially for printing work well, do not stain the rollers to any great extent, require only a short steaming for their fixation, and yield sufficiently bright colours of excellent fastness to washing. Moreover, they are easily "reserved," and are therefore of great value in the "print and cover style" for the production of direct printed effects that could formerly only be obtained, of equal fastness, by the tedious method of dyeing on a previously printed, aged, and fixed mordant.

The Sulphide colours will stand a much larger quantity of "hydrosulphite" than is required for their reduction, and this allows of their being used as "discharge colours" on Paranitraniline red and other Insoluble azo colours, and also on direct dyestuffs. They are not very bright colours, but for quiet effects on flannelettes, and in all cases where fastness is required, they are exceedingly useful. For combined brightness, fulness, and fastness, nothing has hitherto surpassed the vat dyestuffs; but the Sulphide colours are none the less useful for a great variety of styles, and they include a greater range of shades than any other series of vat dyestuffs.

In common with the Ciba colours, Indanthrenes, and Indigo, they can be printed on naphthol-prepared cloth in conjunction with any Insoluble azo colour. They are also dischargeable by the chlorate prussiate method; and, as they are easily reserved by zinc salts, they are applicable to a great variety of styles.

With very few exceptions, the Sulphide colours are sensitive to chlorine, but in other respects they represent one of the fastest classes of colours known. It must, however, not be taken for granted that a Sulphide colour is necessarily fast. There are, in fact, some which could not even be termed moderately fast.

The "reserving" and "discharging" of sulphide colours will be dealt with in another section of this work.

It is impossible to review, or even to mention, all the many excellent Sulphide colours on the market. As a class they are very similar; they are all applied according to the principles illustrated in the foregoing examples of printing pastes, and in general they behave in much the same way as the colours mentioned above.

Indanthrene Colours (B.A.S.F.).

The Indanthrenes are a series of "vat" dyestuffs (derived from anthraquinon) which may be fixed on the fibre without steaming, and are fast to light, soap, acids, and alkalies, but sensitive to chlorine. One brand of Indanthrene blue, that marked G.C.D., is, however, fast to chlorine as well.

The Indanthrene colours, together with Vat red, B.A.S.F./B., come into the market in the form of pastes, which are soluble in alkaline solutions of reducing agents, and their application to direct printing depends upon this property of being reduced, and subsequently re-oxidised, in a manner analogous to Indigo and the Ciba colours. In practice, the reduction is effected in different ways according to the conditions under which the Indanthrenes are to be applied. The darkest shades are obtained by the caustic soda method (without steaming), using iron and stannous salts as the reducing agents. For lighter effects and blotches, or heavy objects, the colour is reduced by a short steaming, using either stannous oxide or "hydrosulphite" (Rongalite C.) and caustic soda or soda ash as reducing agents; and in special cases the glucose process may be employed to advantage, though it does not yield the brightest or fullest shades.

The addition of β-naphthol increases the depth, beauty, and evenness of light and medium shades of the Indanthrenes, so that these colours are admirably adapted to the production of fast multicolour effects in combination with any of the Insoluble azo colours. Like the Ciba colours, too, the Indanthrenes will, under certain conditions, withstand prolonged steaming—an advantage which allows of their being associated with the ordinary steam colours, *e.g.* Alizarin, Persian berries, and other mordant dyestuffs, as well as basic colours; and, in common with the rest of the "vat dyes," they can be printed along with almost any colour that is developed by a short steaming, as for instance Aniline black, Diphenyl black, Paramine brown, the Sulphide colours, etc.

The printing of the Indanthrene dyestuffs on cotton is usually carried out by one or other of the following processes:—

(1) THE CAUSTIC SODA METHOD (without steaming).—In this process, which gives the darkest colours, and is especially suitable for fine shirting and cover patterns, the colouring matter, mixed with tin crystals, sulphate of iron, tartaric acid (optional), and a suitable thickening, is printed on white unprepared cloth, and the goods, after well drying, are passed in the open width through a hot solution of caustic soda. The hydrates of tin and iron (more particularly the iron) thus formed reduce the colouring matter to its leuco-compound, which, in dissolving in the alkali, penetrates into the body of the cloth, where it is subsequently re-oxidised and fixed as an insoluble colour.

For the preparation of the printing pastes the proportions of the various ingredients, as given by the makers, are as follows:—

Dark.	*Med.*	*Light.*	*Pale.*		
200	100	50	25	grms.	colouring matter.
120	60	30	30	,,	ferrous sulphate.
20	10	5	5	,,	stannous chloride.
100	100	50	25	,,	tartaric acid.
560	730	865	915	,,	thickening.
1000	1000	1000	1000		

The tartaric acid, finely ground, is first of all dissolved in the thickening; the stannous chloride is then added, and lastly the ferrous sulphate, which may be dissolved in a sufficiency of water, used in place of a portion of the thickening if this latter is made thick enough at the outset to allow of water being introduced. The whole is well stirred until the salts are completely dissolved, and it is then added gradually to the dyestuff whilst stirring with a stiff wire brush, which is the best means of avoiding specks.

When thoroughly incorporated and quite smooth, the colour is well strained and printed in the ordinary way. The goods may be dried either over steam-heated cylinders or in a hot-air apparatus.

The fixation of the colour is then effected by passing the perfectly dry printed goods through a beck containing a solution of caustic soda 30° Tw. at a temperature of 160°–175° F. The treatment lasts about 30 seconds. In order to prevent the soiling of the "whites," which is liable to occur if a number of printed pieces are passed continuously through the same caustic bath, it is recommended to add 1–10 volumes of "manganese paste" (according to the quantity of colour on the goods) to every 100 volumes of caustic soda in the beck. The manganese paste is prepared by precipitating manganese chloride with caustic soda and "chemick." Thus—

7·5 kilos. manganese chloride 72° Tw.
17·5 ,, water

Add

6·25 ,, caustic soda 53° Tw.
20 ,, bleaching powder sol. 12° Tw.

Mix well before use.

On emerging from the hot caustic bath, the goods must not be squeezed, but given a short run through the air to cool down, and then passed directly into cold caustic soda, out of which they may be passed between squeezing rollers without any fear of the colour "marking off." They are then passed into a series of washing becks furnished with "spirt pipes" or sprays, and plenty of clean cold water, followed by a run through sulphuric acid 4½° Tw., another good wash, and finally a soaping at 175°–212° F. In the case of all but the lightest colours it is advisable to allow the goods to lie in the sulphuric acid for some time before they are finally washed and soaped, the object being to thoroughly remove all traces of iron, which, if allowed to remain, would oxidise to yellow ferric oxide, and thus dull the colours. When the colour used contains more than 10 per cent. of dyestuff the goods are allowed to steep in 3 per cent. sulphuric acid for an hour; if it only contains 10 per cent. or less, it is sufficient to saturate the goods in the acid, and then (without squeezing) allow them to lie in pile for about the same period. They are then washed and soaped. The whole series of operations, up to and including "souring," are best conducted on a continuous machine or in an "open-soaper," one compartment of which is left empty to provide the airing mentioned above, after the treatment in hot caustic soda.

For fine patterns printed in dark and medium shades of Indanthrene colours it is best to use a starch and British gum thickening, or a British gum thickening alone. For lighter shades and heavy patterns a mixture of British gum and gum Senegal is recommended; but gum Senegal alone gives the brightest and most even prints; and although the colours yielded are lighter than with other thickenings, it is advisable to use gum Senegal wherever its price will allow. By itself, starch gives the darkest colours of all, but its employment is restricted, and in general, for any kind of fine pattern, it is mixed with British gum.

BRITISH GUM PASTE.

450	grms.	British gum.
550	,,	water.
1000		

Boil and cool.

GUM SENEGAL THICKENING.

500	grms.	gum Senegal.
500	,,	water.
1000		

STARCH—BRITISH GUM PASTE.

225	grms.	British gum.
75	,,	wheat starch.
700	,,	water.
1000		

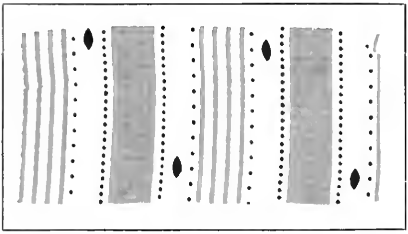
Boil and cool.

In the after-treatment of Indanthrene colours by the caustic soda (without steaming) process, it is of the *utmost importance* to wash out all the caustic soda in the printed pieces as soon as possible after development. If the goods containing dilute soda are exposed to the air for any length of time, the colour not only loses in brightness and depth, but also becomes irregularly developed. For this reason it is preferable to perform all the operations following the printing in a continuous manner, as by so doing the last traces of alkali are effectually neutralised in the final "sour" beck, which must be kept up to the proper degree of acidity by additions of fresh sulphuric acid at regular intervals.

By the above method, and according to the foregoing recipes, all the following colours may be equally well applied :—

Indanthrene blues R.S. and G.C.D. pastes.
,, orange R.T. paste.
,, copper R. ,,
,, claret B ,,
,, dark blue B.O. ,,
,, violets R.T. R. extra R.R. pastes.
,, maroon R. paste.

Indanthrene yellow R. and G. pastes.
,, golden orange G. paste.
,, red R. and G. pastes.
,, brown B. ,,
,, grey B. ,,
,, green B. ,,
Anthraflavone G. paste.



Indanthrene Blue G.C.D. and Indigo pure (B.A.S.F.)
(Stannous Oxide Steaming Method).

When printed in conjunction with Aniline or Diphenyl black, the above printing colours are used for the production of fine and exceedingly fast shirting and blouse prints. With the exception of a short steaming in the ordinary rapid ager, the treatment of the printed goods is exactly as described above. The colours most largely used for this style are the Blues R.S. and G.C.D., the Violet R.T., and the Yellow G.,—the last chiefly for mixing with the blues for fine, fast green shades.

(2) THE STEAMING METHOD.—This process is suitable for all the Indanthrene colours mentioned above.

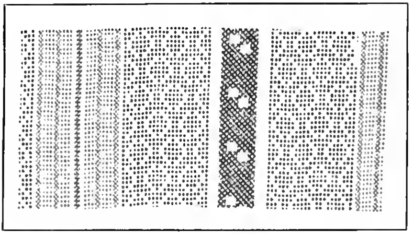
The reduction of the colouring matter is brought about by the action of *stannous oxide* in presence of caustic soda, and under the influence of hot air-free steam. For pale colours the ordinary 2–3 minutes' steaming is sufficient, but dark colours are improved considerably by a longer steaming, or by being steamed twice. In any case the steam ought to be as free from air as possible, and the supply pipe and ventilating arrangements ought to be such as will ensure the constant supply of fresh steam.

The various shades of printing colours are prepared in much the same way as for the preceding process, viz.—

Dark.	*Medium.*	*Light.*	*Pale.*		
200	100	50	20	grms.	Indanthrene colour (any).
80	40	25	25	,,	stannous oxide paste 50 per cent.
50	50	30	30	,,	glycerin.
670	600	600	600	,,	alkaline thickening B.S.
...	210	295	325	,,	dextrin and Senegal paste.
1000	1000	1000	1000		

The oxide of tin is added to the colouring matter, and well stirred in with a steel wire brush to break up any lumps of either ; the other ingredients are then added in the above order, and the whole, after well stirring, is strained and printed.

The addition of 50–100 grammes of a 30 per cent. alcoholic solution of β-naphthol to every 1000 grms. of light and medium printing colours increases the depth of shade and promotes regular development of the colour. It therefore enables a smaller amount of dyestuff to be used, and at the same time improves the quality of the work. For fine patterns the addition of naphthol is unnecessary.



Indanthrene Violet { Blue G.C.D. } (B.A.S.F.).
,, Green { Yellow G. }

After printing, the goods are steamed in the rapid ager for from 5–10 minutes according to the intensity of the shade printed; they are then immediately washed in the full open width, passed through dilute sulphuric acid (1 part acid 168° Tw. to 1000 parts water) to neutralise the last traces of soda, well washed again, and finally soaped at 175° F.

The stannous oxide and alkaline thickening are prepared as follows.—

Alkaline Thickening B.S.

300 grms. 60 per cent. British gum paste.
350 ,, 50 per cent. gum Senegal.

Add to this gradually *in the cold*

1350 grms. caustic soda 90° Tw.

2000

Stannous Oxide 50 per cent.

{ 150 grms. tin crystals.
{ 20 ,, hydrochloric acid 30° Tw.
{ 600 ,, cold water.

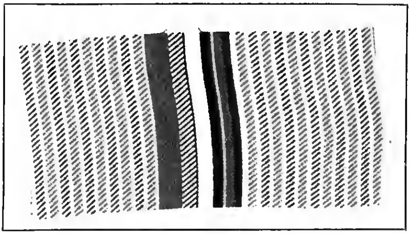
Dissolve and add gradually whilst stirring

{ 70 grms. soda ash in
{ 600 ,, water.

Wash the precipitated oxide with water by decantation and then filter it to a 50 per cent. paste.

If desired, the above method of preparing steam colours can be modified by using Rongalite C. in place of the tin oxide. The results obtained are practically identical; and whether tin or Rongalite is used, the colours, whilst pure and fast, are not so deep as those obtained by the caustic soda-tin-iron method.

In case a proper "hydrosulphite ager" is not available for the steaming, and an ordinary type of Mather & Platt machine has to be used, the quantity of tin oxide (or of Rongalite) must be increased in order to counteract the oxidising action of the air which enters the steaming chamber through the inlet and outlet slits of the machine.



Compound Shades with Indanthrenes (B.A.S.F.).

By this process of applying Indanthrene colours it is possible to obtain combined effects by printing *light shades* of them on β-naphthol-prepared cloth, along with any of the diazo printing colours. The longer steaming, however, that is necessary for the full development of dark and medium shades is detrimental to the azo colours; so that when these latter are intended to work in the same pattern as Indanthrene colours, it is preferable to adopt the preceding process, viz. the caustic soda-tin-iron method.

(3) THE SODA-ASH METHOD (with steaming).—The only difference between this method and the one described last is that soda ash is employed as the alkali, in place of the more energetic caustic soda. In other respects the two methods are identical, at least in so far as the preparation of the printing colours and the after-treatment of the cloth are concerned.

For dark, full shades in outlines and small objects, it is always best to use the "caustic soda steaming process," but for the production of light shades and medium blotches of the greatest uniformity the "soda-ash process" can be employed with advantage. Moreover, the weaker alkalinity of the colours renders them more suitable for printing in combination with Aniline black; and they can also be printed along with the ordinary steam colours—Alizarin, etc.

The reducing agent employed may be either stannous oxide or "hydrosulphite" according to circumstances. The choice of the most suitable will be determined by the results of practical trials made with a view to utilising existing plant to the best advantage. For an ordinary rapid ager working under the best conditions, *i.e.* with a copious supply of air-free steam, the stannous oxide will usually yield more satisfactory results than hydrosulphites of any brand; but with the modern high-temperature agers, Rongalite C., etc. will leave little to be desired in the way of good, fast colours.

According to the particular conditions obtaining then, either of the following reducing pastes may be used.

Reducing Paste I.

100 grms. soda ash.
230 ,, water.
475 ,, British gum and Senegal thickening.
100 ,, glycerin.
45 ,, Rongalite C.
50 ,, water.

1000 or

Reducing Paste II.

100 grms. soda ash.
200 ,, water.
450 ,, British gum and Senegal thickening.
100 ,, glycerin.

Dissolve, cool, and add

50 grms. stannous oxide paste 50 per cent.
100 ,, 30 per cent. alcoholic sol. of β naphthol.

1000

The printing colours consist of—

10 – 120 grms. of Indanthrene colour.
990 – 880 ,, reducing paste I. or II.

1000 1000

After printing, the goods are steamed 5–7 minutes in air-free steam, then thoroughly washed and soured in sulphuric acid at $\frac{1}{5}$° Tw. (about 1 : 850). For very light shades a short steaming of 3–4 minutes is often sufficient; darker shades require the full 7 minutes, and in all cases the longer the steaming the deeper the colour.

For this process the following colours are specially suitable:—

Indanthrene blues R.S. and G.C.D.	Indanthrene yellows R. and G.
" violets R.T., R., and R.R. extra.	" brown B.
" dark blue B.O.	" grey B.
Vat red B.A.S.F./B. paste.	

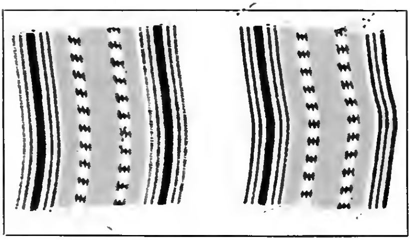
The last—Vat red—gives in pale shades, by the soda-ash method (Reducing Paste I.), beautiful rose pinks of great fastness. For a red it is too blue in tone, and must be modified by the addition of Indanthrene yellow R. It is then applied in exactly the same way as the artificial Indigo (Indigo pure or L. of the Badische). The same remarks apply more or less to all the Indanthrene colours: dark shades require the more strongly alkaline pastes.

VAT RED.

150	grms.	Vat red B.A.S.F./B. paste.
25	"	Indanthrene yellow R. paste.
770	"	alkaline thickening for Indigo.
55	"	Rongalite C. (or hydrosulphite N.F. conc.).
1000		

"VAT RED" PINK.

20	grms.	Vat Red B.A.S.F./B. paste.
980	"	reducing paste I.
1000		



Vat Red B.A.S.F./B. and Indigo.

DARK GREEN.

70	grms.	Indanthrene blue R.S. paste.
30	"	Indanthrene yellow G. paste.
50	"	stannous oxide 50 per cent. paste.
50	"	glycerin.
800	"	alkaline thickening for Indigo.
1000		

Other compound shades may be made by mixing suitable colours according to the well-known principles of colour mixing.

When Indanthrene colours are printed simultaneously with ordinary steam colours, the goods are first steamed as usual for Indanthrenes (4–7 minutes), and then further for $\frac{3}{4}$–1 hour for the fixation of the Alizarins, etc. The sulphuric acid treatment must also be omitted or replaced by one with acetic acid. In general, however, the ordinary washing and soaping will sufficiently clear the goods of alkali.

As is the case with all processes for Indanthrene colours, the steaming and washing ought to be proceeded with as soon after printing as possible. Prolonged exposure to the air, either before or after printing, is certain to result in irregularity in the colours of the finished goods.

Taken altogether, therefore, the employment of Indanthrene colours is best restricted to styles that can be handled quickly, *i.e.* those of which the colours are fully developed by a short run through one or other of the various types of "rapid steam agers."

Glucose Process for Indanthrene Colours.—It has been found possible to print these colouring matters on glucose-prepared cloth in the same way as Indigo; and although one of the preceding three methods is to be preferred wherever it can be applied, it is not unlikely that the "glucose process" will prove to be a valuable alternative method in many cases,—as, for instance, in the alkaline discharging of Turkey red, for the production of a brighter green than can be obtained from a mixture of Chrome yellow and Indigo, which latter is a dull blue compared with Indanthrene blue R.S. or G.C.D.

The best results are obtained by steaming for 2–3 minutes in an ordinary Indigo steamer, whereas for Indigo itself $\frac{1}{2}$-$\frac{3}{4}$ minute is sufficient. The difference between the longer and shorter steaming is very pronounced, the shades produced by the former being twice the depth of those produced by the latter. Probably a still longer steaming would further improve the colours as regards their intensity. In the case of Indanthrene brown B. the difference is not very marked; if anything, judging by a practical trial, the shorter steaming yields the darker shade. With this exception, however, the reverse holds good.

A comparison of the results obtained by the glucose process with those by the stannous oxide method shows that the latter is, in general, the most advantageous. The only colours, of those tested, that come out better in the glucose way are the Indanthrene clarets B. and B. extra and Indanthrene red R. A few of the others appear to be a little brighter, but this may be accounted for by their want of intensity.

The colours prepared in the following way are printed on cloth prepared as for indigo in a 20–30 per cent. solution of glucose and carefully dried.

Printing Colour.

100	grms.	Indanthrene dyestuff.
50	,,	glycerin.
700	,,	alkaline thickening for Indigo.
150	,,	gum-dextrin thickening.
1000		

Print, dry carefully, and then steam at once for 2–3 minutes in damp air-free steam. The steaming is done in either the special Indigo steamer or in the ordinary ager. After steaming well, wash in plenty of fresh cold water, and finally soap at 180° F.

In using Indanthrene colours it is well to take careful note of the following points:—

(1) Indanthrene green B. is sensitive to the action of Rongalite and other hydrosulphites, and it is therefore best applied by the stannous oxide method (Method 2).

(2) Indanthrene yellows R. and G. are preferably printed by the soda-steaming process (Method 3).

(3) Anthraflavone yellow is only suitable for the production of bright greens, fast to light, in combination with the blues R.S. and G.C.D.; by itself it is not very fast to light.

(4) The brightest of the blues (the G.C.D. brand) yields the fullest shades by the tin-iron-caustic-soda method (Method 1); it can also be applied to advantage by the stannous oxide process (Method 2). Caustic soda is essential to its proper development, and consequently Method 3 is unsuitable, since, although it gives bright colours, they do not represent the full value of the quantity of colour used.

(5) On goods prepared with β naphthol, Indanthrene colours come out darker than on either plain or oiled cloth.

(6) Oiled cloth is the best for the steaming processes (2 and 3).

(7) The goods ought not to lie either before or after steaming, otherwise irregularity of colour is certain to occur.

The Algol Colours (Bayer).—This range of dyestuffs includes a variety of exceedingly fast colours, but so far has not been utilised to any great extent in calico printing, chiefly on the score of expense.

The Helindone Colours (M., L. & B.).—With one exception, all the Helindone colours of Messrs Meister, Lucius & Brüning are derivatives of Indigo, or are indigoid in character. They are quite insoluble in the ordinary solvents, but their leuco-compounds dissolve readily in caustic soda, and they may therefore be applied to printing by methods analogous to those employed for other vat colours.

The fastness of the Helindone colours is excellent in all respects. Not only are they exceptionally fast to washing, acids, alkalies, and light (Helindone scarlet S. is inferior to the rest of the group in this respect), but the majority of them also resist the action of bleaching agents to a remarkable extent—a quality which renders them of the utmost value for the production of dress goods, such as muslins, shirtings, blouse materials, etc., all of which are expected to withstand the somewhat drastic treatment meted out to them in most laundries.

A glance at the list given below will be sufficient to show that the Helindone colours, in combination with various Brom-indigoes, are capable of giving an extensive range of useful shades.

Indigo M.L.B./4 B.
,, ,, /5 B.
,, ,, 6 B.
Helindone yellow 3 G.N.
,, ,, 3 G.
,, orange R.

Helindone red 3 B.
,, ,, B.
,, fast scarlet R.
,, scarlet S.
,, brown G.
,, grey B.B.

The above colours may be worked together, and in suitable mixtures yield various shades of green, olive, grey, brown, fawn, and other "mode" colours.

As regards the printing of Helindone colours, various methods have been proposed, but the most generally useful is that in which the printing pastes contain, besides colouring matter, the usual ingredients, viz. caustic soda, glycerin, hydrosulphite, and British gum. In some cases the working qualities of the colour are improved by the addition of olive oil, sulphite of potash, and dissolving salt B. (benzyl-sulphanilate of soda). In other respects the colours are treated, for the most part, exactly like the Ciba colours, which they closely resemble in general properties.

The chief point to observe, in the successful printing of Helindone colours, is to avoid the employment of too much alkali, since an excess tends to impair the purity and intensity of the shades. Helindone red B.[1] *may* be printed without any alkali at all, while the other colours, contrary to most vat dyestuffs, require very little.

For the production of full shades of blue of a tone brighter than Indigo itself, the Brom-indigoes may be employed along with any of the artificial Indigoes. They reduce well with glucose in the presence of caustic soda, and this property enables them to be used either in the ordinary glucose process of Indigo printing, or, in Direct printing, as self colours, in cases where hydrosulphite is not available. On the whole, however, the hydrosulphite method is to be preferred.

The two patterns illustrating the application of the Helindone colours to calico printing have been produced from colours made up as follows:—

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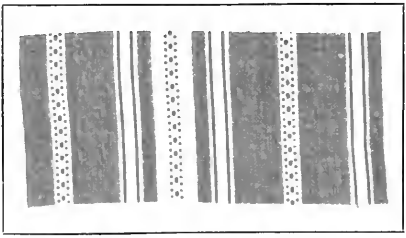
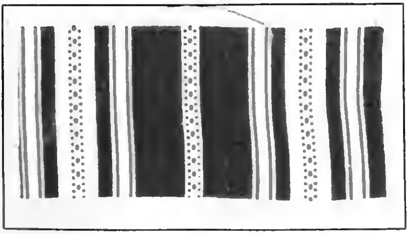
[1] Buckley, *Jour. of Soc. of Dyers and Colourists*, March 1910, p. 60.

	Red.	Green.	Brown.	Blue.
Helindone fast scarlet R. paste	400	...	...	...
,, brown G. paste	...	65	270	...
,, yellow 3 G.N.	...	27	...	...
,, red B. paste	...	...	15	...
Indigo M.L.B./5 B. paste	...	17	...	25
Glycerin	100	100	100	100
Water	40	335	40	511
British gum powder	150	275	250	250
{ Dissolving salt B.	30	20	30	5
{ Water	30	20	30	5
Caustic soda 76° Tw.	60	33	80	15
Hydrosulphite conc. powder	40	13	40	4
Heat until reduced, then cool and add—				
Olive oil	30	30	30	30
Hydrosulphite conc. 50 per cent. solution	100	30	100	30
Sulphite of potash 90° Tw.	...	15	15	...
British gum paste	20	20	...	25
	1000	1000	1000	1000

After printing, the goods are run twice through the rapid ager at 102° C. for three minutes each time; they are then either soaped at the boil or, alternatively, first rinsed, then "chromed" (0·2 per cent. solution of bichromate of soda) at 60° C., rinsed again, and finally soaped at the boil.


Helindone Brown and Indigo M.L.B./5 B.

Helindone scarlet S., Helindone fast scarlet R., and Helindone yellow 3 G.N., when used alone, yield better results if steamed in moist steam at 100°–102° C. Usually, however, the conditions obtaining in the ordinary hydrosulphite ager give sufficiently satisfactory results.


Helindone fast Scarlet R. and Green (Mixture) (M., L. & B.).

A recent addition to the Helindone series is Helindone yellow 3 G., a colouring matter yielding a pure yellow which is fast to light, acids, alkalies, soap, and chlorine.

Helindone yellow 3 G. is best printed in the reduced state with slightly alkaline thickenings, and an addition of dissolving salt B. is advisable in order to obtain the best results, both as regards depth of shade and working quality of colour. The makers recommend the following proportions for a full shade of yellow:—

HELINDONE YELLOW 3 G.

150	grms.	Helindone yellow 3 G.
100	,,	glycerin.
60	,,	caustic soda 76° Tw.
30	,,	dissolving salt B.
150	,,	water.
200	,,	British gum powder.

Heat at 60° C. until the reduction is complete and, when a pure blood-red colour is obtained, add—

30	grms.	olive oil.
50	,,	Hydrosulphite N.F. conc.
50	,,	British gum solution.
150	,,	sulphite of potash 90° Tw.
1000		

Print and treat the goods as described for other Helindone colours.

Printed according to the foregoing instructions, the Helindone colours give brilliant shades that are exceptionally fast to almost all reagents. They withstand the hydrosulphite discharge process, and consequently may be used for obtaining coloured discharge effects on the Direct colours, Azo colours, etc.; and, as they resist the action of oxidising agents to a remarkable extent, they cannot be discharged, like Indigo, by the chromate or chlorate methods. A notable exception is Helindone Grey G.G., which may be discharged with hydrosulphite.

Notes on the Vat Colours.—From the point of view of a colourist pure and simple, the vat colours as a class possess nearly all the qualities that colours are desired to possess. They are easy to apply, they give beautiful shades, and, above all, they are characterised by great fastness. To some extent their properties debar them from being associated with other classes of colouring matters, but this in itself is no great disadvantage, since it makes it imperative to use them only in conjunction with such colours as will withstand the severe after-treatment that is necessary to develop their full beauty and intensity. In any case it is altogether inexpedient to print multicolour patterns in colours that possess widely different degrees of stability, and especially is it so when it is unnecessary to mix up different classes of colouring matters in a given colour scheme. With the exception of a bright *fast* red, almost any desired colour can be obtained from one or other of the series of vat dyestuffs; and as most vat dyestuffs can be used in combination with the Alizarin colours, the absence of a good red is not of much moment. Such reds as Vat red, Helindone red 3 B., and others are quite good enough for compound shades of violet, etc., even if no such bright colours as the Ciba violets were on the market.

Unfortunately, however, there is one great disadvantage attaching to the use of the Ciba, Indanthrene, Algol, and Helindone colours, namely, that of expense. With regard to the Ciba blues and other brominated Indigoes, attention should be drawn to the fact that they are "tinctorially weak," *i.e.* that in consequence of their great molecular weight a larger amount of dyestuff is required to produce a given depth of shade than is the case with such colours as Indigo. The expense of these colours is not only due to their tinctorial weakness, but also to the large percentage of bromine which they contain. Indigo M.L.B./6B., for instance, is the penta-brome compound, and contains therefore about 66 per cent. of bromine, which is not merely an expensive substance itself, but which is the direct cause of the decrease in tinctorial value. With respect to other vat colours, the high price may be equally well attributed to the high cost of manufacture.

For this reason alone the use of vat dyestuffs (with the exception of the sulphide colours) is restricted to the highest class of work in shirtings and dress materials, and then usually to fine patterns only, or such as are printed in pale shades.

It is to be hoped that in the near future the price of these excellent colours will be brought down to a point that will enable calico printers to apply them to a much wider range of styles than commercial considerations warrant them in doing at present.

Steam Mineral Colours.

With the single exception of Prussian blue, the production of mineral pigments on the fibre by steaming is a thing of the past. The shades so obtained are neither so bright nor, of necessity, so intense as those got by first printing a salt of one of the main constituents, and then precipitating the pigment by running through a bath containing the other constituent.

STEAM CHROME YELLOWS AND ORANGES may be obtained, according to H. Schmid, by printing a mixture of a soluble lead salt and an insoluble chromate.

A suitable recipe for the preparation of steam chrome yellow is as under :—

STEAM CHROME YELLOW.

400 grms. 6 per cent. gum tragacanth thickening.
70 ,, acetic acid 9° Tw.
110 ,, lead nitrate }
120 ,, lead acetate } or 250 of lead acetate.

Dissolve and add, when cooled a little,

100 grms. aluminium nitrate acetate 28° Tw.

Cool and add

200 ,, zinc chromate 50 per cent. (or 170 grms. of barium chromate 50 per cent.)

1000

Print, steam for one hour, pass through a hot bath of—

{ 25 grms. sodium sulphate }
{ 0·5 ,, tartaric acid } at 140° F.
{ 1 litre water }

Wash and dry up.

The above gives a lemon-yellow pigment of a composition approximating to $PbCrO_4.PbSO_4$. It also contains a little aluminium oxide, which, as is well known, tends to preserve the delicate tone of "lemon chrome." The small quantity of tartaric acid in the sodium sulphate solution ensures the absence of any free carbonates, which would, of course, be liable to redden the shade of the yellow. At the same time, it probably reduces a minute portion of the chromate, thus helping to preserve the greenish canary yellow of the finest shades of lemon yellow.

A chrome orange proper cannot be obtained by steaming alone, but a much redder shade of yellow, which can afterwards be converted into a pure orange, can be obtained by a modification of the above recipe for the lemon yellow.

STEAM CHROME ORANGE.

200 grms. lead nitrate.
435 ,, 5 per cent. tragacanth thickening.

Dissolve and add when at 80° F.

25 grms. acetate of soda.
340 ,, barium chromate 50 per cent. paste.

1000

Print, steam, and soap.

This printing colour gives a golden or maize yellow, which (if printed with colours that will stand the treatment) may be converted into an orange by passing through boiling lime water (1/1000, or 1 lb. quicklime in 100 gallons of water). When six "lumps" of 120 yards each have passed through, the bath is replenished with 175 grms. of lime per 1000 litres, or 2½ oz. per 100 gallons. After "liming," the goods are well washed and soaped.

The great defect of all lead yellows is that they tend to blacken when exposed to the impure air of towns. This is due to the formation of lead sulphide caused by the presence of sulphuretted hydrogen in the atmosphere.

CADMIUM YELLOW, on the contrary, is a sulphide itself, so that it is quite unaffected by sulphuretted hydrogen. In fact, the chief use of cadmium salts in calico printing is not for the production of the fine but expensive pigment so largely used by artists, but for the preservation of precipitated lead yellows. For this purpose a certain amount of cadmium nitrate is ground up and dissolved in the pigment paste; and so long as any soluble salt of cadmium remains, the sulphuretted hydrogen will combine with it in preference to acting upon the insoluble and more inert lead chromate.

In cases where its expense is not prohibitive, cadmium nitrate may be used for the production of an exceedingly brilliant yellow, which is quite permanent in impure atmospheres, and quite as fast to light and soaping as the various lead yellows. The formation of cadmium sulphide on the fibre by steaming depends upon the action of sodium thiosulphate on a soluble cadmium salt. Whether free sulphur is liberated during the reaction in the steaming chamber, or whether an unstable cadmium thiosulphate is the first product, is not definitely known. The latter explanation is perhaps the more likely, though it is possible to obtain the same result by steaming a mixture of flowers of sulphur and cadmium nitrate.

$$(1)\ Cd(NO_3)_2 + Na_2S_2O_3 = CdS_2O_3 + 2NaNO_3.$$

$$(2)\ CdS_2O_3 + H_2O = CdS + H_2SO_4.$$

Steam.

In any case free mineral acid is liberated, as is proved by the tendering of the fibre. This latter defect is overcome by the addition of sodium acetate. The final result may perhaps be expressed by the following equation:—

$$Cd(NO_3)_2 + Na_2S_2O_3 + H_2O + 2NaC_2H_3O_2 = CdS + 2NaNO_3 + Na_2SO_4 + 2C_2H_4O_2.$$

The recipe given below is based on these lines, and was formerly in use on the large scale.

STEAM CADMIUM YELLOW.

100 grms. cadmium nitrate.
670 ,, 5 per cent. tragacanth thickening.

Dissolve, cool, and add

110 grms. sodium thiosulphate.
120 ,, sodium acetate.

1000

Allow to stand a day or two before use. Then print on white cloth, steam for an hour, wash, and soap.

As a printing colour, Cadmium yellow, in spite of its excellent qualities, has never been employed to anything like the same extent as the lead chromates; and this not merely on account of its greater cost, but because, for most purposes, the "chrome" yellows and oranges are sufficiently permanent, and at the same time adaptable to a greater variety of styles.

PRUSSIAN BLUE.—Prior to the introduction of the aniline colours, Prussian blue was the only really bright blue at the disposal of the calico printer. The usual method of obtaining blue patterns was to pass cloth mordanted (by printing or padding) in ferric oxide through an acidulated solution of potassium ferrocyanide.

$$4Fe(OH)_3 + 3K_4Fe(CN)_6 + 6H_2SO_4 = \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3} + 6K_2SO_4 + 12H_2O.$$

The presence of tin salts imparts a fine purplish tone to the blue, and in all "steam Prussian blues" stannous ferrocyanide plays an important part. Other ingredients also are added to assist the reaction during the steaming operation, *e.g.* mineral acids which liberate the hydroferri- or hydroferrocyanic acids which decompose under the influence of steam with the formation of insoluble Prussian blue, and organic acids which act as solvents (oxalic), and generally accelerate the production of the blue.

Steam Prussian blues consist essentially of stannous and potassium ferrocyanides and acids or acid salts. Most of them, however, contain ferricyanide of potash in addition to the other ingredients, and its presence undoubtedly improves the shade. After printing, they are steamed, and then passed through a warm chrome bath, or a very weak solution of "chemick," to ensure the complete oxidation of any ferrous ferrocyanide which may have escaped oxidation during "steaming."

An exposure to the air for some time would have the same effect, but "chroming" develops the colour instantaneously, and is, moreover, a necessary operation in the production of styles to which Prussian blue is well adapted.

The preparation of printing colours was formerly a matter of profound secrecy among colour mixers, and, as a result of their "rule of thumb" methods, the proportions of the ingredients employed to obtain one and the same effect differed considerably. Each colour mixer worked according to his fancy, hence the existence of a large number of recipes for "steam Prussian blue," which was formerly the only bright blue available, and, as such, one of the most important colours then known.

It would serve no useful purpose to give a selection of these old recipes; many of them are badly balanced, and most of them are better fitted for Turkey-red "discharging" than for steam work; they contain an unnecessarily large excess of acid, and, judging from practical trials of a few of them, they must have caused an immense amount of damage in the way of "tender" cloth.

The following two recipes have given good results in general steam work on the large scale, and will serve as types of the preparation of "steam Prussian blue."

STEAM PRUSSIAN BLUE 1.

350	grms.	water.
70	,,	starch.
10	,,	ammonium chloride.
15	,,	olive oil.

Boil, cool, and add

400	grms.	tin pulp 30 per cent.
60	,,	yellow prussiate of potash (finely ground).
30	,,	red ,, ,, ,,
30	,,	tartaric acid (powdered).
5	,,	oxalic acid.
25	,,	water.
5	,,	sulphuric acid 168° Tw.
100	,,	water.

1100 = 1000 after boiling the first part.

STEAM PRUSSIAN BLUE II.

300	grms.	water.
120	,,	light British gum.
60	,,	yellow Prussiate of potash.
40	,,	ammonium chloride.

Boil, cool, and add

400	,,	tin pulp 30 per cent.
20	,,	red prussiate.
60	,,	boiling water.
10	,,	alum (finely ground).
20	,,	bisulphate of soda [$NaHSO_4$] (powdered).
5	,,	oxalic acid.
5	,,	sulphuric acid 168° Tw.
60	,,	water.

1100 = 1000 when finished.

Print both these blues on either oiled or unoiled cloth; steam the goods for an hour, and then develop the full shade by a short run through a ½ per cent. solution of bichromate of potash at 140° F., wash well, and dry.

TIN PULP for above.

a	430	grms.	yellow prussiate of potash.
	2000	,,	water.
b	450	,,	stannous chloride.
	100	,,	hydrochloric acid.
	2000	,,	water.

Dissolve *a* and *b* separately; add them together; wash the precipitate 4–5 times by decantation, and then filter it to 1500 grms. = about 30 per cent. paste of tin ferrocyanide.

In addition to acting as a simple blue, Prussian blue was also employed as the blue element of fast, deep "steam greens." For this purpose it was combined with Persian berry or Quercitron bark extracts, the tin lakes of which are very bright; so that very good clear greens and olives resulted from the mixture.

STEAM PRUSSIATE GREEN I.

520	grms.	water.
140	,,	Persian berry extract 48° Tw.
65	,,	powdered alum.
145	,,	British gum.
100	,,	yellow prussiate of potash. Boil, cool, and add—
15	,,	stannous chloride.
15	,,	oxalic acid.
110	,,	water.

1110 = 1000 when finished.

STEAM GREEN II.

530	grms.	water.
140	,,	Quercitron bark extact 48° Tw.
60	,,	alum.
145	,,	British gum. Boil, cool a little, and add—
100	,,	tin ferrocyanide (tin pulp) 30 per cent.
10	,,	red prussiate of potash.
50	,,	boiling water.
15	,,	oxalic acid.
50	,,	boiling water.

1100 = 1000 when finished. Print, etc., exactly as for Prussian blue.

The chief drawback of all Prussian blues is that they will not stand soaping. The slightest excess of alkali decomposes them, leaving yellow ferric oxide on the fibre. Exposure for any length of time to strong light causes them to fade somewhat, but they recover their original intensity again if kept in a dark place.

Steam Manganese Brown.—The excellent fastness of Manganese brown or Manganese bronze produced as a plain shade by passing cloth padded in manganese chloride through a solution of caustic soda and bleaching powder, or bichromate of potash and ammonia, led to several attempts being made to obtain the same colour directly by printing and steaming. Of these, the most successful was the method suggested by Balanche, who printed a mixture of manganese chloride, bichromate of soda, and acetate of soda. On steaming, an unstable chromate of manganese is formed which decomposes, with the ultimate formation of the brown oxide. The acetate of soda is added to prevent the tendering of the fibre by the hydrochloric acid liberated during the reaction.

Steam Manganese brown is out of date at the present time, having been displaced by other and more generally applicable colours. The following recipe will serve to illustrate the method of Balanche.

Steam Manganese Brown.

500 grms. water.
10 ,, olive oil.
100 ,, starch.

Boil, turn off steam, and, when cooled a little, add—

150 grms. bichromate of soda.

Cool and add

125 ,, manganese chloride [$MnCl_2.4H_2O$].
125 ,, acetate of soda.

1000

Print, steam, allow to lie an hour or two, and then wash and soap. If the other colours of the design allow of it, the goods are improved by a short run through "chemick" ½° Tw. immediately after steaming, in which case they may be washed and soaped at once without the necessity of lying exposed to the air.

All the steam mineral colours may be used in combination with the vegetable yellows and browns, and with a strong Logwood-iron or Logwood-chrome black; but the styles of work for which they were formerly in demand are now executed by other and more reliable means, and they have fallen into practically complete disuse.

The Loose Steam Style.

This style is characterised by the brilliancy and fugitiveness of its colours. Any colouring matter that will give the required shade is used irrespective of its fastness or its capability of being fixed upon the fibre. The goods are not required to undergo any washing, fixing, or soaping operations, and are ready for finishing as soon as they are steamed. Even steaming is dispensed with, except in cases where it is cheaper or more convenient to use a mordant colour —*e.g.* Logwood black, Alizarin chocolate, Persian berry yellow, etc.—than to make up a special "loose" colour.

The cloth is usually prepared in "oleine," as already described, and the goods, after printing and steaming, are finished at once either by back starching or simply by "hot calendering."

Alizarin is often used for the red in "loose" work, and the olives and browns, blacks and chocolates are, as a rule, fast mordant colours, simply because they are the cheapest; but the pinks are for the most part phthalein colours like Phloxine, Eosine, and Rose Bengale; the yellows Auramine or Thioflavine T.

without tannic acid; and the blues, violets, greens, and oranges are also basic colours without any mordant whatsoever. The basic aniline colours printed on oiled cloth are exceedingly bright, and are to some extent fixed, but they cannot be regarded as fast colours when so applied; in fact they are very "loose" to soap, and much less permanent to light than when fixed as double tannates.

Most of the acid colours are also largely employed in the "loose steam style," either alone or in conjunction with alumina or chrome mordants, with which they form lakes that are just sufficiently insoluble to prevent the colours from running during the processes connected with finishing. They are quite loose to soap.

The Crocein scarlets (Bayer), Scarlet 6 R., etc. (M., L. & B.), Ponceau F.F.R., and Amaranth (Cassella), none of which can be fixed on cotton, are all used for red grounds in "loose work" on calico. They produce excessively brilliant fiery reds, that wash out almost completely on soaping. In short, any colour that will yield the desired effect may be used in "loose work," whether it be fast or loose, a dyestuff proper, or merely a stain. Dark colours like blacks, navy blues, and chocolates, also olives, are generally fast mordant colours, while the lighter and brighter pinks, yellows, greens, and blues are obtained either from the acid colours, phthaleïn colours, or basic colours simply thickened, with or without the addition of "Alizarin oil," or the acetates of aluminium or chromium.

For Eosines and acid colours the following directions may be followed; the basic colours require no special mention.

Eosine Pink (with chrome).

25	grms.	Eosine or Erythrosine.
250	,,	water.
650	,,	starch or tragacanth paste.
75	,,	acetate of chrome 30° Tw.
1000		

All Eosines, Phloxines, Erythrosines, Rose Bengale, Uranine yellow, and other phthaleïn colours may be made up according to this recipe. If desired, the chrome can be left out, but the colours are apt to run in finishing if no chromium salt is present.

Croceïn Scarlet (with alumina).

35	grms.	Croceïn scarlet (any brand).
350	,,	water.
515	,,	tragacanth 5 per cent.
100	,	acetate of alumina 25° Tw.
1000		

This recipe will serve for all brands of oxy-azo colours of the Croceïn class; also for Naphthol yellows, etc., for which alum may be used in place of "red liquor."

The Soluble and Alkali blues may be applied in much the same way.

Soluble Blue.

35	grms.	Alkali or Soluble blue.
300	,,	water.
50	,,	ammonium citrate 20° Tw.
50	,,	neutral Turkey-red oil.
515	,,	starch-tragacanth paste.
50	,,	acetate of chrome 30°.
1000		

All the ammonium and sodium salts of the Rosaniline blue sulphonic acids can be applied in the same way.

The "loose steam style" of printing is used mainly for temporary decorations, and for certain foreign markets where brilliancy and cheapness are more important than fastness. Commercially it may be of some value, but technically and artistically it is of no interest whatever. The designs employed are frequently of the highest class, being those that have already served their purpose in previous years for the home market, but the colours in which they are printed are for the most part outrageously crude and vulgar; and while, perhaps, harmonising well enough with the brilliant surroundings of the East and the Tropics, they are at the same time unsuited to those regions by reason of their general fugitiveness.

"Padding" and "Covering" Styles.

These styles are not restricted to any particular class of colouring matters, and therefore they may be described here as well as elsewhere. In fact the effects obtained by "padding" and "covering" are due more to the mechanical means of applying the colouring matters to the fibre than to the chemical operations concerned in their fixation.

A "padded" or "covered" print displays a pattern, either in white or colour, or both combined, on a plain or figured coloured ground; and differs from an ordinary multicolour print, not in appearance, but in the method of its production, which allows of the same ground roller being used for any number of patterns. These patterns may be printed at separate times, and then all be "covered" or "padded" at once with one roller, thus effecting a great saving in both engraving and material (copper).

A "cover roller" is a copper roller engraved *all over* its surface with a fine delicate pattern, such as, for instance, a fine check, a honeycomb, a continuous trail, a series of fine perpendicular or of oblique lines or spots, etc.; and a "pad" is a roller engraved so as to print a uniform flat tint over the whole of the cloth, *i.e.* dye it on one side only. It is obvious that if a lighter colour is printed, with either of these rollers, on cloth already printed in a darker pattern, the latter will show through the lighter ground, and its darker colour will mask the paler tint of the over-print. When a white pattern is required on a coloured ground obtained in this way, the cloth is first printed with a mixture containing some substance or substances, capable of preventing the fixation of the colour applied by the cover or pad roller. These mixtures are known as "resists" or "reserves," and they act in various ways, sometimes destroying the colouring matter, sometimes preventing its combination with the mordant, and sometimes forming a soluble and stable compound with the mordant, which is washed out of the cloth in subsequent operations. Apart from their chemical action, "resists" also act mechanically by obstructing the entrance of the colour into the body of the cloth to be printed. Occasionally, indeed, their action is entirely mechanical.

The composition, etc., of the numerous "resists" used for different classes of colouring matters and mordants will be dealt with in a special chapter. It may be noted here, however, that citric acid (or tartrate of chromium) is the resist most commonly employed for Alizarin pinks.

The *modus operandi* in producing a red and white pattern on a pink or red ground by steaming is as follows:—

(1) First print on oiled cloth a two-colour design in steam Alizarin red and a thickened solution of tartrate of chromium. Dry the goods well and then—

(2) Over-print them with either a cover or pad roller in steam Alizarin red or pink. Dry well.

(3) Steam for one hour in the continuous steamer, wash well, and soap.

Wherever the tartrate of chromium has been printed, the ground colour printed over it will have been prevented from developing during the steaming operation, and in the final washing and soaping it will be removed entirely, carrying along with it those portions of the undeveloped colour which fell over it in the second printing, and leaving a more or less perfectly white object in its place. The red is, of course, unaffected by the over-printing, and develops in the usual way; so that the final effect obtained is that of a red and white pattern on a pink ground. The ground will be plain or "patterned" according as the roller used in the second- or over-printing was a "pad" or a "cover." A red pattern will, if large enough, show up well on a fine red "*cover*," but it is almost needless to point out that a "*pad*" should always be lighter than the lightest colour in the pattern to be "padded."

By employing suitable resisting agents, similar effects to the above can be obtained with the Insoluble azo colours, Sulphide colours, basic aniline colours, Aniline black, iron and aluminium mordants (dyed style), and, in fact, with almost every group of colouring substances known.

The object of both "resisting" and "discharging" processes is the same, *i.e.* the production of a white or coloured design on a coloured ground that has not been specially engraved for it. The main difference between the two, apart from chemical questions, is that in the case of "resists" the development or fixation of the ground colour is prevented altogether, while in the case of discharges the fully developed ground colour is subsequently destroyed by the oxidising or reducing action of the discharging agents—in a word, bleached out.

Colours produced on the Fibre by Condensation.

In the year 1898 the Farbwerke Höchst patented a process for the direct production and simultaneous fixation of certain basic colours on the fibre.

These colours are obtained by the condensation of the nitroso-bases of tertiary aromatic amines with various phenols, and constitute what are known as the oxazine dyestuffs. They form insoluble lakes with tannic acid, and their mode of application allows of all the components of the lakes being printed on the cloth together and without any previous preparation. A short steaming in the rapid ager is sufficient to develop the colour, which is then further fixed, in the usual way for basic dyestuffs, by a run through tartar emetic.

Several nitroso-bases and several phenols may be used in the production of these colouring matters, but the most interesting, and in fact the only, combination used to any extent on the large scale is Resorcin blue M.R., the result of the condensation of p-nitroso-dimethylaniline with resorcin.

The other bases and phenols yield different shades of blue, which have been distinguished from the above by the brand marks Resorcin or Nitroso-blue A.D., M.D., T.O., etc. They are not in much demand, as the Resorcin blue M.R. gives the most popular shade of navy blue.

Although the Nitroso- or Resorcin-blues are useful for the direct printing of dark navy-blue blotches, their most important application is in the production of imitation Indigo discharges. For this purpose the cloth is slop-padded in a mangle through a solution of the blue mixture; and as the development of the colour is prevented entirely by the presence of reducing agents, it is easily possible, by printing these on the padded and dried cloth, *before steaming*, to obtain fine resist effects in white and colours on a deep indigo-like ground.

Para-nitroso-dimethylaniline comes into commerce either solid or in the form of a 50 per cent. paste, as Nitroso-base M.; and resorcin is supplied either as such, or mixed with the requisite quantity of tannic acid, as Tannoxyphenol R.

The hydrochloride of p-nitroso-dimethylaniline may also be used in place of Nitroso-base M.; it is very soluble in water, but otherwise has no advantage over the base.

In preparing either the printing or the padding colour the following directions are to be observed:—

The nitroso-base is first dissolved in water containing hydrochloric acid and a little glycerin, and is then mixed with the thickening; to this is then added a solution of resorcin or Tannoxyphenol R. in water, and finally a small quantity of oxalic acid. If resorcin is used, the tannic acid is added separately, and either before or after the oxalic acid.

Nitroso-Blue M.R. (for printing), (M., L. & B.) I.

6,000	grms.	acid starch paste.
200	,,	glycerin.
Add		
260	,,	Nitroso-base M. 50 per cent.
207	,,	water.
87	,,	hydrochloric acid 36° Tw.
Mix well and add first		
200	grms.	resorcin in
1470	,,	water.
60	,,	oxalic acid.
500	,,	water.
600	,,	tannic acid 50 per cent. solution in acetic acid.
400	,,	phosphate of soda 20 per cent. solution.
To 10,000	,,	with water.

Print on white cloth, dry gently, steam for 2–3 minutes at 212° F. in the rapid ager, and then fix through tartar emetic exactly as for basic dyestuffs, wash and soap.

With Tannoxyphenol the same procedure is observed, except that the above quantities of resorcin and tannic acid are replaced by 325 grms. of Tannoxyphenol.

The phosphate of soda is introduced to prevent the tendering of the fibre by the acids during steaming.

The amount of tannic used has considerable influence on the shade produced. By diminishing the above quantity a redder and rather darker shade of blue is obtained; by increasing it, the shade becomes greener and a little lighter, and at the same time faster to soaping.

Padding colours are made up in exactly the same way as printing colours, with the exception that the acid starch paste is replaced by water or a thin tragacanth mucilage.

For particulars of the methods of resisting Nitroso-blues, see under "Resists and Discharges."

The drying of Nitroso-blues, whether printed or padded, requires careful attention. If possible, the goods should be dried in hot air, care being taken to prevent them from touching any of the drying chests that may form part of the apparatus. If over-dried, the final shade becomes dull and grey-looking. The best results are obtained when the colour of the dried goods is a pure bright yellow. At the same time, by working with an acid colour containing no phosphate, it is possible, with care, to dry the goods over steam-heated cylinders and yet obtain satisfactory results. In such cases the first three or four cylinders must be wrapped with calico, and the temperature of the rest must be kept down to a point just sufficient to dry properly. The colour given below has given good results in practical trials.

RESORCIN BLUE II.

26	grms.	Nitroso-base M. 50 per cent.
25	,,	water.
20	,,	phosphoric acid 50 per cent.
633	,,	acid starch paste.

Mix and add

20	,,	resorcin.
150	,,	water.
30	,,	tannic acid.
30	,,	acetic acid.
6	,,	oxalic acid
60	,,	water.
1000		

Print, dry gently as described, steam 2–3 minutes at 200° F., fix in tartar emetic and chalk, wash and soap.

Another colour which may be dried over tins is as follows:—

NITROSO-BLUE III.

530	grms.	thick starch tragacanth paste.	
15	,,	glycerin.	
24	,,	Nitroso-blue base M. 50 per cent.	Dissolve lukewarm.
200	,,	acetic acid 9° Tw.	

Mix, cool, and add

20	grms.	resorcin in
100	,,	water.
60	,,	20 per cent. oxalic solution.
60	,,	50 per cent. acetic acid tannin sol.
Make to 1000		

Print, etc., as for Blue II.

Nitroso-blues, being fixed with tannic acid, can be toned at will by the addition of suitable basic dyestuffs, or they can be mixed with existing basic printing colours to produce greens, etc. The usual colours made use of for toning are Auramine, Methyl violet, Methylene blue, and Brilliant and Methylene greens.

Nitroso-blue M.R., when produced according to the first recipe, can be steamed for an hour, after the first short run through the rapid ager, without injuring the shade and without tendering the fibre; so that it is suitable for printing along with Alizarin red and other steam colours.

The Nitroso colours form a group apart from all others; but as they resemble steam colours more than any other class, and as they are applied by direct printing, they have been described along with this style in preference to treating them in a special chapter.

Notes on the Preparation of Compound Shades.

It rarely happens that all the separate colours of a multi-colour pattern are obtained from pure unmixed dyestuffs. In the majority of cases, not more than one or two of the colours of an elaborate colour scheme are so obtained, the rest of them, consisting of various shades of brown, olive, gold, grey, etc., being produced by the admixture of two or more suitable colouring matters. Since by far the greater number of printing colours in everyday use consist of mixtures of this sort—compound shades that are impossible to obtain from any single dyestuff—it is necessary that the calico printer's colourist should not only understand how to apply individual dyestuffs (that is, what thickenings, mordants, etc., to use), but that he should also know how to modify the shades they yield, and how to combine them for the production of the thousand and one soft, delicate, subdued colours that play so important a part in modern high-class textile printing. Merely to match or modify the actual shade of a colour is, at most, a question of a more or less lengthy series of experiments; but to match or modify it as desired, in tho shortest possible time, and in such a manner that its component colours will all behave in, approximately, the same way towards light, soap, and other destructive agencies, requires some knowledge of the theory of colour, and of the properties of the colouring matters employed.

For all practical purposes, the Newtonian theory of colour, which takes red, yellow, and blue as the primary colours, orange, green, and violet or purple as the secondaries, and the various shades of brown, olive, grey, etc., as tertiaries, is the only one applied in textile colouring. But it must be regarded more as a technically valuable, and quite the most convenient, *system of "colour mixing"* rather than as a scientific *theory of colour*; for while it accounts satisfactorily for the effects obtained by the combination of *coloured bodies*, it was based upon an erroneous conception of the nature of colour itself, and consequently it breaks down when applied in explanation of many of the most striking colour phenomena observed by later workers in the field opened up by Newton's own discovery that white light is a compound of seven distinct colours.

The following definitions will make plain the meaning of some of the terms used to distinguish between the various qualities of colour, and in connection with colouring matters.

(1) COLOUR itself is a mental effect produced by the wave pressure of the "ether" on that ultra-sensitive portion of the optic nerve which constitutes the retina of the eye. The waves of undecomposed white light produce the sensation of white, hence colour is the intangible product of the decomposition of light.

(2) COLOURING MATTERS, be they pigments, dyestuffs, or any other substance, are the material agents which decompose immaterial light in such a way that only one of its constituent colours, together with a larger amount of unaltered white light, is reflected from their surfaces. All bodies absorb a certain amount of light. If very little is absorbed, and that little as such, the body is white; but if the absorbed light be decomposed, the body appears coloured, and its particular colour depends upon which of the decomposition products it is unable to retain permanently. Thus a piece of Turkey-red cloth appears red in white light because, while reflecting the greater portion of the red light falling upon it, it absorbs the green rays, the rest complementing each other to form white light. But red is also capable of reflecting orange and purple, and if looked at through blue and yellow glasses will appear purple and orange respectively, owing to the fact that it reflects or returns just those particular shades of the two colours to which the glasses are transparent. The same applies to the various analogous effects obtained with other colours; at the same time it must be observed that, although all coloured bodies are capable of reflecting or are transparent to any one of a certain limited range of colours, they never, under any circumstances, reflect or transmit more than *one* colour at a time, and that colour varies with the kind of light thrown upon them: to put it in another way, the powers of absorption and reflection of coloured bodies vary with the light in which they are viewed. Red absorbs green entirely; therefore when Turkey red is viewed in green light it appears black, since pure green light contains no colour that is reflected by red.

Colouring matters will be referred to as *colours* simply from this point onwards.

(3) Shade.—Strictly speaking, this term refers to the chromatic composition of a colour. Thus Indigo, Prussian blue, and Alizarin blue represent different shades of blue. In a wider sense, "shade" is applied to distinguish between different intensities of the same colour, as for example dark and light "shades" of Indigo. This use of the term is perhaps incorrect, but it is difficult to describe the effects it represents otherwise, except by the use of the following term.

(4) Tint refers to that condition of a colour arising out of its dilution with water, paste, gum solution, or white. Its shade remains the same, but its intensity or depth is reduced. By a "tint" is generally understood a very pale colour.

(5) Reduction is a term used to denote both the thickening paste employed to reduce the intensity of a colour and the reduced colour itself. Thus starch paste is a "reduction," and a four-reduction of Alizarin pink means that one part of standard pink has been added to four parts of starch paste or other thickening.

(6) Tone is the effect produced on a colour by various influences which apparently modify its shade. A yellow spot on a red ground appears to be greener than the same spot on a blue ground; and again, a pink is always a pink in white light, whether the light be dull or bright, but it has a different appearance in each case. The colour remains the same, but its "tone" is modified.

(7) Harmony of Analogy is the effect of arranging a series of similar colours of different shades, strengths, and tints, as, for instance, the combination of yellows, browns, oranges, and chocolates.

(8) Harmony of Contrast, on the contrary, consists in the pleasing arrangement of different colours. Thus a floral design may be arranged to show a harmonious effect by using different colours for the flowers, leaves, stems, and background. For example, red, pink, yellow, and pale blue flowers, green or olive leaves, brown stems, and a dark blue background.

(9) Primary Colours are pure, unmixed colours. In all that relates to textile colouring and the arts generally, the primary colours are red, yellow, and blue. In their purest form they cannot be obtained by any sort of chromatic combination of other colours.

(10) Secondary Colours.—Orange, green, and violet are the result of mixing two primaries in any proportions.

(11) Tertiary Colours.—Browns, greys, and olives contain all three primaries in various proportions. Their qualitative composition (chromatically) is the same, their particular character being due to the predominance of one primary over the others. Tertiary colours result from the mixture of either the three primaries, or a primary and its complementary secondary, or from any two secondaries in any proportions.

(12) Complementary Colours.—Helmholtz and Maxwell regarded those colours as complementary which, when mixed together, produced *white light*. But as no mixture of coloured bodies can possibly yield white, this definition does not apply to dyestuffs, etc., and some other must therefore be found.

As all known colours consist of one or more of the three primaries—red, yellow, and blue—and as it is universally recognised that the presence of each of these (or their compounds) is absolutely essential to the perfect harmony of any colour scheme, it is clear that the absence of any one of them would create a feeling of dissatisfaction. The eye naturally craves for the missing colour—for the completion of the primary triad. So much so is this the case that it is impossible to look for long at a pure primary colour or an inharmonious combination without fatiguing the eye, which becomes to some extent blinded by the strain of continually striving to complete the set of primary colours. In order to avoid this colour weariness, it is customary in examining, say, Turkey red, for the cloth looker to cast his eyes from time to time on some bright-green object, such as green paper. Green being a secondary colour, composed of blue and yellow, makes up the complement, or completes the set of primary colours, and so affords relief to the eye.

The simplest method of determining the complementary of a given colour is to gaze fixedly at a fairly large spot of it for a minute or two, and then to cast the eye on a piece of white paper, when there will appear on the blank paper a similar spot, but of a quite different colour. This colour is the complementary of the one first looked at. If one eye only is used in the first instance, the effect of the complementary colour is much more pronounced by winking rapidly, with each eye alternately, at the white paper. In this way the following colours are found to be complementary:—

Red	to	Bluish-green.
Blue	,,	Yellowish-orange
Yellow	,,	Indigo blue (reddish).
Violet	,,	Greenish-yellow (lemon).
Green	,,	Yellowish-red (scarlet).
Sky-blue	,,	Full orange.

From this it will be seen that the primary colours are each complementary to the secondary colour formed by the mixtures of the other two primaries. The yellow taken as a primary is of a slight greenish tinge, *e.g.* lemon-yellow.

Complementary colours may be described equally well as those which, when mixed together in certain proportions, produce neutral grey or black. To dull or "flatten" the shade of any colour, therefore, it suffices to add a little of its complementary; a small quantity of black is thereby produced, and the principal colour is modified accordingly.

On the other hand, if, instead of mixing two complementary colours together, they are placed side by side, they mutually enhance each other's brilliancy. This is due to the fact that it is impossible to look at any colour for long without the sensation of its complementary being excited on the retina. It follows, therefore, that each colour is seen in its own light (the light that it reflects best), which, of course, adds enormously to the brilliancy of its shade. Complementary colours juxtaposed in this way are said to be in "full contrast." The most telling contrasts are naturally afforded by combinations of the primary colours with their complementary secondaries, but contrasts of a more subdued character also arise out of the analogous arrangements of secondary and tertiary colours. Thus—

Purple,	full contrast with	Yellow,	subdued contrast with	Olive.
Orange,	,, ,, ,,	Blue,	,, ,, ,,	Grey.
Green,	,, ,, ,,	Red,	,, ,, ,,	Brown.

Most of the finest and most artistic products of calico printing are "got up" in harmonious combinations of quiet tertiary colours, with a few touches of the more brilliant primaries and secondaries added here and there to enrich the whole, and give life and interest to what might otherwise be a dull, depressing effect.

At the same time, it must not be supposed that harmony in colour is in any way dependent on the use of broken tertiary shades. Quite otherwise, in fact; for perfectly harmonious results can be secured in any combination, simple or complex, which contains the three primary colours in proper proportions. The only condition of perfect harmony is that they be balanced properly; and so long as this condition is fulfilled, it matters not whether they are present as primaries, secondaries, or tertiaries. Thus the following simple arrangements of—

(1) Red, Blue, and Yellow (brilliant),
(2) Orange, Purple, and Green (bright),
(3) Brown, Bluish-grey, and Olive (subdued),

all form perfectly harmonious combinations, because they each contain the three primaries in one form or another. For the same reason, a combination of the above nine colours would be equally harmonious.

Except in small patterns, the first two combinations given above are unsuitable for the best class of decorative prints. To most people their effect is crude and hard; their brilliancy dazzles rather than satisfies the eye, and they soon become wearisome. Conversely, the combination of brown, grey, and olive, while certainly restful to the eye, is somewhat lacking in character (unless one at least of its elements approaches to the brightness of a secondary colour), and usually requires to be relieved by the addition of a brighter colour. After all, however, the choice of a "colouring" is to a great extent a matter of taste, and is governed largely by the purpose it is intended to serve: if its surroundings are too bright and lively in colour, a calico print will be none the worse for being subdued, whereas in dingy localities a brightly tinted cretonne pattern supplies a real want, and satisfies a feeling for colour, which, if not always understood, is generally experienced.

But while the harmonious arrangement of colours in a design is a branch of calico printing, the importance of which can scarcely be overestimated, it is a branch quite apart from the actual compounding of printing colours, and one which to discuss with any profit would require a separate volume. It belongs essentially to the artistic side of the industry; and as it is concerned with the *appearance* of colours irrespective of their *composition*, its treatment here would be out of place, even if it were possible. In fact, the sole object of the foregoing brief review of some of the more important optical properties of colour and of colouring matters has been to show (*a*) why red, yellow, and blue are still regarded, in the arts, as primary colours; and (*b*) why the "undulatory theory" of light is of little help to the textile colourist. The results obtained by the mixing of *immaterial coloured lights* afford absolutely no indication as to what to expect from a mixture of similarly *coloured material bodies*—pigments, etc. Taken altogether, it is questionable whether any relation at all exists between the production of white light and the production of colour harmony; and it is certain that the establishment of the true theory of light and colour has not conduced to any improvement on the superb colour effects of either the old Venetian artists or the Oriental craftsmen in carpets and pottery.

Application of the foregoing Principles.

The accumulated experience, derived from centuries of practice in the mixing of all descriptions of colouring matters, has demonstrated beyond question that the colour of any material object can be imitated, more or less perfectly, by *suitable* shades of red, yellow, and blue, or mixtures of these. Practically speaking, this means that all colours consist of one or more of the three colour elements, red, yellow, and blue; and therefore, starting out with these three, to which must be added the two extremes of non-colour—black and white—it ought to be possible to prepare an exact replica of any known shade. Further, every single shade of the infinite variety of colours met with in nature corresponds in qualitative chromatic composition with one of the following nine types:—Red, Yellow, Blue, Orange, Green, Purple, Brown, Grey, and Broken Green (Citrine or Olive); that is, all colours are either primaries, secondaries, or tertiaries.

The close relationship existing between the primary colours and their derivates, the secondaries and tertiaries, is clearly shown below. Thus—

THE PRIMARIES :— Red, Yellow, Blue.

THE SECONDARIES :—Orange = Red + Yellow.
Green = Yellow + Blue.
Purple = Blue + Red.

THE TERTIARIES :— Brown = Orange + Purple.
Grey = Green + Purple.
Olive = Green + Orange.

Brown is frequently called russet; and olive is also known as citrine and broken green.

Both the primaries and the secondaries occur in their purest form in the spectrum, and can be obtained by mixing suitable coloured lights, as well as from pigments and dyestuffs. On the contrary, the tertiaries can only exist in the presence of matter, and their formation depends entirely on the absorption of a considerable quantity of light. It is quite impossible to produce a tertiary colour by any mixture of lights. The addition of light to light only results in an increase of light, until finally pure white light is obtained; but the addition of the three primary colours to each other, in the form of pigments or dyestuffs, results in the destruction or absorption of light, and the consequent production of olive, brown, grey, or black, according to the strength and proportions of the colours used.

An analysis of the three typical tertiaries will show that they each contain red, yellow, and blue, and that they owe their difference in colour to the presence of an excess of one of these primary elements. Thus—

$$\text{BROWN} = \begin{cases} \text{Orange} = \begin{cases} \text{Yellow.} \\ \text{Red.} \end{cases} \\ \text{Purple} = \begin{cases} \text{Red.} \\ \text{Blue.} \end{cases} \end{cases}$$

$$\text{GREY} = \begin{cases} \text{Green} = \begin{cases} \text{Yellow.} \\ \text{Blue.} \end{cases} \\ \text{Purple} = \begin{cases} \text{Blue.} \\ \text{Red.} \end{cases} \end{cases}$$

$$\text{OLIVE} = \begin{cases} \text{Green} = \begin{cases} \text{Blue.} \\ \text{Yellow.} \end{cases} \\ \text{Orange} = \begin{cases} \text{Yellow.} \\ \text{Red.} \end{cases} \end{cases}$$

Red predominates in Brown.
Blue ,, ,, Grey.
Yellow ,, ,, Olive.

By varying the proportions of the primaries or secondaries, the above brown, grey, and olive may be made to approach as nearly as required to any of their constituent colours; so that sometimes a brown may be almost indistinguishable from an orange or a purple; an olive may appear almost pure green, yellow, or orange; and a grey may assume the appearance of any colour, since it is easily affected by any variation of its constituents. Further, by mixing the primaries in certain proportions, it is possible to obtain a dense black which, when reduced in strength, yields a useful series of neutral greys. These greys or black are always formed, to a greater or less extent, in any combination of the three primaries, and it is to their presence that the dulness of the resulting tertiary colours is due. Hence tertiary colours of any desired shade can be obtained either by directly mixing the three primaries, or by simply adding the required quantity of previously prepared grey or black to the primary or secondary colours that are to be modified.

So long as a compound colour is composed of only *two* primaries it is a secondary colour, whatever its shade may be, and however much one of its components may be in excess of the other. A purple may be any shade between red and blue; but if it consist of these two colours only without the admixture of any yellow, it is a secondary colour whether it approximate to red on the one side or to blue on the other. Add the slightest trace of yellow, however, and it at once becomes a tertiary colour. The addition may be so small as not to produce any perceptible difference in shade, but, all the same, it results in the formation of a minute quantity of black, which absorbs a corresponding amount of light, and so reduces the luminosity of the mixture.

The "dulling" of a *secondary* colour by the addition of a minute quantity of its complementary *primary* is called technically "toning," and the modification of its shade by increasing one or other of its two component primaries is known generally as "shading." The combined "toning" and "shading" of one or other of the primaries, *or their typical compounds*, constitutes the whole art of colour mixing.

From the foregoing it might be supposed, and not unreasonably, that, given pure primary red, blue, and yellow colouring matters, it would be possible to reproduce exactly every conceivable shade of colour that is to be found in nature and the arts. But neither practical nor theoretical considerations afford the slightest support to any such supposition; for, in the first place, perfectly pure primary colours do not exist except in the spectrum; and secondly, if they did, they would, on theoretical grounds, be totally unsuited for use in mixtures.

Impure primary colours, therefore, possess the qualities of their defects: their employment is not only demanded by theory, but is absolutely unavoidable in practice, because no others are available. But, for a given purpose, their impurity must be of a certain kind, otherwise they yield unsatisfactory results. Hence, in practice, the shades of the red, blue, and yellow elements used in the making of compound colours vary according to the class of colour required. Thus a red inclining to orange and a blue inclining to green would, when mixed together, produce a very dirty shade of purple (if not a brown), whereas if a bluish-red and reddish-blue were employed the resulting purple would be bright and pure. So also scarlet and a warm yellow give the brightest oranges, and greenish-yellow and greenish-blue the purest and most brilliant greens.

In a less degree, the same thing applies to tertiary shades, although in these it is easily possible to adjust the balance of the primaries. Still, in some cases it is difficult to match even a tertiary colour if its elements all possess the same kind of impurity. For instance, take the case of a warm orangy-brown: if its components consist of a crimson, a lemon-yellow (greenish-yellow), and reddish-blue, it is out of the question to expect anything approaching to the shade required; but if the crimson and lemon-yellow be replaced by scarlet and maize-yellow, the desired effect is obtained at once, because the excess of blue is eliminated.

Similarly, in olives excess of blue and red must be avoided; and in greys the blue element must always predominate, unless, of course, the grey is intended to be quite neutral.

Any group of colours employed in the making of an extensive range of compound colours may be most conveniently called a "series," and for the sake of distinguishing it from all other series it ought to be lettered thus, "Series A," etc. In a series of the three primary colours the red ought to be first, the yellow second, and the blue third; and this order ought to be preserved for every other series, whether its members be pure primaries or compound shades. If a fourth member is introduced, it ought to occupy a position between the two colours it most resembles. Thus—

A three-member Series.	*A four-member Series.*
1. Red element.	1. Red element.
2. Yellow element.	2. Yellow element.
3. Blue „	3. Green „
	4. Blue „

The first number denotes the Red element.
„ second „ „ „ Yellow element.
„ third „ „ „ Blue „
} In the first series (three-member).

Thus, calling the first series A, an olive written in the following manner—Olive 1.6.2 A—would imply that it was composed of 1 part of red, 6 parts of yellow, and 2 parts of blue. Any number written after the letter A would denote the extent to which it was diluted by the addition of thickening.

Olive 1.6.2 A 4. =	1	part	Red.
	6	parts	Yellow.
	2	„	Blue.
	36	„	thickening or reduction.

Here the full-strength olive consists of 9 parts by weight or volume; and as the final number (4) after the A indicates that 1 part must be diluted or "reduced" by 4 parts of thickening, the total amount of this latter is therefore 4 × 9, or 36 parts. It may be 36 gallons, quarts, pounds, or kilogrammes, according to the standard in use.

By far the greater number of compound colours in general use are quiet tertiary shades; and as these can be mixed as well from secondaries, or even from other and comparatively bright tertiaries, as from primaries, it is by no means essential that the members of every "series" should consist of primary colours, or of colours approximating to the primaries. Indeed, with the exception of bright oranges, purples, and yellowish-greens, very few compound colours call for the use of primary colours at all. Hence in practice the red element varies between orange and reddish-purple, the blue element between green and violet, and the yellow element between yellowish-orange and lemon-yellow. Within these limits all shades of colour may be used in different series intended for the production of browns, olives, greys, drabs, fawns, terra-cottas, buffs, and mode shades of every description.

In making use of abstract colours to illustrate the foregoing system of colour mixing, it has been impossible to give more than a rough indication of the composition of the several representative types of compound colours. The following concrete examples will supply this deficiency, the percentage of each dyestuff contained by the separate "elements" of each series of colours being given, together with the mordant used. The amount of mordant and the kind of thickening used must be determined by the properties of the dyestuff and the style of work in hand. When alterations in thickening are desired it is usual to indicate these by adding additional letters to the colour after the reduction number; thus Olive 1.8.2 A 4 G.T. means that the whole colour is thickened with gum tragacanth—the abbreviation G.T. being the initials of the thickening agent. Similarly, G.S. and G.A. represent gum Senegal and gum Arabic respectively; and so on for any other special thickening. The absence of any letters after the reduction number is usually taken to mean that the colour is made up with starch paste.

Series of Colours for Compound Shades.

General Rules of the Series.—In series of three members the colours are always arranged as nearly as possible in the order in which their types occur in the spectrum. This is a matter of convenience only, and may be modified at will; but it enables the composition of a shade to be recognised more readily if every colour is worked on the same general principle. In four-member series the same rule is observed, the only difference being in the manner of writing the colours on the printer's work sheet. Each series is given a distinctive letter or letters; the composition of the colours made from it is denoted by figures following the name of the colour; the order in which these figures occur corresponds to the order of the members in the series, and their value represents the relative proportions of the constituents of the compound colour they yield. The reduction of the strength of a colour is indicated by the final number after the distinctive series letter. Thus a series containing Orange, Yellow, Green, and Blue may bear the distinctive mark of X, and a brown written as Brown 4.2.0.1 X. 20 would consist of—

$$\left.\begin{cases}4 \text{ parts Orange X}\\ 2 \quad ,, \quad \text{Yellow X}\\ \quad \text{No Green and}\\ 1 \text{ part Blue X}\end{cases}\right\} = 7 \text{ parts.}$$

$$140 \text{ parts starch paste} = (7 \times 20).$$

Or put it this way:—

		Constituents.					
Name of Colour.		*Orange.*	*Yellow.*	*Green.*	*Blue.*	*Series.*	*Reduction.*
Brown	=	4	2	0	1	X	20
Olive	=	1	6	6	1	X	
Gold	=	1	8	0	0	X	10

In this manner, once the constitution of a series is known, it is possible to ascertain at a glance the composition of any colour derived from it: and thus the work of the colour mixer is both simplified and expedited, since it is much easier to remember a few series of colours than hundreds of disconnected and unsystematic recipes.

With from twenty to thirty well-selected series it is possible to match practically any compound shade that is ever likely to be required in ordinary steam "styles."

The series given below will serve as examples of the methods adopted on a works scale. They are in actual use, and have yielded consistently good results in practice.

SERIES A.L. (Steam mordant colours).

1st. Red A.L. (10 per cent. Alizarin (blue shade) (20 per cent. paste) alumina mordant).
2nd. Yellow A.L. (30 per cent. Persian berry ext. 48° Tw., chrome mordant).
3rd. Green A.L. (15 per cent. Alizarin green, chrome mordant).
4th. Blue A.L. (6 per cent. Alizarin blue S., ,, ,,).

Examples:—

Olive 1.6.6.1 A.L.
Brown 6.4.1.1 A.L.
Grey 1.2.1.8 A.L.
Salmon 10.2.0.0 A.L. 5.
Buff 3.10.0.1 A.L. 12.
Chocolate 8.1.21 A.L.
Fawn 5.6.1.0 A.L. 5.
Old Rose 11.0.0.1 A.L.
Claret 11.0.1.0 A.L.
Old Gold 1.10.0.1 A.L. 5.
Drab 3.6.0.3 A.L. 5.
Gobelin Blue 0.0.10.2 A.L. 2.

etc. etc.

SERIES B.

1st. Orange B. (15 per cent. Alizarin orange (20 per cent.) with chrome).
2nd. Yellow B. (10 per cent. Azo alizarin yellow R.F.S. (Geigy), chrome mordant).
3rd. Green B. (4 per cent. Alizarin viridine (powder) chrome mordant).
4th. Blue A.L. (see above).

Examples :—

Apple Green 0.2.1.0 B. 10.
Fawn 2.1.1.0 B. 6.
Brown 4.2.0.1 B.
,, 4.6.0.1 B.
Mode 1.2.0.1 B. 10.
,, 3.3.0.2 B. 10.
Olive 1.3.6.1 B.
Reseda 1.0.4.0 B. 8, etc.

SERIES C.

1st. Purple C. (4 per cent. Chrome violet (Geigy) with chrome mordant).
2nd. Yellow C. { 7½ per cent. Bark extract / 7½ per cent. Persian berry extract } with chrome mordant
3rd. Blue A.L. (see above).

Examples :—

Grey 1.1.6 C. 10.
Violet 6.0.1 C. 10.

SERIES P.B. (for pigment blotches).

1st. Red P.B. (10 per cent. Vermilion with albumen and tragacanth).
2nd. Buff P.B. (10 per cent. Yellow ochre with ,, ,, ,,).
3rd. Blue P.B. (5 per cent. Ultramarine ,, ,, ,, ,,).
4th. Black P.B. (10 per cent. Lampblack ,, ,, ,, ,,).

Examples :—

Salmon 6.1.0.0 P.B. 6.
,, 9.1.0.0 P.B. 6.
Drab 3.8.0.1 P.B. 6.
Silver grey 6.0.6.5 P.B. 6.
Fawn 5.8.1.1 P.B. 6.
Lavender 6.0.6.0 P.B. 6.
Slate 1.0.3.0 P.B. 6.
Electric blue 1.0.9.0 P.B. 6.
Linen 1.8.1.0 P.B. 6.
Stone 0.3.0.1 P.B. 6.

SERIES B.C. (Basic Colours).

1st. Pink B.C. (2 per cent. Rhodamine 6 G. with tannic acid).
2nd. Yellow B.C. (2 per cent. Auramine O. conc. ,, ,, ,,).
3rd. Blue B.C. (2 per cent. Methylene blue N. ,, ,, ,,).

Examples :—

Orange 1.4.0 B.C.
Green 0.6.1 B.C.
Violet 1.0.1 B.C.
Olive 1.12.2 B.C.

SERIES D.

1st. Claret D. 15 per cent. Alizarin, yellow shade (20 per cent.), with chrome mordant.
2nd. Yellow C. (see series C).
3rd. Blue A.L. (see series A.L.).

Examples :—

Terra-cotta 1.2.0 D.
Old Gold 0.24.1 D. 8.
Claret 1.0.0 D.
Plum 4.0.1 D.
Lilac 1.0.4 D. 10.
Drab 1.3.1 D. 10.
Fawn 1.6.1 D. 10.
Brown 2.4.1 D.
Grey 1.4.8 D. 10.
Olive 0.4.1 D. 1 etc.

In a similar manner series can be made from any class of colouring matter that is capable of being applied by printing. For this purpose, therefore, the "Direct colours," the "Sulphur colours," the "Ciba colours," and the Indanthrenes are all suitable. A useful series of the latter with Vat Red B.A.S.F. is as follows:—

SERIES I.

1*st.* Vat Red B.A.S.F. (15 per cent. Vat red with caustic soda and Rongalite).
2*nd.* Indanthrene yellow (15 per cent. Ind. yellow G. with caustic soda and Rongalite).
3*rd.* Indanthrene blue (15 per cent. Ind. blue R.S. with caustic soda and Rongalite).

Examples:—

Green 0.1.2 I. (Light) Green 0.1.2 I. 3.
Red 1.0.0 I.
Purple 2.0.1 I.
Brown 4.2.1 I., etc.

The above half dozen or so series will be sufficient to show with what facility it is possible to obtain a vast variety of shades by simply altering the proportions of the few constituent colours. Examples could be multiplied, but the above will serve to illustrate the principles of the method—a method which, with such modifications and amplifications as the common-sense of the colourist will suggest, may be applied to any and every style of work in which compound colours play an important part.

While a series consisting of three members—red, yellow, and blue—contains all the elements essential to the production of shades belonging to every known class of colour, it is found in practice that four-member series are more generally useful, because more variety can be got out of them. The addition of a fairly bright green, such as Alizarin viridine, for instance, considerably increases the scope of a series, and enables very pure shades of quiet "Gobelin" blues and greens to be produced free from flatness.

In the mixing of tertiary shades of any description it is advisable, on practical grounds, to avoid, as far as possible, the use of unnecessarily bright colours. If such brilliant colours as Rhodamine, Auramine, Malachite green, and Methylene blue have been mixed together to give a complex mode shade (olive, fawn, drab, grey, etc.), it will be found, on making a second batch, that the slightest excess of any one of them over the amount previously employed will make a tremendous difference in the resulting shade of colour; and that, as a rule, it is extremely difficult to get the same shade twice alike, more especially if it be light and of a delicate tone. Colours that are composed of three or more bright luminous colours are always very difficult to match accurately, and accordingly they ought never to be made, except for special styles in which only one class of dyestuff is available—*e.g.* the tannin discharge style, for which only basic colours can be used. Even then, if quiet mode shades are required, it is better, if possible, to execute the work by some other process—say the chlorate discharge on slop-padded mordant colours, or by dyeing Alizarin colours on discharged chrome mordanted cloth—which will allow of the same effect being produced by more reliable means.

On the other hand, if the bright, pure, luminous colours are replaced by more subdued colours, such as Alizarin, Alizarin orange, Persian berries, Quercitron bark, Alizarin yellows, Alizarin viridine, Alizarin blue, etc., in combination with chromium mordants, the shades produced by their combinations are much easier to match and to bring up to standard, because a slight excess of any one of them does not produce anything like so decided an effect as when the brighter dyestuffs are used.

Further, in order to prevent undue loss of harmony in the colour scheme of a multicolour pattern when seen under gaslight, etc., all the compound shades in the pattern ought to be made, as far as possible, from the same constituents, *i.e.* the same "series" of colours. By this means the absorption spectra of the olives, browns, golds, drabs, or greys used in the colouring will be more or less similar to each other (though the composition of the colours differ, of course; yellow predominating in the golds, blue in the greys, red and yellow in the browns, and blue and yellow in the olives); that is to say, rather, that they will bear the same approximate relation to each other in gaslight as they do in daylight; and therefore, although the colouring may differ considerably from the daylight effect, it will at least not lose a great deal in balance or harmony. But if widely *different* constituents are used for the *various* compound shades, it is more than likely that what appears perfectly harmonious in daylight will in gaslight become a mere botch of badly-balanced and inharmonious colours.

The same chaotic effect is produced, under any conditions, in course of time, if the component parts of the several compound shades do not possess about equal powers of resistance to the action of light, soap, and other agencies. Many beautiful colours fade to quite horrible shades; others wash out almost immediately; and others, again, lose their purity and freshness when diluted or reduced. When such colours are mixed with others which are much "faster," to make compound shades, these latter rapidly alter when exposed to light, or they may be changed completely by the first washing, the result in either case being that the whole balance of the colour combination in the pattern is upset and its effect completely spoiled. Too much attention, therefore, cannot be paid to the selection of the members of a series if the best and most durable results are to be obtained.

In testing a group of colours for mixing properties, their fastness to light, soap, chlorine, and perspiration (acetic acid) ought to be compared, their suitability for working with a common thickening ascertained, and a range of gradated tints of each colour prepared, so as to make sure that no colour is employed which alters in tone on reduction.

The advantages of working according to some such system as that outlined in the preceding pages are that (1) fewer standard colours are required; (2) the composition of any compound shade can be seen at a glance; (3) the nomenclature of colour mixing is simplified, and at the same time made more graphic; (4) the particulars of the whole of the colours used in a works can be entered up in a comparatively small book, thus doing away with the folios that accumulate so rapidly in colour shops, where every little mixture is given a special name which affords no clue to its composition; (5) the saving of time, arising out of the fact that thousands of shades can be made without necessitating a single reference to a notebook; (6) the disorganisation of work, which frequently happens when a change is made in the *personnel* of a colour shop, is reduced to a minimum; and (7) that with a few well-selected series of colours it is possible to obtain an infinite variety of shades, each one of which possesses properties more or less identical with those of all other shades mixed from the same elements. If these elements have been chosen with care every colour made from them—olives, browns, greys, fawns, drabs, salmons, etc.—will be equally "fast," so that an elaborate colour scheme can be built up entirely from three or four simple colours, without any fear of one colour fading or washing-out more than another. Of course, light colours are always apt to fade more rapidly than dark ones of the same composition, but, apart from this common defect, colours of the same "series" behave in the same way; and if care has been taken in the first instance to select the *fastest* colours available for a given class of work, it is possible to obtain a range of pale shades that compare favourably in fastness to light with the standard colours from which they are mixed. Altogether, the unequal fading of a combination of colours of similar composition is not so pronounced as to detract from the system of colour mixing just described; in fact, experience has demonstrated that multicoloured prints worked on the above methodical lines preserve their balance in a remarkable degree.

Many exceedingly valuable colouring matters cannot be worked in series; but these are, for the most part, used for special purposes; and as they are unsuitable for the preparation of compound shades, they call for no mention here.

The few examples of "series" already given are only suitable for "steam work," but the same principle can be applied to any other class of work, and in the following pages other illustrations of its varied usefulness will be found in the descriptions of the "discharge styles," etc.

Useful "series" can be made from all classes of dyestuffs, and for any style of printing in which compound shades are used. Once the simplicity, convenience, reliability, and scope of the systematic method of colour mixing outlined above are recognised, its advantages over the haphazard methods still in use in many printworks will be obvious.

It must be understood, however, that a mixture of colours is never employed if the desired result can be obtained by using a single colouring matter; for mixtures are liable to irregularity.

The introduction of the coal-tar colours not only revolutionised textile colouring in general, but in particular resulted in raising the "Direct Printed or Steam Style" from a position of insignificance to one of paramount importance. Almost every addition to the now enormously long list of coal-tar colouring matters increased the range of effects producible by means of direct printing; and at the present time it is scarcely too much to say that work executed by this method forms by far the greater proportion of the total sum of calico and other textile fabrics printed on the large scale.

(2) THE DYED STYLE.

The "dyed style" is the oldest, and is still one of the most important, of all the numerous styles of printing in use at the present time. In a simple and primitive form it was largely practised by the ancient Hindoos, Chinese, and Egyptians, many of whose methods are still in use in the East Indies; similar methods are also employed by the natives of the West Coast and in the interior of Africa. In Europe and America, however, the "dyed style" has been brought to a high pitch of perfection, and, in common with other branches of calico printing, its development has proceeded on scientific lines.

Chemical research has not merely disclosed, but has improved upon the most cherished secrets of the old-time dyer; so that nowadays anything of value that he knew is to be found in almost any good text-book, and many of the things that he practised have been discarded as utterly worthless. At the same time good *practical* dyers are just as necessary as ever they were; for, although the art of dyeing has been shorn of the mysterious, it is by no means a craft that can be taken up by a chemist fresh from the university. It requires a good deal of experience to dye even a regular plain shade in large quantities; and when the process is complicated by the presence of different strengths of mordants, the necessity for keeping the white parts of printed goods clean, and the matching of shades on different qualities of cloth, it requires a good deal more than laboratory practice to produce successful results.

The "dyed style" differs from the "direct printed or steam style" in the manner of applying the colours to, and fixing them upon, the cloth. Instead of the colours and their mordants being mixed together in a thickened paste, printed simultaneously on the cloth and fixed at the same time by a process of steaming, they are applied separately and in two quite distinct stages, each of which comprises a series of operations peculiar to itself. These stages are known respectively as Mordanting and Dyeing. The former may be effected either by printing a thickened mordant in the desired pattern on the cloth, or by slop-padding the cloth in a solution of the mordant, and afterwards discharging it with an "acid" in the required pattern. In both cases the object is the same, viz. to fix a mordant on the cloth *locally*, so that when it is afterwards treated in dye liquor the dyestuff will only attach itself permanently to those parts of the cloth to which the mordant has been applied. The *dyeing operation* may be performed in any convenient form of apparatus. That usually preferred for the general work of calico printing is the spiral dye beck already described; but for certain styles the "jigger" may also be used with advantage; and for very heavy goods, like molletons, corduroys, and velveteens, the old-fashioned wince dye beck cannot be improved upon when large quantities are dyed at a time.

The "dyed style" may be produced in different ways according to circumstances, but the following will afford the simplest illustration of the practical application of the principles involved. The cloth is first printed, either by block or roller, with one or more thickened mordants. The composition of the mordants will vary with the colour to be dyed. After drying, the mordants are fixed in a suitable manner; the cloth is then well washed, and finally dyed by being passed into a hot solution of dyestuff, through which it is made to circulate continuously until the required depth of shade is attained. During this operation the dyestuff combines with the mordant or mordants to form an insoluble colour lake or lakes analogous to those obtained by the very different method of "steaming." On leaving the dye bath the whole surface of the cloth is more or less stained with colour; but that on the unprinted (*i.e.* unmordanted) portions only adheres mechanically, and can be entirely removed by washing and soaping the goods, thus leaving a coloured design on a white ground.

From the foregoing it will be seen that the essential operations in the "dyed style" are: (1) the printing-on of the mordant, or its application in some other way; (2) the fixing of the mordant; (3) washing out the excess of the fixing agent; (4) dyeing; and (5) washing and soaping the dyed cloth to remove all loosely adhering colour, and to clear the white parts of the pattern. These five operations, with such modifications and additions as are demanded by circumstances, are common to all the numerous phases of the dyed style.

The terms "dyed style," "dyed work," and "dyed way" were formerly applied exclusively to goods mordanted with iron and aluminium salts, and dyed up afterwards in Madder, Logwood, Quercitron bark, and other vegetable dyestuffs. At the present time no such distinction exists; and the "dyed style" now comprises all classes of work in which any mordant whatsoever is first applied to the cloth, and subsequently combined in the dye bath with a colouring matter capable of forming an insoluble coloured compound with it.

Most of the colours used in dyeing can also be (and are) applied by "direct printing." Hence the "dyed style" is not so much characterised by the use of special colours and mordants as by the methods employed in their application to, and fixation upon, the cloth. Nevertheless the kind of colour employed influences the *modus operandi* of dyeing to a considerable extent. Different classes of colouring matters and mordants demand different treatments; and as these treatments point to so many variations of process, the "dyed style" does not consist of an unalterable sequence of operations, but of several quite distinct processes. Of these the most important are the following:—

(*a*) The "Madder" style and its modifications.
(*b*) The "Basic" style.
(*c*) The "Chrome Mordant" style.

A slight modification of the Madder style allows of any basic aniline colour being dyed on cloth mordanted for Alizarin colours—a facility permitting of cloth printed in a single mordant being dyed up in an immense variety of shades, including those obtained from Alizarin, basic colours, and most of the vegetable dyestuffs still in use.

(*a*) **The "Madder" Style.**—This style owes its name to the fact that formerly Madder was the chief dyestuff used in its production. It still retains its old name, although Madder has been superseded entirely by its artificial competitor, Alizarin, which, chemically, is identical with the essential red colouring principle of the madder root.

The Madder style is the oldest, the most important, and the most largely practised of the "dyed styles" at present in vogue. It yields an extensive range of exceedingly fine colours, fast both to light and soap; and it possesses an advantage over all other "printed and dyed styles" in that various shades of red, pink, maroon, chocolate, and purple, together with black, can all be associated in a multicolour pattern, and dyed simultaneously by *one operation* and with the *single dyestuff, Alizarin.*

In these multicolour effects, advantage is taken of the property possessed by Alizarin of forming differently coloured lakes with different mordants. Thus the colour of the lake produced with aluminium salts is red; with iron salts, black or purple, according to the strength of the mordant; and with mixtures of iron and aluminium mordants, various shades of maroon, which become chocolates as the proportion of iron increases. Other colours, such as Chrome yellow, Catechu brown, Alizarin blue, and Indigo may also be introduced into multicolour prints, but they require special treatment, and the blues especially require careful handling when used in combination with Chrome yellow, although formerly Indigo was largely used in this connection.

The only mordants used on the large scale in the "madder style" are the *crude* acetates of iron and aluminium—the "black liquors" and "red liquors" of commerce. The properties and composition of these mordants have already been discussed, but it may not be out of place here to recapitulate the practical reasons for preferring the crude impure salts to the pure normal acetates. In the case of iron, the pure salt not only oxidises very rapidly in solution, but when printed it oxidises both irregularly and to a point beyond that at which good results are obtainable. As previously noted, the best colours can only be dyed on an iron mordant when it exists on the cloth in a condition intermediate between the ferrous and ferric states. When the pure ferrous acetate is employed, its conversion into the highest state of oxidation takes place so rapidly that, in practice, it is found impossible to control it sufficiently well to enable it to be used with any degree of certainty. On the other hand, the crude pyrolignite of iron or "black liquor" contains organic impurities which, while not detracting from the beauty of the final shade, retard the rate of its oxidation to such an extent that under proper conditions it is possible to arrest it at exactly the point required to secure the best results. Aluminium only forms one oxide (Al_2O_3), and so cannot be over-oxidised; but it also forms various basic salts, each of which possesses a different affinity for Alizarin. If, therefore, the mordant used for printing decomposes very readily, it is apt to produce salts of varying basicity on the cloth, and hence to yield irregular shades on dyeing. Experience has proved that pure aluminium acetate yields neither such regular results nor such full rich colours as an acetate in which a portion of the acetic acid is replaced by sulphuric acid, *i.e.* a sulphate-acetate. Moreover, pure acetate of alumina decomposes on standing, and loses strength by depositing alumina or an insoluble and very basic acetate; access of light accelerates the rate of this spontaneous decomposition. Again, when thickened and printed, the pure acetate is very susceptible to the action of dry heat, and is easily "*burned*" by too great a temperature in drying after printing; it also possesses the property, when dried on the cloth, of repelling water, so that in "dunging" it prevents the fixing liquors from penetrating into the body of the material, and thus gives rise to another cause of irregular work. These defects can be overcome by the addition of acetic acid to the normal acetate; but care must be taken to avoid making it too acid, as otherwise it does not thicken well, and works badly owing to its solvent action on the edge of the steel "doctors." On the whole, therefore, a crude acetate or "red liquor," made from sulphate of alumina and calcium acetate, and corresponding approximately to the formula $Al_2(SO_4)(C_2H_3O_2)_3(OH)$, is preferred to the normal salt, since any precipitate it may deposit on boiling with the thickening re-dissolves on cooling, and in printing, drying, ageing, and dunging it behaves, as shown by experience, in a satisfactory manner.

In any case, excessive heat in drying must be avoided, otherwise all iron and aluminium mordants are liable to be dehydrated, in which state their affinity for colouring matters is reduced considerably, and they yield poor, thin shades in the dye bath.

After printing and drying, the next stage in the production of Madder work is the fixation of the mordants on the cloth. For this purpose the printed goods are first "aged" and then "dunged." During the ageing the thickening materials are softened, allowing the mordant to penetrate thoroughly into the fibres of the cloth; large quantities of acetic acid are evolved, and the mordant is converted into a more or less insoluble basic salt which adheres or is fixed firmly to the cloth. The "dunging" process completes the fixation of the mordant by precipitating those portions of it which have been unacted upon in ageing; it also prevents the unprinted parts of the cloth from becoming mordanted by any soluble mordant running into them from the printed parts during the subsequent operation of dyeing; and finally, it removes all the thickening used in printing, thus leaving the cloth perfectly free to the action of the dyestuff. If any thickening were allowed to remain it would act as a mechanical resist, by interposing an obstruction between the mordant and the dyestuff.

As previously stated, the process of ageing consists in exposing the printed goods to the action of warm moist air for varying periods, the duration of which depends on the work in hand. The process, and the precaution to be observed, have been discussed at length in another part of the present volume, under the heading of "The Treatment of Goods after Printing," and little more remains to be said on the subject. Any of the methods there described may be adopted, but for general work Crum's Ageing Machine is the most convenient; its action is intermediate between that of the "hanging room" and the "Mather & Platt Rapid Steamer" or "Steam Ager"; it is quicker than the one, and more reliable, on the whole, than the other, especially for iron mordants, which require very gentle oxidation if the best results are to be secured. The time required to pass through Crum's continuous ageing chamber is twenty minutes, and the state of the atmosphere ought to correspond with about 36° C. dry bulb and 33° C. wet bulb thermometers. On leaving the ageing chamber, the goods are loosely bundled in 2–4 piece lots and allowed to lie for several days in the room surrounding the chamber. The temperature of this outer room is usually maintained at 33° C. dry and 29° C. wet bulb thermometers, or as close as possible to these points. In this way the ageing process is completed with the least possible trouble, and without taking up anything like the immense amount of space occupied by the old-fashioned hanging rooms. For aluminium mordants, either alone or in combination with Aniline black, the rapid ager may be used if desired. The time required in passing through the chamber is from two to four minutes, through an atmosphere of low-pressure steam at a temperature of 75° C. to 90° C. In other respects the process is identical with the preceding.

"Dunging" has likewise been described in detail in the earlier pages of this work, and nothing more need be said about it beyond giving a few particulars of the composition and working of the "dunging liquors" used in illustrating the practical examples of the "Madder styles," which are to follow later.

After "ageing" and "dunging," the goods are dyed in any convenient manner and with any suitable dyestuff.

Washing, soaping, and clearing follow the dyeing operation: and as these processes vary with different classes of work, their description will be given along with that of the practical methods.

By far the greater proportion of "dyed work" produced at the present time consists of single-colour patterns in red, chocolate, and purple. Black and white styles were also produced in large quantities at one time by dyeing Logwood on a strong iron mordant, but "steam" Aniline black has now displaced Logwood almost entirely for this purpose, and also for most Madder styles in which black occurs in combination with red, pink, chocolate, and purple. With very few exceptions, all multicolour patterns, containing more than two or three shades of a colour or colours, are nowadays executed by the "steam style." Occasionally a combination of red, pink, chocolate, purple, and black is produced in the dye beck, but the style is practically obsolete, although it yields exceedingly fast and very pleasing effects.

The thickened mordants used in the "Madder style" are called "*colours*" not because they contain any colouring matter, but because they give definite shades when dyed up in Alizarin. Thickened red liquor is always known as "red" in the colour shop, although it gives different colours with different dyestuffs—*e.g.* yellow with Bark extract and Persian berries; blue with Alizarin blue; purple with Gallo-purple or Gallo-cyanine; and brown with Anthracene-brown. Similarly, thickened iron mordants are known as blacks or purples according to their strength: and mixtures of iron and aluminium mordants generally go under the name of chocolates. This is simply because their chief use is for the production of these colours with Alizarin.

MADDER RED PROCESS.—Print on white unprepared cloth the following "red":—

6T. RED.[1]

100	grms.	wheat starch.
50	,,	flour.
900	,,	red liquor 6° Tw.
20	,,	olive oil.
·5	,,	Magenta.

Boil, cool, and add

12·5 grms. tin crystals.

1000 after cooling.

The stannous chloride (tin crystals) is added to prevent the fixation of any iron, which would, of course, dull the shade of the red by forming a small quantity of purple in the dye bath: and the Magenta is merely added for "sightening,"

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[1] 6T. Red denotes that the colour is made from red liquor at 6° Tw.

that is, to give a decided colour to the paste, so that the printer can see what he is doing. The "sightening" all washes out in "dunging."

After carefully drying, the goods are "aged" and then dunged as under:—

First Dunging.

The goods are passed at *full width* through the "fly dunging" machine (see page 150), the first three compartments of which are filled with the following liquor,

2000 litres water,
15 kilos. chalk,
2½ ,, phosphate of soda,
70–85 ,, cow-dung,

and the last with water alone.

The treatment occupies 2–5 minutes and is conducted at a temperature of 60° C. After washing, the goods are "dunged" a second time, in the rope form, in the following:—

Second Dunging.

500 litres water.
1½ kilos. chalk.
¼ kilo. phosphate of soda.
8–12 kilos. cow-dung.

This liquor is contained in a spiral dunging beck, similar to a dye beck; and the goods are worked in it for 20–30 or more minutes at a temperature of 50°–60° C. After a thorough wash, to remove completely every trace of the dunging solution and the thickening materials, the goods are ready (without drying) for dyeing.

In works where large quantities of Madder-dyed goods are regularly produced, the "second dunging" is performed in a continuous manner. For this purpose three or more becks are arranged to work together, the cloth passing from the first into the second, from the second into the third, and so on through the whole range.

Cow-dung imparts a somewhat yellowish-green appearance to the mordanted parts of the cloth, especially if used in excess, but as a rule the tint is too slight to affect the shade of deep colours. It may be strong enough, however, to dull the brightness of light reds and pinks; and where this is to be suspected from the general appearance of other goods, one of the many dung substitutes may be used with advantage.

Of these, the most commonly employed are phosphate of soda, arsenate of soda, silicate of soda, and sometimes, though rarely, silicate of lime. Chalk is an ingredient common to nearly all "dunging liquors," and occasionally, too, a small quantity of ammonia is added. The following solutions may be taken as typical of the composition of these dunging liquors:—

	I.	II.	III.	IV.	
Phosphate of soda . .	1½–6	...	...	. .	parts by weight.
Arsenate of soda . .	...	2–5	...	...	,,
Silicate of soda 32° Tw. .	...	...	20	...	,,
Silicate of lime . .	...	...	...	1000	(saturated solution).
Chalk	7½	7½	7½	7½	parts by weight.
Water	1000	1000	1000	...	,,

Silicate of soda is not generally employed as a dunging agent on account of its liability to contain an excess of alkali, either in the form of free caustic soda or carbonate of soda. Properly prepared, however, and free from this defect, it may be used with safety, even for weak aluminium mordants. Taken altogether it is, however, perhaps the least suitable fixing agent for aluminium mordants, since the resulting colours are neither so bright nor so full as when the other dung substitutes are employed.

Silicate of lime is an extremely insoluble salt, and to ensure an efficient dunging by its means the bath must always contain an excess in order to keep up its strength.

It frequently happens that the thickening materials of printing pastes are difficult to remove in dunging, especially if the cloth has been printed in a heavy pattern, in thick colour, and with newly engraved rollers. In such cases the most effectual method of removing the thickening is to add malt or bran to the dunging liquors, and to prolong the second dunging operation. Thus—

First Dunging.

60° C.
2000 litres water.
35 kilos. good quality silicate of soda 32° Tw.
4 ,, phosphate of soda.
30 ,, malt or bran.

Second Dunging.

60° C.
500 litres water.
2 kilos. chalk.
$\frac{1}{4}$ kilo. phosphate of soda.
5 kilos. malt or bran.

If, after 45 minutes' treatment in the second dung liquor, some of the thickening still adheres to the goods, it can be finally removed by working them for 15 minutes in an infusion of malt or bran at a temperature of 50°–60° C. The diastase ferment of malt and bran acts on the starch, converting it into easily soluble sugars.

When cow-dung is used it is rarely necessary to add malt or bran to the dunging liquors, since, in addition to fixing the mordants, cow-dung also acts energetically on the thickening materials used in printing, and renders them soluble in warm water. On the whole, cow-dung is the favourite fixing agent with practical dyers; and it must be admitted that, taking everything into consideration, it yields the best and most regular work. Experience proves that, other things being equal, cow-dung acts effectively, and imparts a softer feel to the cloth in less time than any other "dunging agent" yet discovered. Its only drawbacks are, that it is irregular in composition, that it sometimes stains the cloth, and that it requires changing more frequently than the soluble dung substitutes cited above. Properly handled, however, it gives excellent results, both as regards depth and quality of colour.

After a thorough wash in any type of spiral washing machine, the properly dunged goods are split up into conveniently sized lots and dyed in Alizarin together with certain additions, such as sumach, tannic acid, glue size, Turkey-red oil, and chalk—the latter being employed only if the water be deficient in lime, the presence of which is absolutely essential to the production of a bright red. The sumach or tannic acid tends to increase the fastness of the colour, and in conjunction with the glue size prevents the white parts of the pattern from becoming unduly stained; the Turkey-red oil, which should contain a fair quantity of free fatty acid, enhances the beauty of the shade, increases its depth, and promotes the penetration of the Alizarin into the body of the cloth.

The composition of the dye bath and the proportions of its constituents vary with the strength and quantity of the mordant printed on the cloth. A small spot pattern requires a much weaker dye bath than a heavy stripe printed in the same colour, and the same pattern printed in two colours of different strengths requires the dye bath to be regulated accordingly. Thus 6 T. Red (Aluminium acetate 6° Tw.) requires really six times as much Alizarin as 1 T. Red which is six times weaker, and similarly for all other strengths of mordants. If an excess of dyestuff is employed, there is always a risk of the "whites" being badly stained. In order to avoid this as much as possible, the proportion of glue size is increased for patterns containing large masses of white, such, for instance, as widely-set spot patterns. On the other hand, when the entire surface of the cloth is printed, as in many furniture patterns, the use of glue may be dispensed with altogether.

For an average kind of pattern, covering about half the surface of the cloth, and printed in the 6 T. Red already given, the following dye bath will be about correct.

DYE BATH (for 100 kilos. of cloth).

5500	grms.	Alizarin 20 per cent. paste.
1000	,,	glue.
2000	,,	water.
2000	,,	Turkey-red oil (3 parts neutralised).
750	,,	chalk.
550	,,	dried and powdered sumach.
2000	litres	water.

The pieces, in the rope state, are run into a spiral dye beck containing the above ingredients. They are dyed in the cold for 15 minutes, then the temperature is gradually raised in 15 minutes to 40° C., and after another 20 minutes to 60° C., and finally, after dyeing at 60° C. for 20 minutes, to 75° C., at which temperature the goods are worked for 15–20 minutes. They are then taken out and well washed through a series of square beater machines (see p. 162). If the "whites" are not satisfactory, the goods are then further treated in an infusion of bran (2 per cent.) for 15 minutes at 75°–90° C., and then thoroughly washed and hydro-extracted, or, if they cannot be dealt with at once, dried.

At this stage the colour of the dyed pieces is a dull brown red, totally unlike an Alizarin red. To convert this dull Alizarin alumina lake into a full rich and bright red, the goods are oiled, steamed, and finally well soaped until the "whites" are pure.

Any of the ordinary "soluble oils" of commerce may be used for brightening dyed reds, but a much better result is obtained by using one of the specially prepared oil mixtures containing tin and oxalic acid. Of these, the two given below have yielded excellent results on the large scale.

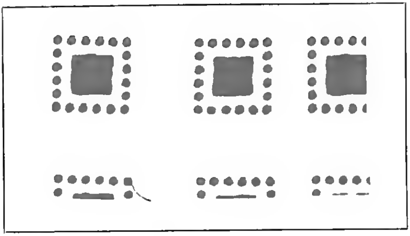
BRIGHTENING OIL I.

200	grms.	Turkey-red oil 25 per cent. (sodium sulphoricinoleate).
15	,,	stannous sulphoricinoleate.
15	,,	ammonia.
125	,,	oxalate of ammonia 3° Tw.
645	,,	water.
		= 5 per cent. fatty acid.

BRIGHTENING OIL II.

200	grms.	Turkey-red oil 25 per cent.
3	,,	oxalic acid.
2½	,,	tin crystals.
600	,,	water: add ammonia until the precipitate formed is redissolved and make up to—
1000 = 5 per cent. fatty acid.		

The cloth (preferably dry) is padded through either of the above solutions, dried, and then steamed in a "cottage" at 5 lbs. pressure for one hour. After washing, the goods are soaped 15–20 minutes at 75° C. in a solution of 3 parts of soap per 1000 of water. If the whites still retain a pinkish tinge, the pieces, after being well washed out of the soap becks, are finally "cleared" by being passed through a solution of bleaching powder ¼°–½° Tw., steamed wet for a minute, washed, and dried up over cylinders. The "*clearing*" is effected in the machine already described.



Madder Red (dyed).

The effect of oiling as above is to intensify the depth and increase the brilliancy of the red, while at the same time the oxalic acid liberated in steaming produces a very pure, clear white. The oil combines with the colour lake to form an Alizarin alumina tin fatty compound of extreme fastness to light and soap.

Before the discovery of the "soluble oils," the brightening of dyed reds was always done by boiling them with a neutral soap, to which was added a very small percentage of "tin crystals." The process was long, and no better than the modern oiling and steaming method.

Madder Orange is produced in exactly the same way as the red, with the sole exception that Alizarin orange is used in place of Alizarin. It is rarely employed alone, being for the most part used in combination with Aniline black. The same printing colour, viz. 6 T. Red, serves for orange, and indeed for all colours dyed on an alumina mordant.

As already mentioned, the name 6 T. Red is merely a convenient expression of the strength of the aluminium acetate printed. Weaker and stronger colours are distinguished in the same way. Thus—

½	T. Red (aluminium acetate	½° Tw.	thickened) gives	Light Pink.
1½	,, ,, ,,	1½° Tw.	,, ,,	Dark ,,
6	,, ,, ,,	6° Tw.	,, ,,	Medium Red.
8	,, ,, ,,	8° Tw.	,, ,,	Full rich ,,
12	,, ,, ,,	12° Tw.	,, ,,	Crimson.

The shade of red produced varies with the shade of Alizarin used in dyeing. Scarlets are dyed with the "yellow shades"; pinks and crimsons with the "blue shades." In the latter cases, too, it is advisable to use a brightening oil without tin, since tin tends to make the shade yellowish and very fiery—a desirable quality in scarlets, but a defect in crimsons and pinks.

In addition to various shades of red, pink, orange, and salmon, the above simple aluminium mordants are all suitable for the production of a great number of yellows, browns, clarets, fawns, olives, etc., all dyed directly on the "dunged" cloth, and finished off with no further after-treatment than a thorough washing and soaping, with perhaps a run through the "chemicking" machine to brighten the whites when these have suffered in dyeing from too great an excess of dyestuff, too long an immersion, or too high a temperature. It is important to observe that, in order to preserve the purity of the "whites" (the unprinted parts of the cloth), the dyeing should always be conducted at as low a temperature as is consistent with the production of a "fast" colour lake.

The following colours are all suitable for dyeing on aluminium mordants :—

Alizarin bordeaux.
,, orange.
,, red, all brands.
,, brown.
,, blue (in mixtures only).
Quercitron bark extract.
Persian berry extract.
Anthracene brown.
Gallo-purple.
Logwood (in mixtures).

A fine shade of *claret*, much clearer in tone than can be obtained on any aluminium and iron mixed mordant, can be produced on *8T.Red* by dyeing the cloth in a mixture of Alizarin bordeaux and Alizarin (blue shade).

Dye Bath for Claret (100 kilos. cloth).
6 kilos. Alizarin 20 per cent. paste (blue shade).
1½ ,, Alizarin bordeaux B.B.D. paste.
¾ ,, tannic acid.
10 ,, glue size 15 per cent.
1500–2000 litres water.
Dye as for Alizarin red ; wash, oil, steam, wash, and soap.

Mixtures of Quercitron bark or Persian berry extracts, with small quantities of Alizarin, Alizarin bordeaux, Anthracene brown, Alizarin orange, give rise to a vast variety of compound shades when dyed on "8. T. Red" mordant. As a rule, however, all compound shades except the most brilliant are dyed on "chocolate mordants" of various kinds. Chocolate mordants are mixtures of iron and aluminium acetates.

"**Alkaline**" **Reds**, so called, are merely Madder reds, dyed on an alumina mordant, prepared by thickening "alkaline mordant" or *aluminiate of soda* ($Al_2O_3.Na_2O$). For fixing the alumina on the fibre, the printed goods are either simply exposed to the action of the atmospheric carbonic acid or passed for from two to four minutes through a solution of "sal ammoniac" (ammonium chloride), or through a solution of phosphoric acid prepared by the double decomposition of superphosphate of lime and sulphuric acid.

$$(1)\ Na_2Al_2O_3 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3.$$
$$(2)\ Na_2Al_2O_3 + 2NH_4Cl + 2H_2O = 2NaCl + 2NH_3 + 2Al(OH)_3.$$

In each case, the precipitation being effected in presence of moisture, the oxide of aluminium is deposited on the fibre as the hydrate. With ammonium chloride care must be taken to avoid an excessive accumulation of ammonia in the bath, since it is liable to dissolve or "strip" a portion of the alumina from the cloth.

The chloride and sulphate of zinc have been proposed as fixing agents for "alkaline red mordant," but, while they answer perfectly for the purpose, they possess no particular advantages over other fixing agents, and, if used at all in practice, they serve merely as alternatives.

Perhaps the best and most reliable fixing agent is that proposed by B. W. Gerland, viz. phosphoric acid. It is very effective, does not strip the fibre of alumina (phosphate of alumina is insoluble), and can be very cheaply prepared from the commercial superphosphate of lime by the action of warm dilute sulphuric acid. The essential constituent of "superphosphate" is calcium phosphate ; sulphuric acid precipitates the calcium as sulphate, leaving phosphoric acid in solution.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The insoluble calcium sulphate is filtered off and the clear filtrate of phosphoric acid reduced with water, as required, to the requisite working strength—about 8° Tw. on the average.

Solutions of "alkaline mordant" are best thickened with maize starch and a little tragacanth. Wheat starch and flour are both unsuitable, by reason of the fact that they become ropy and gelatinous when treated with strong alkalies.

Well torrefied British gum, *i.e.* dark British gum, is also an excellent thickening agent, but it gives lighter reds than maize starch, and is therefore only useful for pinks.

The following example of the method of producing "alkaline red" is taken from practice :—

PRINTING COLOUR (10 Alk. Red).

8 parts by weight maize starch.
50 ,, ,, ,, water.

Boil, turn off steam, and add

2 parts by weight Turkey red oil.
10 ,, ,, ,, tragacanth thickening 6 per cent.

Cool and add gradually

30 parts by weight alkaline red mordant 30° Tw.

100

Heat again to 75° C. and then cool.

The above colour corresponds to alkaline mordant at 10° Tw., plus, of course, the thickening.

Print on white, unoiled cloth : dry : hang overnight in a cool, airy hanging room to soften the thickening : and then fix by a two or three minutes' run through either of the following baths :—

Fixing Bath I.—Ammonium chloride solution 10° Tw. at 60° C.

Fixing Bath II.—Phosphoric acid 8°–10° Tw. at 60° C.

The fixing is most conveniently performed in the ordinary "fly dunging" machine.

After a thorough wash, the fixed pieces are treated exactly like ordinary "Madder styles" ; that is, they are dyed, washed, oiled, dried, steamed, washed, soaped, and (if necessary) lightly cleared in "bleaching liquor."

Cloth mordanted by means of aluminate of soda is identical in its behaviour towards colouring matters with cloth mordanted in the usual way with aluminium acetate and other *acid* aluminium salts.

The great advantages of aluminate of soda as a mordant for printing are, that it will stand drying at a comparatively high temperature without injury ; that, owing to its nature, it is not liable to contract iron stains ; and that it penetrates well into the cloth, thus yielding good, solid colours, and allowing of "reversible effects" being produced with ease on thin cloth and by ordinary printing on one side. Moreover, the "alkaline red" process is quicker than the regular Madder process, and for this reason it has largely displaced the latter for the production of the "red and white" prints. On the other hand, aluminate of soda is much more limited in its application than the acetates of alumina, since its alkalinity precludes its association with Aniline black and the iron mordants in direct multicolour patterns. As a resist under Aniline black "covers," however, it yields fast red, black and white effects. It is rarely used at the present time for this purpose, other quicker and more modern methods having displaced it.

Madder Chocolates.—These colours are obtained by dyeing Alizarin on a mixed mordant of iron and alumina. They therefore consist essentially of mixtures of Madder red and Madder purple, since the Alizarin iron lake is purple.

According to the proportion of iron in the mordant, Madder chocolates vary in shade from maroon to plum ; the smaller the quantity of iron the redder the shade, the greater the quantity of iron the darker and bluer the shade.

For convenience of working, the amount of aluminium acetate (red liquor) taken is generally a simple multiple of the amount of "iron liquor" (pyrolignite) taken, and this relation is most commonly expressed numerically in the distinctive name given to the colour. Thus:—

		Red Liquor 8° Tw.		*Iron Liquor 24° Tw.*
8 Chocolate	=	8 parts	and	1 part.
16 ,,		16 ,,	,,	1 ,,
20 ,,		20 ,,	,,	1 ,,
40 ,,		40 ,,	,,	1 ,,

etc.

Lighter shades of these colours are indicated in various ways in different works. The one mentioned, when dealing with the mixing of compound shades, is perhaps as convenient as any. Thus, a colour written "8 Chocolate 2" means that 1 part of 8 Chocolate (see above) is reduced in strength by the addition of 2 parts of starch or flour paste; or is made correspondingly weaker in the first instance. Similarly:—

20 Chocolate ¼ = 4 parts of 20 Chocolate and 1 part of paste,
16 ,, 4 = 1 ,, 16 ,, ,, 4 ,,

and so on.

The processes of printing, ageing, dunging, and dyeing Madder chocolates are exactly the same as those for reds. In the oiling, however, tin crystals and oxalic acid are, of course, left out, as they would effect the reduction of the iron mordant, and thus give rise to irregular work.

Some printers prefer to age all goods printed in iron mordants in the old-fashioned hanging rooms, and where these are available it is perhaps the safest method to adopt. The oxidation of the iron requires to be carefully effected, and it can certainly be carried out more evenly and regulated with greater precision in the hanging rooms, where the goods are suspended in single folds, and every part of the cloth is subjected to the same atmospheric conditions of heat and humidity, than when the goods are bundled up and allowed to lie in piles, with only the outer folds of the bundle fully exposed to the action of the air, as is the case when the "continuous ageing" machines are made use of. If hanging rooms are not available, the goods, after passing through either Crum's machine or the rapid ager, must be piled, as loosely as possible, in small lots, and turned over frequently during a period of two to four days, in order to equalise the oxidation.

The following is an example of a Madder chocolate printing colour largely used in practice for the production of dark shades.

20 CHOCOLATE.

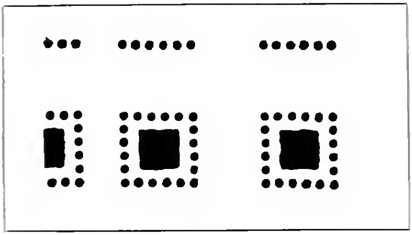
120	parts by weight of	flour.
40	,, ,,	olive oil.
800	,, ,,	"red liquor" 8° Tw.
40	,, ,,	iron liquor 24° Tw.
0·5	,, ,,	Magenta (for "sightening").
1000		

Boil and cool.

Print on white, unprepared cloth, age, dung, dye, wash, oil, steam, wash, soap, and clear (if necessary) in chemick as for reds.

The strength of the dye bath varies with the amount of mordant printed on the cloth. For an average pattern covering half the cloth about 7½ per cent.

of Alizarin on the weight of the cloth would give a full shade on "20 chocolate," the other ingredients of the dye bath, glue and chalk, being the same as for reds. It ought to be observed that tannin or sumach are omitted from chocolate dye baths on account of the black compound they form with iron salts; they may be replaced, if desired, by bran, but the addition of bran is not necessary, although it tends to preserve the purity of the "whites."



Madder Chocolate.

In addition to Chocolates, many other shades can be dyed on iron-alumina mordants, and in some such cases tannic acid or sumach plays an important part as a dyestuff in modifying the shade of the colour.

Examples:—

(1) Fawn on "12 Chocolate 1."

Dye bath (for 100 kilogrammes cloth printed in a heavy "blotch").

1·200 kilos. Alizarin (yellow shade) 20 per cent. paste.
40 ,, Persian berry liq. 18° Tw.
6·400 ,, dried sumach.
0·275 ,, ammonia ·880.
2000 litres water.

Dye for 80 minutes in all.—15 minutes in the cold, 15 minutes at 40° C., 15 minutes at 50°–60° C., and the rest of the time at 75° C. Wash well after dyeing, and then soap at 60° C. for 10 minutes with 2 grammes of soap per litre of water.

(2) Warm Dark Brown on "20 Chocolate."

For 100 *kilos. cloth.*

3 kilos. Anthracene brown (in paste).
3 ,, Alizarin orange 20 per cent.
6 ,, 20 per cent. glue solution.
2000 litres water.

Dry, wash, soap, and clear.

(3) Dark Olive on "40 Chocolate."

For 100 kilos. cloth.

8 kilos. Alizarin orange 15 per cent.
6 ,, sumach powder.
6 ,, 20 per cent. glue solution.
2000 litres water.

Dry, well wash, and then re-dye in—

2½ kilos. Methylene green (extra yellow).
½ ,, Auramine O.
15 ,, alum.
½ ,, sulphuric acid 168° Tw.
1500 litres water.

Dye at 50° C., wash well, treat 15 minutes in an infusion of bran at 80° C., wash well, soap, wash, and clear. The addition of alum and sulphuric acid aids in keeping the "whites" clean. Alizarin itself acts as a mordant for basic colours, but for fast colours it is always advisable to use tannin matters along with it, since they form much more insoluble lakes with the basic dyestuffs applied in the second dyeing, or "topping" as it is termed technically.

The foregoing examples of compound shades will show that the "Madder style" is capable of a good deal of variation. Many other instances could be given, but they would be simply repetitions of the above with different dyestuffs, and as such would only take up space without affording any corresponding advantage.

Madder Purples.—The production of Madder purples is strictly analogous to that of all other Madder colours; but, unless in combination with red, they are never oiled and steamed, the clearing of the "whites" and the brightening of the colour being effected by repeated soapings at the boil, varied occasionally by a treatment in bran or in chemick.

Madder purples and Madder blacks are both obtained by dyeing Alizarin on iron mordants; in fact, the only real difference between them is that in blacks the iron mordant used is many times stronger than in purples; so that, in the abstract, a Madder black is, to all intents and purposes, an intense purple, so dark as to appear black by comparison. When placed side by side with an Aniline or a Logwood black, however, its purple tone is at once apparent.

The iron mordant used for purples is the pyrolignite of iron already described. To this is usually added a certain proportion of arsenious acid, the object being to retard the rate of oxidation. The arsenious acid (As_2O_3) is introduced in various ways: (1) by boiling it up with iron liquor; (2) in the form of a solution in water, glycerine, or acetic acid and ammonium chloride; and (3) by preparing the cloth in a weak aqueous solution before printing. All such solutions are known as "purple fixing liquors," and their composition is so much a matter of fancy that probably no two printers use the same formula.

Depierre gives the following as a suitable preparation of iron for "dyed purples":—

{ 100 litres. iron liquor 24° Tw. (pyrolignite).
{ 1 kilo. white arsenic (As_2O_3).

Boil ½ hour, settle, and decant the clear liquor for use.

A separate "fixing liquor" for adding to the iron liquor during the boiling of the printing paste is made up as under. It has been used with success for a long number of years on the large scale.

PURPLE FIXING LIQUOR.

80 litres water.
20 ,, acetic acid 9° Tw.
10 kilos. sal ammoniac (NH_4Cl).
10 ,, arsenious acid.

Boil until dissolved; then allow to settle, and decant the clear solution for use.

The solution used for preparing the cloth before printing is as follows:—

M. PREPARE.

3 – 5	grms.	arsenious acid.
3 – 5	,,	sodium chlorate.
994 – 990	,,	water.
1000 1000		

The object of the sodium chlorate is to form arsenate of iron during the "ageing,"—a salt which oxidises very slowly, and which is not liable to oxidise beyond the point required to yield the best results on dyeing. The same prepare is sometimes used for chocolate mordants with the same end in view. If the purple printing colour itself contains arsenious acid, the preparation of the cloth is restricted to the application of sodium chlorate alone.

Whether the employment of arsenical fixing liquors and chlorate of soda, with or without the addition of ammonium chloride, common salt, or glycerin, is absolutely essential to the production of the best Madder purples, has never yet been definitely ascertained. Some calico printers have maintained that all such additions are superfluous, while others have been equally emphatic to the contrary. The whole question is probably one of plant and process more than of anything else. In works where the ageing arrangements are particularly favourable to the slow and gentle oxidation of the iron mordants, it may be easily possible to obtain first-class work without the assistance of any "fixing liquors" in the printing colours; and in such cases it would be manifestly absurd to increase the cost of production by making useless additions. On the other hand, most calico printers bear witness to the value of arsenious acid in promoting regular work; and, taken altogether, the balance of evidence seems to be in favour of employing it, either alone or in combination with glycerin, ammonium chloride, or common salt, and sometimes chlorate of soda or potash.

The thickening used for Madder purples may be either flour, starch, or British gum—the last usually for a variation of the "Madder style" known as the "cover and pad style," which will be dealt with later. "Paste purples" (P. purples) give shades almost as dark again as "Gum purples," the strength of the mordant being the same in both instances. This is, of course, on a par with what occurs with all classes of colouring matters, but it must be borne in mind when it is necessary to change the thickening for any technical reason.

The nomenclature of Madder purples is similar to that of the chocolates, with this difference, that the figure in front of the name indicates the volume of water taken to dilute one volume of pyrolignite of iron standing at 24° Tw. Thus—

12 P. purple = 12 vols. of water to 1 vol. iron liquor 24° Tw. or 12 : 1
40 ,, = 40 ,, ,, ,, 40 : 1
240 ,, = 240 ,, ,, ,, 240 : 1

The letter "P." denotes that the solution is thickened with starch or flour; "G." would indicate British gum. Any other distinctive signs such as "S.," "F.," or "BG.," etc., might be used as agreed upon. The name of the colour is immaterial so long as its signification is understood.

Apart from the employment of arsenical fixing liquors, the preliminary preparation of the cloth, and the omission of the oiling process, the *modus operandi* of purple dyeing is practically that of Madder reds and chocolates.

The following formulæ will illustrate the method of boiling Madder purple printing colours.

20 P. Purple (Medium).

200	litres	water.
10	,,	iron liquor 24° Tw. containing 1 per cent. As_2O_3.
26	kilos.	flour.
3	,,	olive oil.
0·1	,,	Methyl violet (for sightening).

Boil and cool.

200 P. Purple (Pale Lavender).

200	litres	water.
1	,,	iron liquor 24° Tw.
¼	,,	fixing liquor. (See page 347.)
25	kilos.	flour.
2½	,,	olive oil.
0·1	,,	Methyl violet.

Boil and cool.

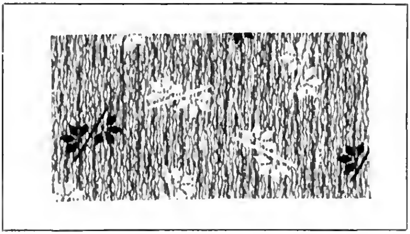
Print both the above on white cloth prepared in a solution of 3 grammes chlorate of soda per litre; dry, age, dung twice; wash, dye in Alizarin (blue shade); wash well; bran for 15 minutes at 90° C.; wash well, and then soap at 90°–100° C. for 15 minutes, or until the whites are clean. Finally, if necessary, clear lightly in bleaching powder and soap and wash again.

For 20 P. purple (a heavy pattern) the following dye bath will yield a fully dyed shade on 100 kilos. of cloth.

3	kilos.	Alizarin blue shade 20 per cent.
6	,,	glue size 25 per cent.
$\frac{1}{4}$	,,	chalk (if necessary).
2000		litres water.

Weaker shades of purple require weaker dye baths; but the dye bath ought not to be *too dilute*, otherwise the dyeing will take too long. On the contrary, too great an excess of Alizarin will inevitably stain the "whites" badly, making it impossible to clear them properly without impoverishing the colour.

Modern Madder purples are in general of a brighter and livelier shade than those dyed before the introduction of the coal-tar colours. This is due not merely to the use of artificial Alizarin, which is free from the brown colouring matters contained by the madder root, but also, and mainly, to the almost universal practice of "topping" Madder purples with Methyl violet. The Alizarin acts as a mordant for the basic violet, and the resulting compound shade is much purer and brighter than the simple Alizarin iron lake. "Topped" purples are fairly fast to soap, but the basic colour soon fades when exposed to light, leaving the original Madder purple somewhat less bright than it was before topping. On the whole, therefore, the "topping" of dyed purples is more in the nature of an expedient to enhance the appearance of the goods temporarily than of a permanent improvement in the quality of the colour.



Madder Purple.

The "topping" is done, after the dyed goods have been well soaped and washed to clear the "whites," in solutions of Methyl violet, varying in strength from $\frac{1}{16}$ to $\frac{1}{4}$ per cent. of dyestuff, reckoned on the weight of the goods, and according both to the depth of the purple to be treated and the shade desired. It is usually performed at about 40°–45° C., and a little acetic acid is generally added to the bath to preserve the purity of the white parts of the cloth. Care must be taken to avoid any excess of acid, otherwise the tone of the Madder purple will be changed to an unpleasant yellowish-grey. After topping, the goods are again well washed in warm water, lightly soaped, and finally well washed and dried.

Madder Black.—Blacks dyed with Alizarin on an iron mordant are only employed in combination with dyed reds, chocolates, and purples; and even for this purpose they have been almost entirely superseded by Aniline blacks, which yield a much finer shade and give a very much sharper impression of the pattern. Still Madder blacks do find occasional use in some styles, and, apart from other considerations, any mention of the Madder style would be incomplete without some note on the methods of obtaining a black, along with other colours, by dyeing.

For small objects on lightly engraved rollers the strength of "iron liquor" required to give a black on dyeing in Alizarin is from 12°–16° Tw.; heavier patterns often yield good results with 8°–10° Tw.

12° T. Black.

45	litres	iron liquor 24° Tw.
35	,,	water.
10	,,	purple fixing liquor. (See page 347.)
10	kilos.	flour.
$2\frac{1}{2}$	,,	British gum.
$2\frac{1}{2}$	,,	olive oil.

Boil and cool. Sighten with Logwood.

Logwood is sometimes added to the above to intensify and modify the shade. Print on cloth prepared in chlorate of soda as under:—

M. Prepare.

5	grms.	chlorate of soda.
1000	,,	water.

Dry; age by hanging 4 days at 30° C. dry bulb, 27° C. wet bulb; dung; wash and dye in any dye bath suitable for the other colours printed in the combination; wash, soap, and clear.

Multicolour Patterns in the "Madder Style."

The Madder style, pure and simple, does not allow of much variety being obtained in the way of colour combinations. At most it is only possible to produce, *by dyeing*, combinations of four types of colour, *e.g.* red, chocolate, purple, and black, but it so happens that Catechu and lead sulphate can be fixed on the cloth sufficiently permanently to withstand all the operations connected with the dyeing and clearing of Madder colours. This fact permits of Catechu brown and Chrome yellow or orange being associated with any of the dyed colours already mentioned, so that it is possible to obtain combinations of six different classes of colours in the Madder style by a few simple modifications of process. Catechu and Chrome yellows used in this connection are generally known as "Madder brown" and "Madder orange" respectively—a terminology not quite correct, but one readily understood under the circumstances.

Patterns containing Chrome yellow are always printed on cloth prepared in sodium sulphate, with the obvious object of precipitating insoluble lead sulphate in the fibres of the material. This lead sulphate withstands all the operations of dyeing, etc., and is finally converted into Chrome yellow by a treatment in bichromate of potash.

The introduction of Catechu makes it necessary to age the goods for from four to six days in a warm, moist atmosphere, and in hanging rooms where a good circulation of air can be maintained. The fixation of Catechu is effected by a process of oxidation, and if this is incomplete the resulting colour is correspondingly "loose" and washes off in dyeing. Similar conditions of ageing are suitable, even essential, for sulphide and vanadium Aniline blacks, and are, likewise, the best for aluminium and iron mordants. Simple air oxidation, however prolonged, does not develop the colour of Catechu to anything like the same extent as bichromate of potash does; hence Catechu browns in the Madder dyed styles are always rather light in shade, the use of bichromate of potash before dyeing being inadmissible. The presence of copper salts and ammonium chloride promotes a more complete oxidation; and the shade is also intensified by the addition of red liquor, which, by attracting colour from the dye bath, makes it darker, and at the same time rather redder in tone.

CATECHU "MADDER" BROWNS.

	I.	II.
Catechu sol. 25 per cent.	65 litres.	65 litres.
Water	9 ,,	4 ,,
Starch	10 kilos.	10 kilos.
Gum tragacanth 6 per cent.	8 litres.	8 litres.
Ammonium chloride	3 kilos.	3 kilos.
Olive oil	3 ,,	3 ,,
Boil, cool, and add		
Nitrate of copper 80° Tw.	4 litres.	4 litres.
Red liquor 8° Tw.	none.	5 ,,

CATECHU SOLUTION 25 per cent.

25 kilos. Catechu in cubes.
40 ,, water.
35 ,, acetic acid 9° Tw.

Boil 6 hours, make up to the original volume, stir well, and allow to settle for from 24 to 36 hours. Then decant the supernatant liquor for use as above; or the liquor may be thickened with gum Senegal 4 lbs. per gallon, in which case a printing colour can be made by adding copper nitrate, ammonium chloride, and a little reduction, thus:—

60 litres thickened Catechu solution 25 per cent.
5 ,, nitrate of copper 80° Tw.
5 ,, gum Senegal sol. 60 per cent.
5 kilos. ammonium chloride.

For "Madder yellows" the best salt to use is a basic lead acetate made by boiling the normal acetate with litharge. Thus—

9 litres water.
6 kilos. lead acetate.
2¼ ,, litharge.

Boil one hour; replace the evaporated water; settle and filter.

LEAD OR "MADDER" YELLOW.

100 litres basic acetate of lead as above,
25 kilos. light British gum,

or

40 kilos. powdered gum Senegal.

Heat till dissolved, and then cool.

The rollers used for printing Catechu browns and lead yellows in the "dyed Madder styles" ought to be strongly engraved in order to transfer a heavy charge of colour to the cloth, and thereby compensate for the loss of depth which these colours are apt to suffer during the long series of severe operations that are essential to the dyeing and clearing of the Alizarin colours.

The following is a summary of the various stages in the production of a six-colour print in red, yellow, brown, purple, chocolate, and black:—

(*a*) PREPARATION OF THE CLOTH.—Slop pad in a mangle through—

250 grms. sulphate of soda.
50 ,, chlorate of soda.
10 litres water.

Dry over steam heated cylinders.

(*b*) Printing.—On the prepared cloth print a six-colour pattern in—

(1) "Madder" yellow as above.
(2) 8 T. red (Madder red).
(3) Catechu Madder brown I.
(4) 20 Chocolate ½ (Madder chocolate).
(5) 20 P. purple (Madder purple).
(6) 16 T. black (Madder black), or a Sulphide Aniline black.

(*c*) Ageing.—Pass through Crum's continuous ageing chamber for 20 minutes at 32° C. dry bulb, 28° C. wet bulb thermometers, and then hang three to four days under similar conditions of heat and humidity. During this latter part of the ageing process the Catechu browns and the Aniline black (if any) are oxidised and developed as far as is possible at this stage.

(*d*) Dunging.—After ageing, the printed pieces are dunged as usual, but without cow-dung when yellows are present.

First dunging for 3 minutes at 60° C.:—

10 kilos. phosphate of soda,
10 ,, chalk,
200 ,, sulphate of soda,
1000 litres water,

in the continuous "fly dunging" machine. Wash and dung a second time in—

2½ kilos. phosphate of soda.
2½ ,, chalk.
100 ,, sulphate of soda.
1000 litres water.

for half an hour at 50°–60° C., in the spiral becks. Wash well and dye.

(*e*) Dyeing.—For a fairly heavy "sprig" or "spray" pattern take for the dye bath per 100 kilos. of cloth—

3–4 kilos. Alizarin 20 per cent. paste.
4 ,, 25 per cent. glue size.
2½ ,, Turkey-red oil.
½ ,, chalk.
4 ,, bran (optional).
2000–2500 litres water.

Dye ¼ hour in the cold, then gradually raise the temperature during the course of ¾ hour to 70°–75° C., at which temperature continue the dyeing for ½ hour. Then bran ¼ hour; wash and clear.

(*f*) Clearing.—Treat the washed goods for 10 minutes at 50° C. in—

(1) { 1200 litres water.
2 ,, bleaching powder solution 8° Tw.
2 ,, soda ash solution 8° Tw. }
(2) Wash, soap ¼ hour at 90° C. with 2 grms. soap per litre. Wash well.
(3) Repeat operations (1) and (2).
(4) ,, ,, ,,
(5) Wash again and then raise the Chrome yellow or orange.

(*g*) Raising: Treat the goods for 10 minutes at 60° C. in—

{ 1000 litres water.
5 kilos. bichromate of soda.
2½ ,, sulphuric acid 168° Tw. }

Wash well; and then, if an orange is required, pass the goods into a warm solution of the following:—

{ 1000 litres water.
1 kilo. bichromate of soda.
1 ,, quick lime. }

Treat for about 10 minutes at 30°–40° C.; then wash well and soap.

These multicolour patterns produced by dyeing are very fast, but they are not particularly bright, and their cost of production is very high compared with that of similar work executed by direct printing in colours developed by steaming.

FURNITURE AND UPHOLSTERY GOODS.—A style largely employed in the furnishing trade consists of a heavy "repp" cloth printed "en camaïeux" in different shades of red. The patterns mostly used for this purpose are Renaissance scrolls, rococo designs, and large stripes, either plain or fancy; they cover the whole surface of the cloth, not a vestige of white being left. This allows of the mordants being printed on *oiled cloth*. In all Madder styles containing white objects or spaces in the pattern, the use of Turkey-red oil *before dyeing* is altogether inadmissible, since it attracts a certain amount of colour from the dye bath to the white unprinted parts of the cloth, and this colour adheres so obstinately to those parts that it is practically impossible to remove it, except at the cost of impoverishing the brilliancy and strength of the colours on the mordanted parts. This defect, however, becomes an advantage in patterns on a red, pink, or any other colour of a Madder-dyed ground, because the presence of an insoluble oil alumina mordant not only gives the brightest shades, but it also admits of the goods being treated by a process closely approximating to the dyeing of Turkey red, which is by far the fastest and most brilliant of all the colours derived from Alizarin.

The majority of such patterns used for furniture, etc., consist of four colours—chocolate, dark red, light red, and pink. The first three of these are printed in the ordinary way on the printing machine or by hand block; the last is applied by slop-padding the goods in a weak mordant after the printed mordants have been "aged" and "dunged." The weaker or pink mordant may be applied before printing and immediately after oiling the cloth, if desired, but in practice the best results have been obtained by operating in the way described. The "ageing" and "dunging" are then repeated to fix the pink mordant, after which the dyeing is proceeded with in exactly the same manner as for ordinary Madder reds. Oiling in Turkey-red oil and steaming under pressure follow the dyeing; and finally, the colours are specially "brightened" by a treatment in dilute mineral acid and, after washing, in "soda chemick."

The preliminary preparing of the cloth in oil is effected in a padding mangle with a large trough or beck, the object being thoroughly to saturate the cloth. The drying is done over steam-heated *copper* cylinders. The cloth employed is bleached as for Turkey reds; that is, it is simply boiled two or three times in caustic soda, and then washed, soured, washed, and dried without any treatment in bleaching powder. A synopsis of a process largely used in practice for the production of a "Chocolate, red and pink" effect is given below.

1st operation.—Pad the cloth in a 5 per cent. solution of olive oil oleine and dry over copper cylinders.

2nd operation.—Repeat operation 1, dry and stove in hanging room at 75° C.

3rd operation.—Pass through a solution of soda ash $1\frac{1}{2}°$ Tw. and wash.

4th operation.—Repeat operations 2 and 3.

5th operation.—Steam the goods in bundles for 1 hour at 4 lbs. pressure, then allow them to lie in pile in a warm room for two days.

6th operation.—Print for the Chocolate:—10 Chocolate.
,, ,, Dark red:—14 T. Red.
,, ,, Light red:—4 T. Red.

7th operation.—Age in any of the ways already described, but preferably by hanging 2–4 days in a chamber heated to 36° C., and containing moisture equal to 32° C. wet bulb thermometer.

8th operation.—Fix in a continuous "fly dung" machine in—

4000 litres water.
60 ,, arsenate of soda 18° Tw.
20 ,, cow-dung.
2 kilos. chalk.

Pass the goods in the open width through the above at 60° C., and at such a speed that the treatment occupies 4 minutes. Then wash and dung in—

4000 litres water,
20 ,, arsenate of soda 18° Tw.,
30 ,, cow-dung,

at 40° C. for from $\frac{1}{4}$ hour to 20 minutes. Wash well in spiral becks and dry over copper cylinders.

9th operation.—Pad the dried goods in the open width through a solution of "red liquor" $\frac{1}{2}$° Tw.—dry.

10th operation.—Age through Crum's machine at 32° C., allow to lie overnight in loose pile, and then fix again through the first "dunging" liquor given in operation 8. Wash well and dye.

11th operation.—Dyeing.—Dye with 10 per cent. Alizarin 20 per cent. paste (blue shade), 3 per cent. sumach, 1 per cent chalk, $2\frac{1}{2}$ per cent. Turkey-red oil, 3 per cent. glue size 25 per cent., and a sufficiency of water. Dye $\frac{1}{4}$ hour in the cold; then raise the temperature gradually in $\frac{3}{4}$ hour to 80° C., and dye at that for $\frac{1}{2}$ hour or longer. Wash well "out of dye," hydro-extract the goods, and then open them out to the full width, and, without drying them, proceed to the next operation.

12th operation.—Preparing.—Pad the goods in a 5 per cent. solution of Turkey-red oil, and dry them over cylinders.

13th operation.—Steam the dry oiled pieces for an hour at 5 lbs. pressure. Wash well and soap.

14th operation.—Soap at the boil for $\frac{1}{4}$ hour. Wash well.

15th operation.—Soap at the boil for $\frac{1}{4}$ hour. Wash well.

16th operation.—Pass for 2 minutes through hydrochloric acid $\frac{3}{4}$° Tw.

17th operation.—Wash well and pass for 4 minutes through a solution of soda chemick 2°–3° Tw. Wash well and dry.

Operations 16 and 17 are carried out in continuous machines, as the cloth must not be allowed to lie after its treatments in acid and soda chemick solutions, either of which would rapidly destroy the light red and the pink. As a matter of fact, these two operations are only performed when the very brightest colours are demanded.

Various shades of maroon and claret reds are obtained in the above manner by applying mixed iron and alumina mordants to the oiled cloth, and afterwards dyeing in Alizarin. After dyeing, the goods are treated as described up to the 14th and 15th operations.

Certain shades of brown, olive, old gold, fawn, and blue are also produced in the same way by replacing Alizarin with any other members of the group of mordant colours that will dye up on iron and alumina mordants. Thus it is possible to obtain quite a series of fast shades by simply varying either the mordant or the dyestuff as the case may be, the process remaining the same in its main features. For colours other than Alizarin reds, one "oiling" of the cloth before dyeing is usually enough, or it may be dispensed with altogether in some cases.

Brown effects are obtained either by mixtures of Persian berry or Quercitron bark extracts and Alizarin, or from Anthracene brown, and other shades by suitable mixtures of these with Gallocyanine, Cœruleïn, Galleïn, and Alizarin orange, etc. Some of these "fancy" colours are dyed as under:—

Brown I.— (Fawn)	1½	per cent.	Alizarin 20 per cent. paste	Alumina mordants.
	35	,,	Quercitron bark extract 48° Tw.	
	½	,,	Gallocyanine paste	
Brown II.—	6	,,	Alizarin orange 20 per cent.	Alumina or Chocolate mordants.
	4	,,	Anthracene brown 30 per cent.	
Purple.—	20	,,	Gallein paste 10 per cent.	Alumina or Iron mordants.
Olive I.—	10	,,	Cœrulein S. 20 per cent. paste	Alumina mordants are the best.
Olive II.—	30	,,	Persian berry extract 48° Tw.	
	5	,,	Cœrulein S. 20 per cent. paste	
Old Gold.—	40	,,	Persian berry extract 48° Tw. on 20 Chocolate and its reductions.	

After dyeing, the above shades only require a good washing and soaping for the completion of the process; no oiling or steaming is necessary.

Except for the best quality of goods, and then almost exclusively for reds, the above method of producing the so-called "cameo" effects in three or four shades of one colour has been superseded by the more rapid method of direct printing, or the "steam style" of printing. The best modern "steam" colours are little, if at all, inferior in fastness to most of the "fancy" dyed colours, and they possess the immense advantage of being easily and rapidly corrected for shade if they are "off colour." Moreover, the steam style affords greater scope to the colourist in the harmonising of his colour scheme, since it permits him to introduce gradations of tone as well as gradations of shade, and that, too, with the most delicate of colours—a facility not afforded by the "Madder style," in which gradations of tone are dependent on the variation of the iron content of the mixed mordants, and consequently are limited to the greater or less dulling of a particular colour. Increase in the proportion of iron means the flattening of all compound Madder colours by the introduction of black (or what comes to practically the same thing, of purple), so that it is impossible to obtain gradations such as result from varying the proportions of the members of a "series" of colours, like those already dealt with when speaking of the mixing of compound shades.

Dyed Madder Colours and Steam Colours.

In connection with the "Madder style," it must be mentioned that certain steam colours are capable of being combined with aluminium and iron mordants in the production of multicolour effects, of which the red, chocolate, and purple are obtained in the Alizarin dye-bath in the usual way. The only steam colour that is used to any extent for this purpose is *Alizarin blue.* With very few exceptions, the mordant colours require prolonged steaming for their proper fixation, and are therefore unsuited for use along with "red and iron liquors." But Alizarin blue and one or two other blues of the same group (also Chrome violet blue) can be very well fixed, with a chromium mordant, by running twice through a rapid ager. This short steaming does not harm the iron and aluminium mordants, and it fixes the blue so well that it resists the action of the dye bath perfectly. After steaming, the goods are treated exactly as described for ordinary Madder colours. Aniline black can, of course, be added to the combination—also Catechu brown and lead yellow.

Example.—Print a seven-colour pattern in the following colours:—6 T. Red, 12 Chocolate, 20 P. Purple, Catechu Madder brown, Madder yellow (lead), Aniline black (prussiate), and Alizarin blue.

ALIZARIN BLUE for Madder work.

60 grms. Alizarin blue S.
790 ,,
150 ,, acetate of chrome 25° Tw.
———
1000

Print on cloth prepared with 4 oz. sodium sulphate and ½ oz. chlorate of soda per gallon; pass twice through the "rapid ager"; allow to lie or to hang a day or two, to age the red, chocolate and purple mordants and the brown; and then "dung" and dye in Alizarin according to the instructions already given for Madder styles containing lead yellow. After dyeing, wash and bran the pieces for half an hour at 50°–60° C. to clear the white: wash again and develop the yellow in a warm ½ per cent. solution of bichromate of potash. Then wash again and soap at 60° C.

In working this style, care must be taken to avoid an excess of chromium mordant in the blue, otherwise the blue will be converted into a dirty blackish purple during the operation of dyeing. The excess of mordant becomes fixed on the fibre and attracts Alizarin from the dye bath, so that the resulting colour is a mixture of Alizarin blue and Alizarin claret (the Chrome-Alizarin lake).

In order, too, to keep the white parts of the cloth as clean as possible, and to facilitate their "clearing," the dye bath should contain no more Alizarin than is absolutely necessary for the production of full shades of red, chocolate and purple; and the dyeing should be conducted at not above 50° C. until the bath is almost exhausted, at which point the temperature may be raised to 75°–80° C. Alizarin blue is very susceptible to the action of chlorine, and therefore the clearing of the "white" must be performed almost wholly with bran and soap. A *very light* "chloring" afterwards may be given if the white is not passable, but it is a risky operation, unless the blue is very dark.

Dark blue, orange, and white patterns for the East are obtained in a similar way by dyeing Alizarin orange on a red mordant printed in combination with Alizarin blue. Phenocyanine blues and Cœrulein olive have also been used along with dyed Madder colours, in imitation of some of the "Battick styles."

"Batticking" proper is a "resist" process practised by the Javanese and others, and will be touched upon later. But certain other goods, also produced in Java, have been called "batticks," and have been imitated more or less successfully by means of the Madder dyeing process combined with Aniline black and Alizarin blue. In this class of work a dark blue is often found in combination with a black or chocolate, and the peculiarity of this black or chocolate is, that it is entirely surrounded by a soft, "fuzzy" outline of red or orange. This characteristic outline has the appearance of having been produced by the spreading of some constituent of the principal colour beyond its proper limits; indeed, it is very similar to the defect known as "bleeding," and the colours used in Europe to imitate it are called technically "bleeding blacks and chocolates."

These Blacks and Chocolates consist of mixtures, in various proportions, of Aniline black and red liquor. In practice a mixture of prussiate and sulphocyanide of copper Aniline blacks have been found to give excellent results, but other Aniline blacks are also suitable.

"BLEEDING" BLACK.

{ 2 parts Aniline black (prussiate).
{ 2 ,, Aniline black (sulphocyanide of copper).
1 part red liquor.

CHOCOLATE.

2 parts above mixed black.
1 part red liquor, slightly thickened.

These colours are printed along with Alizarin blue and ordinary Aniline black in a two- or three-colour pattern on the printing machine or by block. The goods are then run quickly through damp steam in a long rapid ager to develop the black, and are afterwards allowed to lie overnight in a cool place, so as not to dry too much. In the morning they are padded with a sloppy paste of acetic acid, and are dried very slowly at a low heat. The roller used must be a heavy pad, in order to saturate the cloth thoroughly with acid. The effect of this padding is to dissolve any basic salt of aluminium that may have been formed in the "ageing" of the black part of the colour; but its main purpose is to cause the red-liquor thus re-dissolved to spread or "bleed" beyond the space occupied by the now insoluble Aniline black. If the first padding does not do this effectually the cloth is padded again. The extent to which the black has "bled" may be tested by dunging and dyeing a small fent in Alizarin. When satisfactory, the goods are aged, dunged, and dyed as usual for the Madder styles. Alizarin gives a black or chocolate with a red edge; Alizarin orange gives black or brown with an orange edge, and other dyestuffs give edges corresponding to the colour of their aluminium lakes.

A good black with a strong red edge or outline is not easy to obtain, nor are the Chocolates very regular in shade; but as the whole process is intended to imitate native hand work, these irregularities are not very serious defects, unless they are too pronounced.

"Cover and Pad" Style.—This important and extensively practised variation from the ordinary Madder style is based upon the solubility of iron and aluminium oxides in solutions of citric and tartaric acids, and of citrates and tartrates; in other words, the presence of these solvents prevents the precipitation of iron and aluminium oxides, hydrates, and basic salts on the fibre, and consequently renders impossible their fixation on the cloth as mordants.

In the practical application of the solvent properties of the above-mentioned substances to the production of white patterns on a dyed ground, a thickened solution of any one of them, say citrate of soda, is first printed on white cloth in any desired pattern. The cloth is then well dried and re-printed with a thickened aluminium or iron mordant in the usual way, in either a fine "all-over" design or a uniform flat ground, covering the entire surface of one side of the cloth.

Wherever the citrate of soda falls under the over-printed mordant the fixation of this latter on the cloth is prevented, with the result that during the operation of dunging it is washed out entirely from those parts of the cloth to which the citrate has been applied; so that on dyeing in Alizarin, etc., a white pattern on a plain or figured coloured ground is obtained,—a pattern corresponding, of course, to that first printed in citrate of soda.

If, in the second- or over-printing, a fine all-over pattern is applied, the cloth is said to be "covered," and the roller used is known as a *covering roller or cover*, whereas when a plain uniform ground is printed, the cloth is said to be "padded," the roller employed being called a *pad roller* or a *pad*. An ordinary "pad" is simply a copper roller engraved over its entire surface with a series of oblique and closely set furrows or lines; a "pin pad" is also engraved evenly over its whole surface, but with minute dots instead of furrows. Both are used for the same purpose, and generally in sequence, with the object of producing a fuller and more even grounding.

A white pattern on a figured background of two different shades of the same or two different colours is obtained by (1) printing an acid or a citrate first; then "covering" in, say, a dark purple, and finally "padding" in a lighter purple; (2) —for a red and chocolate background—covering in a "red liquor" containing a sufficient quantity of tin crystals ($SnCl_2$) to prevent the fixation of the iron contained by the Chocolate mordant subsequently padded over it; and (3), for a red and purple background, covering in the same resist red liquor, followed by padding in weak iron liquor. The operations of ageing, dunging, and dyeing in each of these cases are identical with those already given in describing the ordinary "Madder" style.

Thickened solutions of citrates, tartrates, citric acid, and tartaric acid all go under the general name of "acids."

They are also described as "resists" or "discharges" according to whether they are applied to the cloth before or after the mordants.

Stannous chloride (tin crystals) acts as a resist for iron mordants only, but is only used along with acetate of alumina for "resist reds," since the citrates, etc., give much better and cleaner whites. As a matter of fact, a certain amount of tin is fixed on the fibre, and this, while adding brilliancy to the dyed red, would detract from the purity of the white, because tin is itself a mordant for Alizarin. The Alizarin tin lake is a bright orange.

Citric acid and the citrates are by far the most commonly employed "resists" for all classes of Madder work. They are very effective in all respects, but being exceedingly hygroscopic they absorb a large amount of moisture during the "ageing" process, and are apt to spread into the surrounding parts of the cloth by capillary attraction. This defect, known variously as "swelling," "bleeding," "spewing," etc., is particularly liable to occur if they are too strong for the mordant employed, or if the goods are allowed to get too damp in the ageing chambers. To some extent it can be remedied by the addition of China clay to the printing paste, and by making the latter as thick as is consistent with good printing qualities, but it is always liable to occur under any conditions if the "acid" is too concentrated for the work it has to do.

Tartaric acid and the tartrates are less apt to "swell" than the citrates and citric acid. They are excellent resists, and for Madder purples tartaric acid is perhaps the best "acid" to use, although citrate of soda, citrate of chromium, tartrates of soda, tartrate of chromium and citric acid are all employed with success for this purpose by different firms. Tartrate of chromium is employed largely on the Continent as a resist under all Madder mordants except the strongest, such as 14 T. Red, 18 T. Black, and other colours previously given.

Its chief advantage is that it "swells" very little, and can therefore be used without China clay, which tends to fill up the lines of the engraving.

For very strong alumina and iron mordants it is often necessary to add a small quantity of sulphuric acid, in the form of bisulphate of soda ($NaHSO_4$), to the citric acid and the citrate resists for the purpose of procuring a pure well-cut white. Oxalic acid is also used to the same end, but in both cases ageing in the rapid ager must be avoided if possible, as oxalic and the mineral acids attack the fibre, and, at a high temperature and under the influence of steam, tender it rapidly.

The strength of the simple citric and tartaric acid resists is usually expressed in percentages or in grammes per litre.

Thus 5 per cent. = 50 grms. per litre.

Other resists, being somewhat more complex, are named in the same way as reductions of ordinary colours. Thus an "acid" marked, say, "M. acid 2/3" consists of two parts of gum or starch paste and three parts of standard "M. acid."

In the following recipes will be found formulæ representative of most of the "acids" and "resists" in general use for Madder colours.

5 per cent. T. Acid.

1 litre British gum solution.
50 grms. tartaric acid.

5 per cent. C. Acid.

800 c.c. British gum paste.
200 „ 50 per cent. China clay.
50 grms. citric acid.

Sighten with Indigo extract. Both these acids are used as resists under weak iron mordants for purples. Other resists may be employed equally well, but the above are simple and effective, and have, moreover, been adopted on account of the good results they yield.

M. Acid (for Reds and Chocolates).
320 litres lime juice 48° Tw.
320 ,, neutral citrate L.J.
72 kilos. dark British gum.
40 ,, light ,, ,,
40 ,, starch.
7½ litres turpentine.
Boil and cool.

Neutral Citrate L.J. = (lime juice 48° Tw. neutralised with caustic soda 70° Tw.).

Resist C. (Reds and Chocolates).
35 litres tartrate of chromium 40° Tw.
10 ,, water.
25 kilos. dark British gum.
10 ,, citric acid.
5 ,, oxalic acid.
12½ ,, British gum paste.
Boil and cool.

M.S. Resist :—(Reds, Chocolates).
160 litres lime juice 48° Tw.
16 kilos. starch.
40 ,, water.
48 ,, light British gum.
28 ,, sulphate of soda.
Boil, cool to 50° C., and add—
8 kilos. sulphuric acid 168° Tw.
20 litres water.
Cool before use.

X. Acid.
60 litres lime juice 48° Tw.
40 ,, caustic soda 70° Tw.
20 kilos. dark British gum.
15 ,, light ,, ,,
Heat to 85° C. and cool.

Resist S. (Reds, Chocolates and Purples).
6 litres 50 per cent. gum Senegal solution.
2·75 kilos. citric acid.
1 ,, bisulphate of soda 52° Tw.
0·25 ,, turpentine.
Add a little safranine to sighten.

R.B. Resist (to resist alumina mordants and Aniline black).
20 litres water.
6 kilos. citric acid.
Add carefully
10 kilos. soda ash
and then thicken with
1¼ kilos. glycerin.
8 ,, light British gum.

Resist Red (Chocolate and Purple mordants).

Resist red consists of the ordinary 6 T. or 8 T. Reds, plus an extra quantity of tin crystals. The percentage of tin crystals may be indicated thus: 8 T. Red 5 per cent. T. The amount of tin varies with the strength of the iron mordant to be resisted, but it rarely exceeds 75 grms. per litre of colour, although for fine patterns, and for resisting heavy iron mordants, as much as 100 grms. per litre (1 lb. per gal.) is sometimes used. Stannous chloride (tin crystals) acts as a resist or a reserve by reason of its reducing powers: during the "ageing" process the oxidation of the iron on those parts of the cloth to which "resist red" has been applied is prevented, while the fixation of alumina which is independent of actual oxidation takes place as usual, so that on dyeing in Alizarin a red on a purple or a chocolate ground is obtained. Any depth of red can be dyed by varying the concentration of the "red liquor" employed.

The successful production of bright, full "resist reds" depends quite as much upon the composition of the "red liquor" as upon its percentage of available alumina. Two red liquors which yield practically identical results in ordinary Madder work are often found to give widely different results when used for *resists* under iron mordants, although under other conditions they both deposit the same amount of alumina on the fibre in the ageing and dunging operations. This matter was investigated, on a practical scale, by the late Mr J. W. Jones of Middleton, and formed the subject of a paper by him entitled "On the composition and testing of Tin Red liquors" (*Textile Colourist*, vol. i p. 189, 1876). As the result of a long series of trials, he found that when a red liquor of 16° Tw. contained an amount of undecomposed sulphate of alumina corresponding to *more* than $2\frac{3}{4}$ per cent. SO_4 it was unsuitable for "resist Madder reds." The unsuitability took the form of poor, thin, dull colours; hence, since most commercial red liquors are sulphate-acetates of alumina, it is essential, in order to secure the best results, to ascertain beforehand whether they contain too much free sulphate for resist reds. If so, they can easily be rectified by the addition of either a little normal acetate, or by precipitating the sulphuric acid with a calculated quantity of acetate of lime or acetate of lead.

RESIST 12 T. RED $7\frac{1}{2}$ per cent. T. (for strong Chocolate pads and covers)

100 litres red liquor 12° Tw.
20 kilos. flour.
$2\frac{1}{2}$ litres oil (olive).

Boil, cool, and add

$7\frac{1}{2}$ kilos. tin crystals.

For purple "covers" and "pads" $1\frac{1}{2}$–$7\frac{1}{2}$ per cent. of stannous chloride is used according to the strength of the purple mordant.

"Resist" or "Reserve" yellows consist of nitrate of lead and varying percentages of citric or tartaric acids. They are treated as already described for "Madder yellows." As a rule, "resist yellows" are thickened with flour in preference to starch or British gum, a little oil being added in the boiling to soften the paste and improve its working properties.

5. T. RESIST YELLOW (for dark purple covers and pads).

100 litres water.
30 kilos. lead nitrate.
10 ,, flour.
$1\frac{1}{4}$ litres olive oil.

Boil and add

5 kilos. powdered tartaric acid.
$2\frac{1}{2}$,, Indigo extract for sightening.

For weaker purple mordants the tartaric acid is reduced. Cover patterns in general require a rather weaker resist than "pads" printed in the same mordant. The following strengths of "acids," "resists," or "reserves" are arranged to be printed on goods afterwards padded with two rollers at once—the one a "pin" and the other a "line" pad.

5 per cent. T. acid	under	20 P. Purple (on M. prep., see p. 347).
3 per cent. ,,	,,	100 ,, ,,
2 per cent. ,,	,,	240 ,, ,,
Resist C.	,,	8 Chocolate, 8 P. Purple ,,
Resist S.	,,	12 Chocolate, 8 T. Red, 6 P. Purple
M.S. Resist	,,	12 T. Red.
,,	,,	12 T. Black (M. prep.).
M.S. Resist ½	,,	6 T. Red.
,,	,,	8 T. Red.
M.S. Resist 1¼	,,	4 Chocolate 1½.
M. acid	,,	12 T. Red, 8 Chocolate, 12 Choc., etc.
,,	,,	10 T. Black (M. prep.).
R.B. Resist	,,	Aniline Black Cover and 6 or 8 T. Red Pad.
Resist 12 T. Red 7½ per cent. T.	,,	8 Chocolate, M. prep.
,, ,, ,, 5 ,,	,,	20 P. Purple.
5 T. Resist Yellow	,,	,,
2 T. Resist Yellow	,,	240 P. Purple, etc.

Another Yellow resist under strong Red and Chocolate mordants is made as follows:—

Strong Resist Yellow.

80	litres	water.
20	,,	citrate of soda 32° Tw.
10	kilos.	China clay.
10	,,	flour.
30	,,	lead nitrate.
1¼	,,	olive oil.

Boil, cool, and add

20	,,	citric acid (powdered).
3	,,	Indigo extract (sightening only).

If any of the foregoing "reserves" "run" or "swell" in the process it is advisable to grind them up with about 10 per cent. China clay, or, better still, the clay may be introduced during the preparation.

In "resist styles" that are both "covered" and "padded," the covering and padding are usually done in two separate printings; but an arrangement by W. W. Wilson and the Calico Printers' Association is in use for the continuous printing of the two on an ordinary machine. The cloth, after passing under the covering roller, runs into a drying chamber, situated under the printing machine, from whence it re-enters the machine and is at once printed by the padding roller. This arrangement has not been generally adopted by calico printers.

Colours for "cover" patterns are almost invariably thickened with flour and starch in order to ensure a sharp impression; padding colours, on the contrary, are as often as not thickened with British gum or a mixture of British gum and flour, and they are, as a rule, worked much thinner than ordinary printing colours, the object, of course, being to secure a good level ground colour by allowing the mordant to soak into the cloth.

The fact that any cover pattern can be printed over any other pattern (in "resist colours") makes it possible to obtain an endless variety of combinations of patterns, and within the limits of the colours suited to the process, of colour also.

The following concrete examples of some of the effects producible by covering and padding cloth previously printed with "acids" or "resists" will give some idea of the possibilities of the process.

(1) White Design on a Chocolate ground spotted with Red.—First print M.S. resist or M. acid on M. prepared cloth; then dry and "cover" in resist 8 T. Red 7½ per cent. T. with a spot pattern; dry again, and finally pad in 8 Chocolate; dry.

(2) White on a Purple and Red ground.—Print M.S. resist; dry and cover in resist 12 T. Red 5 per cent. T.: dry and pad on 20 P. Purple.

(3) White, Purple, and Black on Purple ground.—Print 3 per cent. T. acid, 12 P. Purple, and 10 T. Black or Sulphide Aniline Black, on M. prepared cloth. Dry and pad 100 P. Purple or 60 Gum Purple.

(4) White, Yellow, and Red on Dark Chocolate ground.—M. prepared cloth. Print M.S. resist, Strong Resist Yellow, and Resist 8 T. Red 7½ T. Dry and pad with 8 Chocolate or 4 Chocolate ½.

(5) White, Yellow, Purple, and Black on Purple ground.—M. prepared cloth. Print 2 per cent. T. acid, 2 T. Resist Yellow, 8 P. Purple, and 10 T. Black. Dry and pad in 200 P. Purple or 120 Gum Purple.

(6) White, Red, Yellow, Purple, Brown, and Black on a Purple and White ground.—On M. prepared cloth. Print first 5 per cent. T. acid, Resist 14 T. Red 5 per cent. T., 5 T. resist Yellow, 16 P. Purple, Catechu Madder Brown, and 10 T. Black. Then dry and "cover" in 20 P. Purple.

(7) White and Aniline Black under Aniline Black cover and Madder Red pad.—First print R.B. resist and Aniline black; then dry and cover Aniline black (prussiate); dry and pass twice through the "rapid ager"; pad in 6 T. Red, and proceed as for the ordinary Madder style.

After the *final* printing all resist styles are passed through Crum's Ageing Chamber, hung up 2–4 days, and then dunged and dyed, etc., as usual, according to methods already described. Patterns containing "resist yellows" are treated in exactly the same way as "Madder yellows," but if they have no white in them the clearing operations in weak bleaching powder may be omitted.

A style of "resist work" in which both sides of the cloth are alike, is produced by printing first of all one of the foregoing "acids," and then, after drying well, padding the goods "straight through the nip" in a padding mangle; that is, passing the cloth between the india-rubber and brass bowls of the mangle without allowing it to pass through the liquor contained in the box below them. The lower or brass bowl revolves, partly immersed in the padding liquor, and carries sufficient of it up to the cloth to thoroughly saturate it (see fig. 50). From the mangle the cloth runs immediately on to a set of drying cylinders, and is dried as rapidly as possible to avoid any chance of the printed resists spreading beyond their proper limits. Resists for this style of work are best thickened with flour or starch, both of which are more insoluble than the gums. China clay may also be added with advantage. In other respects the treatment of these goods is as above, viz. like all Madder dyed goods.

Discharging of Slop-padded Mordants.

This modification of the Madder style is exactly the reverse of that just described. The cloth is first mordanted uniformly all over by padding through solutions of iron or aluminium acetate, and then thoroughly dried in hot air; the patterns are then printed upon it in strongly acid discharging mixtures, which act in precisely the same manner as the preceding "resists" and "acids." After printing, the cloth is aged, dunged, and dyed in much the same way as the ordinary Madder styles, but the acid, being printed on partly fixed mordants, must be allowed sufficient time to react with them, or its action must be intensified by a short steaming in the rapid ager, followed by a 24 hours' hanging in a warm, moist atmosphere. The latter procedure is most commonly adopted at the present time.

The original method of drying in hot air was to pass the padded goods through a long brick chamber—the "hot flue"—which was heated by the hot air rising from the surface of an exposed iron or fire-brick flue (or series of flues) running from end to end of it. The flue itself was heated from a furnace placed at one end of the apparatus. In modern "hot flues" the heating of the air is effected by means of steam chests and batteries of gilled steam pipes combined with a fan which blows hot air through the whole chamber The padding mangle, of which a section is shown in fig. 49, is directly connected with the "hot flue," so that the mordanted goods pass directly from the mangle into the drying chamber.

The process of producing white patterns on coloured grounds by the discharging of slop-padded mordants, followed by dyeing in Madder and other colouring matters, was formerly distinguished from all other kinds of dyed work by the name of the "Foulard" or Padding Style,—a name which at one time indicated that the colours were dyed on iron or alumina mordants. The definition of the "Padding style" has now been extended, however, to include all classes of work, in which either the mordants or the colours are, of necessity, applied by slop-padding in a mangle, so that the discharging of padded Red and Chocolate mordants is no longer *the* padding style, but only *a* padding style,—one amongst many.

Reverting to the application of alumina and iron mordants, it may be noted that the "padding style" is almost exclusively confined to the production of dark, full colours; and this because, as is well known to practical men, it is somewhat difficult to mordant cloth evenly in the padding mangle with very dilute mordants, which are liable to dissociate irregularly in the hot flue. This defect has, to a great extent, been remedied in the modern "hot flues," which are heated by steam and a forced draught of hot air; but alongside these improved means of drying, equal advance has been made in the art of dyeing; and although it is now possible to slop-pad very weak Madder-red, Chocolate, and Purple mordants with considerable certainty of success, other methods than Madder dyeing have been devised for the production of "discharge effects" on light grounds.

After padding and drying, the mordanted cloth is printed with other mordants for colours or black, and with one of the following acid discharges for white:—

DISCHARGE WHITE I.

{ 4 kilos. starch.
{ 2½ litres water.
6¼ ,, gum tragacanth thickening 1½ per cent.
15 ,, lime juice 48° Tw.

Boil and add
4 kilos. bisulphate of soda.

Cool and add
¾ kilo. oxalic acid.

DISCHARGE WHITE II.

300 grms. citric acid.
10 ,, oxalic acid.
690 ,, British gum paste.

DISCHARGE WHITE III.

40 kilos. citric acid.
1¼ ,, oxalic acid.
100 litres water.
5 kilos. China clay.
25 ,, British gum.

The printed cloth is aged by hanging for 2 to 4 days, either with or without a previous run through the "rapid ager," and is then dunged twice, first at the *boil* for 3 minutes in the continuous fly dunging machine, and second for half an hour as usual at 60° C. After dunging it may be dyed with any suitable dyestuff. The "fly dunging" at the boil enables the "acids" to *cut* the mordants much more effectually than they would at a lower temperature.

(1) Black and White on Red ground:—(1) Pad the cloth in red liquor at 10° Tw. dry. (2) Print on 6 T. Black and Discharge White I. dry. (3) Age, dung, and dye in Alizarin as for reds. (4) Oil, steam, soap, and clear.

(2) White on Brown or Cinnamon ground.—(1) Pad the cloth in 40 Chocolate liquor (40 parts Red liquor, 8 Tw., and 1 part Iron liquor, 24° Tw.); dry. (2) Print on Discharge White III.—dry. (3) Age, dung, and dye in the following:—

1½ per cent.	Alizarin, yellow shade, 20 per cent.
15 ,,	Bark extract 48° Tw.
10 ,,	Persian berry extract 48° Tw.
½ ,,	chalk.
20 ,,	glue solution 15 per cent.

On the weight of the cloth.

(4) Wash well, bran for ¾ hour, steam, and clear.

(3) White on Black ground.—(1) Pad in the following:—

3 parts	Iron liquor 24° Tw.
5 ,,	Red liquor 14° Tw.
2 ,,	water.

Dry. (2) Print on Discharge White II. (3) Age, dung, and dye in—

10 per cent.	Logwood ext. 40° Tw.
1 ,,	sumach ext. 48° Tw.
1 ,,	chalk.
20 ,,	glue size 15 per cent.
½ ,,	soda ash.
½ ,,	Turkey-red oil.

On the weight of the cloth.

(4) Wash well, bran at 80° C. for half an hour, wash, dry, and clear in bleaching powder solution ⅛° Tw. A light soaping enhances the brilliancy of the white after "chemicking."

(4) White on Claret ground.—Proceed as in (1), but dye up in Alizarin Bordeaux.

(5) Yellow on Red ground.—Proceed as in (1), and after dyeing and clearing the red, pad in a weak solution of a basic acetate of lead; dry partially, and pass through ammonia vapour to fix the lead as hydrate, and then develop chrome yellow by a run through bichromate of soda, 5 grms. per litre. Wash well and dry.

Scores of other colours can be dyed on slop-padded and discharged red and black liquors, but the above will serve to illustrate the methods of work without giving further examples.

Combined styles with Madder dyed colours and Indigo have never been produced in very large quantities, on account of the practical difficulties that crop up between the ageing and the dunging of the printed mordants. Many attempts have been made to combine the Madder style with the glucose process of Indigo printing, and some good work has been done in this way, but on the whole the process is difficult to work successfully on the large scale. The Indigo loses in depth of shade during the drastic clearing operations that are essential to the production of a bright red and a pure white; and again, after the reduced Indigo has been re-oxidised in cool hanging rooms, it ought to be washed well in cold water, whereas the mordants printed along with it require dunging in hot solutions. In any case one or the other must suffer to some extent, and consequently the style is but little used.

Aniline black in combination with alumina and iron mordants constitutes one of the most important of all styles of printing. The process of ageing is common to both, and the dunging operations not only fix the mordants but at the same time improve the black; and if a Prussiate black is employed, the iron it contains acts as a mordant, thereby tending to tone the shade of the black, while increasing its depth.

Goods printed in Madder red and chocolate mordants and sulphide or vanadium Aniline blacks are always aged by hanging in the ageing chambers for 3 to 4 days (if this system is available); if printed with the prussiate Aniline black, the black is developed by one or two runs through the rapid ager, followed at once by a passage through gaseous ammonia to neutralise the free mineral acid liberated by the steaming. In other respects the treatment of the goods is identical with that given in the description of the previous processes for ordinary printed mordants such as 6 T. red, 20 Chocolate, etc.

(*b*) **The "Basic" Style.**—Of late years the employment of basic Aniline colours in the dyed styles has increased considerably. They yield a vast variety of beautiful shades, moderately fast to light and soap; and as they can be dyed on any insoluble tannate, it is possible to apply them to the production of effects analogous to those obtained by "Madder dyeing" in most of its aspects. For this purpose it suffices merely to treat goods mordanted with red or iron liquor in a boiling solution of some tannin matter, and then, after a good washing, dye them in a slightly acid solution of a basic colour. Both iron and alumina form insoluble tannates, and these fix basic colours practically as well as tannate of antimony. From this it is evident that any iron or alumina mordant, whether printed directly, or resisted, or discharged, can be utilised for obtaining a range of effects altogether too wide to enumerate in detail. In this way (by tanning iron and alumina mordants) most of the "Madder styles" can be reproduced in a series of bright colours otherwise unobtainable by any dyeing process in vogue before the discovery of coal-tar dyestuffs.

Another method of applying basic colours by dyeing is to print tannic acid on the cloth, then fix in tartar emetic, wash well and dye. By printing several strengths of tannic acid, various shades of the same colour are obtained by a single operation in the dye beck; and the tone of these same shades can be varied either by fixing the tannic acid with copperas ($FeSO_4$) instead of with tartar emetic, or by treating the tannate of antimony mordanted cloth in a solution of copperas before dyeing. In both instances the bluish-grey tannate of iron is formed, and this modifies the tone of the colour subsequently dyed.

Still another, and perhaps the most important method of applying basic colours in dyed styles of calico printing, is that based upon the observation that tannic acid and tannate of antimony mordants are capable of being discharged by caustic soda under the influence of steam. The cloth is first mordanted all over by padding, and is then printed with a thickened solution of caustic soda, steamed, washed, and dyed in a basic colour. The caustic soda dissolves out the mordant from the printed parts, and in the dye bath these parts remain undyed, so that they form white figures on a coloured ground. For working details of the Tannin Discharge Style, see "Discharge Styles."

(*a*) BASIC COLOURS ON ALUMINA AND IRON MORDANTS.—Patterns produced in this way are printed as usual with red or chocolate mordants, and for black, with Aniline black. After ageing and dunging they are "tanned" in tannic acid or one of its many substitutes, *soaped lightly*, well washed and dyed. The soaping is not absolutely essential, but it facilitates, in a marked degree, the production of a pure white and a good full quality of colour.

BLACK AND WHITE ON VARIOUS GROUNDS.

Process :—

(*a*) Print Aniline black (prussiate) and 4 T. red.

(*b*) Age twice through the rapid ager, and after "gassing" in ammonia vapour allow to lie two days in loose bundles.

(*c*) Dung, wash and "tan" in—for 100 lbs. cloth (full pattern)—

2 per cent. tannic acid } Dye half an hour at 70° C., wash well in
$\frac{1}{16}$,, ammonia } warm water.

(*d*) Soap at 50° C. for 10 minutes in 1 part soap per 1000 of water. This process is optional. Wash well until free from soap.

(*e*) Dye as follows for medium shades :—

½–2½ per cent. dyestuff.
2 ,, acetic acid 6° Tw.
1½ ,, alum.
water (a sufficiency).

Raise the temperature of the dye bath to 80° C. in half an hour, and then dye a further ½ hour at that. Wash well.

(*f*) Soap at 60°–70° C. until the whites are clean, and then finish with a thorough wash.

Examples :—

Rose pink	½ per cent.	Rhodamine B.
Blue	¼ per cent.–½ per cent.	Methylene blue N.
Electric	½ ,,	New blue L (Cassella).
Green	½ ,,	Methylene green (yellow shade).
	½ ,,	Auramine O.
Orange	1½ ,,	Auramine O.
	¼ ,,	Rhodamine 6 G.
Violet	¼ ,,	Methyl violet.

Darker shades are obtained by operating on exactly the same lines, but with a stronger alumina mordant to start with, followed by a corresponding increase in the quantities of tannin and dyestuff.

Thus :—

	Print.	*Tan.*	*Dye.*
Navy blue . . .	6 T. Red	3% tannic acid	3% Fast cotton blue T.A.I. (M., L. & B.).
Crimson . . .	,,	,,	1½% Methyl violet 6 R.
Plum	8 T. Red	4% ,,	1½% Fast cotton blue T.A.I. 1¼% Methyl violet 6 R.
Peacock green, dark	6 T. Red	3% ,,	3% Methylene green (yellow shade).
Olive	,,	,,	2% Fast cotton blue T.A.I. 1½% Auramine O.
Myrtle . . .	8 T. Red	4% ,,	2% Indigo blue J. A. (Geigy). 3% Thioflavine T.
Dark Blue . . .	8 Choc.	3% ,,	2% Marine blue S.

Any of the above colours dyed on a Chocolate mordant give duller shades, the dulness depending on the proportion of iron present. Two- and three-colour effects are obtained by printing different strengths of mordant, say, 14 T. red, 4 T. red, and ½ T. red. Tan and dye as above.

(*b*) BASIC COLOURS ON PRINTED TANNIN MORDANTS.—In this method a thickened solution of tannic acid is printed on white cloth, and then fixed thereon by a run through tartar emetic or any other suitable antimony salt. If quieter shades are required, the fixing in antimony may be followed by a short treatment in a weak solution of ferrous sulphate. This style is not much used, although it yields good "cameo" effects in a single dyeing.

TWO-COLOUR EFFECT ON WHITE GROUND.

Process:—

(*a*) Print on white cloth the two following thickened solutions of tannic acid:—

5% TANNIN MORDANT.	¾% TANNIN MORDANT.
500 grms. tannic acid.	1½ litres 5% tan. mord.
2 litres acetic acid 9° Tw.	½ ,, acetic acid 9° Tw.
5½ ,, gum tragacanth 6%.	4½ ,, tragacanth 6%.
2½ ,, water.	3½ ,, water.
10 litres	10 litres

(*b*) Dry after printing, and age twice through the rapid ager. Ageing is not essential unless the pattern contains Aniline black, but it is advantageous, as it seems to fix the tannic acid on the fibre better. Fix in the ordinary tartar-emetic bath—

15–20 kilos. tartar emetic,
5 ,, chalk,
1000 litres water,

and wash well.

(*c*) Dye in any basic colour which does not stain the white parts of the pattern permanently.

For Pink say 1 per cent. Rhodamine 6 G.
,, Blue ,, 2 ,, Thionine blue O.
,, Yellow ,, 2 ,, Acridine yellow G.
,, Green ,, { 1½ ,, Acridine yellow G.
{ ½ ,, Thionine blue O.
,, Navy Blue 2–3 ,, New blue L.

and various mixtures of Pink, Blue, and Yellow, for browns, olives, and other mode shades.

The dyeing of mixtures of basic colours in the dye beck or in the jigger presents many difficulties in practice, especially if the shades dyed are delicate and light in tone. Some dyestuffs combine with the mordant very quickly, even in the cold, while others dye up more slowly, the result being that, in most cases, the ultimate colour is more or less uneven in shade. Greater regularity can be secured by the addition of acetic acid to the dye bath, but this cannot be carried beyond a certain limit, and even then it is not a perfect levelling agent, although with care good results are obtained. The best method of dyeing level shades with small percentages of mixed basic dyestuffs is to *slop-pad* the mordanted goods through an acid solution of the colours, instead of dyeing them in a larger bulk of water, as is necessarily the case in the dye beck, and to a less degree in the jigger. After padding, the goods are dried over steam heated cylinders or through a "hot flue," and then passed, in the rope state, into a dye beck filled with boiling water—the "scalding off" beck. During this process of "scalding off," which lasts 15–30 minutes, the dyestuff is completely fixed on the fibre, and the colour that washes out of the unmordanted parts of the cloth is so completely taken up by the mordanted parts that the water in the dye beck is scarcely stained. Indeed, the fixation of the colour is so far advanced after padding and drying that cold water hardly affects the mordanted parts of the cloth at all, dissolving out only that portion of the colour which adheres to the "whites" or unprinted parts.

In order to obtain regular results the pressure of the squeezer bowls of the padding mangle ought to be regulated in such a way that the cloth carries its own weight of dye liquor into the drying apparatus; and a three-bowl mangle ought to be used in preference to a two-bowl machine, because it is possible to arrange it so as to allow of the cloth passing twice through the padding liquor, with a "squeeze" between each passage,—an advantage which ensures a better penetration of the dyestuff into the body of the fabric.

Examples:—

Light Olive (100 kilos. cloth).

1 per cent. dyestuff =
30 grms. Rhodamine 6 G.
725 ,, Acridine yellow G.
245 ,, Thionine blue O.
10 litres acetic acid 9° Tw.
90 ,, water.

Fawn (100 kilos. cloth)

1 per cent. dyestuff =
80 grms. Rhodamine 6 G.
900 ,, Acridine yellow G.
20 ,, Thionine blue O.
10 litres acetic acid 9° Tw.
90 ,, water.

Slop-pad any tannin-mordanted cloth in the above dye liquors, at a speed and with a pressure on the mangle bowls that will allow the cloth to absorb its own weight of liquor. Then dry; "scald off" for 20 minutes at the boil; wash and soap as required.

The two chief advantages of the slop-padding method of dyeing basic aniline colours are – (1) great uniformity of shade; and (2) increased output, due to the speed at which the goods are dyed. A saving of dyestuff is also effected, because practically none comes off in the hot water becks, while in ordinary dyeing the bath is rarely exhausted. Purer colours, too, are obtained, and any modifications of shade that may be necessary are rapidly and easily made. To see the shade yielded by any mixture, all that is required is to dip a part of the cloth under treatment into the dye liquor, pass it at once through the mangle by hand, dry it sharply, and wash it immediately in about 25 times its own weight of boiling water; then dry it again, and compare it with the standard to be matched.

The disadvantages of working as above are—(1) that the cloth requires drying before padding; and (2) that the drying apparatus must be cleaned for each colour dyed. If, however, the first few dry cans are wrapped with calico, this second objection is of little moment. Most of the soiling takes place on the first four or five cans, and if these be wrapped it is a simple matter to change the wrapping. Of course, if pinks follow greens, the whole range will require cleaning by running "wet grey cloths" for some time, taking care to see that their position on the cans is altered continually so as to make sure that the whole working surface of the drying cylinders (cans) is clean. But, as a rule, pinks and similar delicate colours are padded on mangles specially reserved for what are known as "clean colours," the "dirty colours"—greens, blues, slates, purples, etc.—being dyed on other machines.

The slop-padding method is only economical for large quantities of goods. The extra drying operation is then more than counterbalanced by the improved quality of the work as regards uniformity and evenness of shade in the different lots, and increased speed of production, owing to the fact that hundreds of pieces can be dyed continuously. For small orders the ordinary methods of dyeing are the cheapest and most convenient; and even if they are somewhat liable to give irregular results, and demand more care in their working, they at least do away with the necessities of previously drying the cloth, and of cleaning down the drying machines at frequent intervals.

(*c*) The Chrome Mordant Dyed Style.

Chromium mordants, except when mixed with colouring matters as in the steam style, are rarely printed on cloth alone, owing to the practical difficulties in fixing them satisfactorily when so applied. The ordinary chromium acetates, sulphate-acetates, and nitrate-acetates all deposit a certain amount of chromium oxide on the fibre, but it is unevenly distributed, and as a rule gives irregular work when dyed up.

It might be supposed that chromium acetates would behave like the acetates of iron and aluminium, but this is not the case by any means. Such chromium compounds as are capable of application by printing are too stable to dissociate during the "ageing" process, *with one exception*,—they do not seem in practice even to decompose fully—certainly not regularly—on steaming. On the other hand, those compounds that readily yield their chromium to the fibre are only suitable for padding in a slop-padding mangle, because, although they dissociate easily enough, they do so too rapidly and unevenly during their run through the drying apparatus of the printing machine. Moreover, in presence of thickening agents, they are exceedingly liable to decompose spontaneously, with disastrous results if the printing is proceeded with before the decomposition of the "colour" is observed. On the whole, therefore, chromium mordants may be regarded as unsuitable for printing, except in combination with colouring matters as in the "steam style."

The above-mentioned exception to the general rule is not, properly speaking, a chromium compound, but a mixture of bichromate of potash, magnesium acetate, sodium thiosulphate, and a little ammonia. This mixture, thickened with starch paste or British gum, is stable in the cold, or at the ordinary temperature and without access of light, but when printed, dried, and steamed the constituents react upon each other. Under the influence of steam and magnesium acetate, the thiosulphate reduces the bichromate to the basic state, and chromic oxide is deposited on the fibre. The printed goods are then either washed at once, or they may be passed quickly through a 5 per cent. solution of soda ash at the boil, in order to ensure the complete precipitation of the chromic oxide. Any colour that is used with chromium mordants in the "steam style" is suitable for dyeing on chromium mordanted cloth obtained as above.

The dyeing is carried out as already described for Madder colours, the only difference being that the goods require no oiling or steaming, though these processes do in some cases improve the brilliancy of both colours and white. As a rule, however, a good soaping, followed by a light "chemicking," is quite sufficient to clear the "whites."

Either a steam Logwood black or a prussiate Aniline black may be printed in combination with this mordant; both resist the dyeing operation, but Aniline black must be used if it is intended to fix the mordant in soda ash after steaming. A recipe for the preparation of a steam chrome mordant will be found in the chapter on Mordants.

Acetate of chrome and basic sulphate of chrome, thickened with tragacanth, are sometimes used for printing on goods mordanted with chromium oxide (by any of the usual padding processes). They are fixed by a short steaming and a run through boiling soda ash. On dyeing, a two-tone effect is obtained: or if black and a discharge acid have been printed along with strong chrome mordants, on cloth lightly mordanted all over with any of the mordants suitable for that purpose, a four-colour effect is produced, consisting of a black, white, and dark chrome colour, on a lighter ground of the latter. Used in this way, basic acetates and sulphates of chrome are useful mordants, but used alone, on white cloth, their irregularities are too pronounced for them to be of much use in practice except for multicolour dyed work, in which their unevenness is, to some extent, masked by the other shades.

A reduction mordant similar to, and suggested by, the above steam chrome mordant of Koechlin was worked out by one of the authors in 1904. It was never introduced on the large scale, although it gave satisfactory and consistently good results in a series of bulk trials. The original experiments were made with the old hydrosulphite N.F. (M., L. & B.), but in the following formulæ this has been replaced by Hyraldite C. extra pat. (Cassella), though any similar sulphoxylate will answer quite as well. Of the two recipes given below, the second is perhaps the better; strict comparison, however, was not made.

	I.		II.	
Bichromate of soda . .	3,000	grms.	3,000	grms.
Caustic soda 88° Tw. . .	2,000	,,	...	,,
Water . .	10,000	,,	9,600	,,
Sodium acetate . .	...	,,	2,750	,,
Ammonia 25 per cent. . .	...	,,	500	,,
Hyraldite C. extra pat. . .	1,500	,,	1,500	,,
Gum tragacanth 6 per cent. .	33,500	,,	32,650	,,
	50,000		50,000	

Print on white cloth, dry, age twice through a hydrosulphite ager at 100°–102° C.; pass for 2 minutes through a boiling 2 per cent. solution of soda ash; wash well and dye in Alizarin, Cœrulein, Alizarin heliotrope B B., Alizarin orange, Anthracene brown, Gallocyanine, Persian berries, or Quercitron bark, or any other mordant colour which gives a pleasing shade on chrome mordants.

By replacing the greater part of the tragacanth with water, the same mixture may be used for slop-padding with excellent results, as judged by the limited number of experiments made.

Taken altogether, the "printing-on" of chromium mordants is of comparatively little importance. Similar effects and a greater variety of them can be obtained more easily, rapidly, and with greater certainty of success from the same colours by *direct printing*, as in the steam style.

The discharging of *padded* chrome mordants, and of padded "steam chrome colours," is one of the more important branches of modern calico printing. The previously mordanted cloth is printed with citric acid, and then "aged," fixed, and dyed. The acid dissolves out the mordant, with the result that a white pattern on a coloured ground is obtained. Similar styles are produced by printing oxidation discharges on cloth padded with ordinary "steam colours." The padded goods are dried, printed at once with the discharge, and steamed as usual. Details of these processes will be given in the section dealing with "Discharge and Resist Styles."

Remarks on the Dyed Style in general.

In all dyed styles in which part of the cloth is left unmordanted, or in which very light colours are employed, it is essential to the attainment of successful results, as represented by bright level colours and pure whites, that the following precautions be observed:—

(1) The cloth must be thoroughly bleached. To test this, dye a fent off the pieces in question in Alizarin before the cloth is put into work: no streaks, cloudy patches, or stains of any sort ought to be apparent, and the slight tint given by the Alizarin ought to come out on soaping.

(2) Cloth that has been used for "back greys" ought not to be employed for the dyed styles. It is often very difficult to bleach out the last traces of the colour and mordants that have been transferred to "back greys" from the printed cloth; and if they are allowed to remain, they invariably dye up, showing as a faint secondary pattern. Such "back greys" may appear perfectly white after bleaching, and are quite suitable for the "steam styles" or Aniline black discharge styles, but for the Madder styles it is best to avoid all risk by employing new "greys" only. These should be bleached until they are perfectly free from all foreign matters whatsoever, otherwise they are practically certain to contract stains in dyeing.

(3) The mordants must be properly fixed by the "ageing" and "dunging" processes, and before the goods are entered into the dye bath they must be freed from all traces of the thickening agents used in printing. Neglect of these points means uneven colours or stained "whites."

(4) In order to secure pure whites, the dyed goods must be thoroughly washed in water to remove all loosely adhering dyestuff before they are submitted to the oiling and steaming processes.

(5) The dyeing must be conducted at a temperature not exceeding 75° C. for Alizarin and other mordant dyestuffs, unless the cloth be prepared in oil, when it may, with advantage, be dyed at a higher temperature.

(6) The final operations of soaping must be sufficiently drastic to clear the whites and brighten the colour, by removing that portion of the latter which lies, more or less, on the surface only. Too much reliance ought not to be placed on the bleaching properties of the bleaching solution used in the last operation of all. If this has to be repeated two or three times to brighten up a dirty "white," the colour is certain to suffer both in brightness and depth.

(7) In dyeing basic colours, keep the dye bath on the acid side by the addition of acetic, formic, or sulphuric acid or potash alum. These assist greatly in preserving the purity of the white.

Other dyed styles based upon one or other of the foregoing are in use, but they are either modifications or combinations of those already given, and call for no special mention.

Patterns produced by the discharging of Turkey red, Indigo, etc., may be regarded, in a sense, as belonging to the "Dyed Styles." Their characteristic features, however, are due entirely to the application of discharging agents, and therefore, although the preliminary dyeing of the cloth is certainly an essential (and the first) stage in their production, they must be classed as "discharges"; and as such they will be described, along with other "Discharge Styles," in another part of this work. The dyeing of the cloth, however, may be conveniently dealt with here.

Turkey Red.

Turkey red is merely a Madder or Alizarin red, dyed by a special and lengthy process which renders it not only excessively bright, but also extremely fast to all the various destructive agencies to which textile fabrics are exposed.

Turkey red may be considered as quite fast to light, soap, weak mineral acids in the cold, weak alkalies, and to all but the most powerful oxidising and reducing agents. In short, it is one of the fastest colours known.

The dyeing of Turkey red is a special branch of the industry practised only by a few large firms. It involves a long series of consecutive operations, for the proper performance of which an extensive installation of special plant is required; hence it can never form part of the routine work of the smaller printworks, whose output all told would be too small to cover cost of production. Turkey red of a sort is dyed in many works, but it compares very unfavourably with the magnificent productions of the great firms who make it a speciality.

The distinguishing feature of Turkey red is the preparation of the cloth in olive oil or its preparations, the "Turkey-red oils" of commerce. Castor oil oleines and other sulphated oils are also used with success.

The employment of pure hot olive oil, with its accompanying processes of drying at a high temperature and passing through "soda" baths, has become almost, if not altogether, obsolete since the introduction of "soluble oils." Formerly it was necessary to pad the cloth 4–8 times through olive oil emulsions, followed by long exposures to the air, and a 2 hours' drying in stoves at 60° C. after each padding. The oiling, therefore, took several days to accomplish, not to speak of the time subsequently occupied in "soda-ing," steeping in water to get rid of the soda, treating in sumach, mordanting, dyeing, and clearing. The whole process was a question of weeks.

The greatest improvement in Turkey-red dyeing, and one which shortened the process to days, was made by Steiner of Accrington, who impregnated the cloth with the necessary amount of oil in a single operation. This was effected by padding the cloth through *hot* olive oil, kept at a constant temperature of 110° C. The oxidation of the oil was commenced by hanging the goods for 2 hours in a stove (hanging chamber) maintained at 70° C. The goods were then taken out and passed, in the open width, 6–7 times through a solution of soda ash 4° Tw., followed by a stoving of 2 hours at 75° C. after *each* passage. They were finally "soda-ed" at 40° C. in a $\frac{1}{2}$° Tw. solution of soda ash, dried 2 hours at 70° C. after washing out the soda, and then mordanted, dyed, and cleared in much the same way as in modern processes.

Steiner's process, in turn, gave way to the present-day methods, which yield equally good reds, and, when properly carried out, equally fast ones. For discharge work, it is not necessary to dye a shade quite as fast as is required for plain reds, for in any case the red ground will long outlast the colours printed upon it; and if it is fast enough to withstand a run through a powerful decolorising agent like "chemick" at 16°–18° Tw., it leaves little to be desired on the score of fastness.

Those interested in the old processes will find detailed accounts of their practical working in *A Manual of Dyeing*, by Knecht, Rawson, and Loewenthal, or in *The Dyeing of Textile Fabrics*, by the late J. J. Hummel.

In most modern processes the frequent and tedious operations of passing the cloth through alternate baths of olive oil emulsions and solutions of sodium carbonate, followed by "stoving" after each, have been replaced by a *single* run through soluble "Turkey-red oils," followed by one "stoving" or one "steaming" process. This is especially the case for Turkey reds that are intended for discharging. For the fastest reds, however, the oiling and stoving are often repeated four or five times, and the treatment in dilute alkaline solutions is also practised, with questionable reason; probably it is a survival of the older methods, though it is not unlikely that a final run through soda ash removes superfluous oil from the cloth, and renders it more capable of attracting the mordant.

The Turkey-red oil (oleine, sulphated oil, soluble oil, etc.) used may be prepared from either olive or castor oils. As already described, these are treated with sulphuric acid, and the resulting sulphated compounds are neutralised with caustic soda, ammonia, or a mixture of the two. These neutralised oils are the Turkey-red oils of commerce.

The steaming or stoving of the cloth after oiling is not absolutely essential to the production of a bright, full red, but the oil must be decomposed at some stage of the process, and therefore, if the cloth has been mordanted in aluminium salts before steaming, the necessary decomposition of the oleine is brought about by dyeing at the boil. Oiled cloth, whether steamed or not, possesses the property of attracting and fixing the mordant: and, according to Liechti and

Suida, on *unsteamed* cloth the mordant consists of the aluminium compounds of both the ethers and the fatty acids, while on *steamed* cloth it consists of normal aluminium oxyoleate or trioxyoleate, according as olive or castor oil has been employed.

The addition of tin to the aluminium-oil mordant improves the shade of the red. The tin may be introduced as stannate of soda into the oil prepare, or as stannous chloride into the acetate, or the basic sulphate of alumina mordant.

Lime is another essential constituent of the Turkey-red lake; and if the water used for dyeing is not calcareous, an addition of chalk or acetate of lime must be made to the dye bath. It can also be introduced by fixing the aluminium mordant in a warm dunging bath containing chalk—a process which is usually adopted, if only to ensure the complete fixation of the mordant.

In the dyeing operation the temperature is better kept at about 70° C., especially if the cloth is only lightly charged with oil; if, however, a larger amount of oil is present in the fibres, the temperature may be raised, at the end of the dyeing, to the boil, though no useful purpose is served thereby, unless it happen that the oil-prepared cloth has been mordanted in alumina without a previous stoving or steaming, in which case the oil mordants undergo the necessary decomposition at the higher temperature.

On emerging from the dye bath the goods are of a dull reddish-brown shade, totally unlike the brilliant red into which they are converted by subsequent processes. This brown colour is a compound of aluminium alizarate and basic aluminium oxyoleate or trioxyoleate, together with a small quantity of calcium oxyoleate. When its basicity is neutralised by means of a second oiling and steaming it becomes a bright red, the brilliancy of which is further increased by subjecting the goods to a long boil in soap and a small quantity of stannous chloride, followed by a quick run through acid, and a final run through hypochlorite of soda.

The following is a *résumé* of a process used on the large scale for the production of a bluish Turkey red dyed specially for discharging: the cloth used is only half bleached, experience having shown that the finest reds are obtained on goods that have not been treated in bleaching powder solutions. Half-bleaching consists in boiling the grey cloth three times in caustic soda, followed by souring and washing after each boil. The first boil lasts for 10 hours at 8–15 lbs. pressure in any type of kier; the second and third boils occupy 8 and 6 hours respectively at from 4–15 lbs. pressure The goods are not dried after bleaching, but simply squeezed to free them from excess of water; they are then sent directly through the processes given below.

Turkey Red for Discharging.

(1) Slop-pad the cloth direct from the bleach-house, and, before drying, through a 1 per cent. solution of olive oil oleine, and then dry over copper cylinders.

(2) Prepare (slop-pad) in 5 per cent. olive oil oleine; stove two hours at 70°–75° C.; pass through a solution of carbonate of soda at 1½° Tw.; wash through one beck in the open width, and dry. The soda and wash becks are worked in sequence, and the drying machine is also arranged to work with them, so that the process is continuous.

(3) Prepare again in 5 per cent. oleine, dry, and steam in loose bundle form for 1½ hours at 4 lbs. pressure (cottage steamer).

(4) Prepare the cloth after steaming in—

7½	kilos.	stannate of soda.
30	litres	ricinoleate of ammonia 50 per cent.
1000	„	water.

The solution is contained in a machine similar to a "fly dunging" range, and provided with a pair of mangle bowls at the exit end. The cloth runs through at the rate of 30 yards per minute, and is in the liquor about 3 minutes; dry and stove 2 hours at 60° C., or simply dry and allow to lie in pile until wanted.

(5) Mordant, in a similar machine, through basic sulphate of alumina 8° Tw. or red liquor 8° Tw., both at a temperature of 35° C. Dry over copper cylinders.

(6) Repeat (5), and allow to lie a day or two.

BASIC SULPHATE OF ALUMINA.

300 kilos. alum.
3000 litres water.

Add gradually

41¼ kilos. soda ash.
1000 litres water.

(7) When the goods are wanted for dyeing, fix them in a solution of binarsenate of soda and chalk at 40°–50° C. The fixing is performed in a continuous machine of at least 4 becks, provided with top and bottom rollers, over which the cloth travels in the open width.

1ST BECK.

5000 litres water.
100 ,, binarsenate of soda 18° Tw.
50 ,, glue size 15 per cent.
2½ kilos. chalk.

2ND BECK.

5000 litres water.
5 ,, binarsenate of soda 18° Tw.

3RD and 4TH BECKS.—Warm water.

After fixing as above, wash again, and proceed without any drying to—

(8) DYEING.

6 per cent. Alizarin 20 per cent. blue shade.
5 ,, ,, ,, yellow shade.
1½ ,, ground sumach.
2½ ,, Turkey-red oil 20 per cent.

Raise the temperature of the dye bath gradually during the course of an hour to 75°–80° C., and continue dyeing at that temperature for half an hour. Take out of dye, wash well, squeeze, and without drying—

(9) Prepare in 5 per cent. olive-oil oleine, partly neutralised with ammonia. Dry, and then—

(10) Steam for 1 hour at 5 lbs. pressure. Wash and clear.

(11) *First Clearing.*—Boil the goods for 3 hours at 4 lbs. pressure with 4 per cent. soap (palm oil, cotton-seed oil, or Marseilles), 3 per cent. soda crystals, 0·2 per cent. stannous chloride, 2 per cent. oleine (40 per cent.), and a sufficiency of water. Wash well in spiral washing machines, and proceed to the second clearing without drying the goods.

(12) *Second Clearing.*—Boil again for 3 hours at 3–4 lbs. pressure with 2 per cent. soap, 3 per cent. castor-oil soap (50 per cent.), 0·2 per cent. stannous chloride, and sufficient ammonia to dissolve the stannous ricinoleate precipitated: take out, wash thoroughly to remove all traces of soap, and, without drying, proceed to the final brightening processes.

The boilers in which these clearing operations are carried out are of different types: some are practically identical with and work with the same intermittent action as the ordinary low-pressure bleaching kier, that is, the clearing liquor is circulated through the goods by means of a puffer pipe and a steam jet or a steam injector; others are simply large "jacketed" or double-cased pans, like a colour pan, but stronger, and fitted with lids which can be bolted down to make a steam-tight joint with the rim of the pan. Steam may be admitted to the interior of the pan, and the lid carries a safety valve. The liquor, therefore, can be boiled both by live steam and by the steam circulating between the inner and outer casings of the pan. Whatever type of "clearing boiler" is adopted, it must be made of copper, since it is obvious that, at high temperatures, the goods would be stained by coming into contact with iron. In many works the "clearing boilers" serve the double purpose of "clearing" and "steaming" the dyed goods. For the second steaming (operation 10) the oiled and dried goods are packed loosely in the boiler, and then steamed as long as required at the necessary pressure.

(13) *Brightening.*—After the "second clearing" the now bright red cloth is further treated in order to give it the well-known brilliancy of a true Turkey red. For this purpose it is passed in the rope form through successive baths of—(1) hydrochloric acid 1½°–2° Tw.; (2) cold water; (3) and (4) warm water; (5) soap; (6) and (7) hot water; (8) cold water; (9) soda chemick 3°–4° Tw.; and (10) water. All these operations are performed in a continuous machine, furnished with squeezing bowls at convenient intervals, to prevent the successive baths becoming too highly contaminated with the liquor carried forward by the cloth from the preceding becks.

(14) Finally, the cloth is washed thoroughly, hydro-extracted, and dried by hanging in stoves, at a low temperature.

A faster and more intense Turkey red is obtained by padding the cloth 4 times in a 5 per cent. solution of ammonio-soda olive-oil oleine, followed each time by a 24 hours' stoving at 70°–75° C. A light treatment in dilute soda ash (1° Tw.) is then given, and, after drying, the cloth is mordanted, dyed, cleared, and brightened as above.

Another method of dyeing Turkey red was worked out and patented by Erban & Specht. In this process the Alizarin is dissolved in ammonia and then diluted with lime-free water, and mixed with the requisite quantity of Turkey-red oil. The cloth is padded in this solution, dried in the "hot flue," and then passed at once through a second bath containing the necessary mordants. The development and fixation of the colour lake is brought about by steaming the goods for 2 hours, commencing without pressure, and finishing at a pressure of 2 atm. After well washing, the red is treated as already described.

Turkey Red (Erban-Specht Process).

(1) Pad the bleached goods in—
20 kilos. Alizarin paste 20 per cent.
5 litres ammonia 25 per cent.
40 ,, ammonio-soda oleine 25 per cent
lime-free water to 100 litres or—

(2) Dye in the hot flue, allow to cool, and then pass cold through the following mordant:—
2 litres red liquor 8° Tw.
½ ,, acetate of lime 28° Tw.
7½ ,, water.

Dry in the hot flue and then—

(3) Steam for 2 hours as follows:—
1 hour without pressure.
½ ,, at a pressure of 1 atmosphere.
½ ,, ,, ,, 2 atmospheres.

(4) Wash well, and soap with 2 per cent. soap at the boil for 15 minutes.

(5, 6, 7, 8, etc.) Clearing and brightening operations as for other Turkey reds.

It may be noted in passing that Erban & Specht's process is applicable to other mordant colours, and also to iron and chromium mordants. It is not much used for Turkey-red dyeing in this country, if at all.

Goods intended for discharging by the "acid" process may be dyed with any brand of Alizarin; free chlorine destroys both blue and yellow shades of red. On the other hand, the *caustic soda* discharging process is best suited for the yellow shades, the blue shades yielding good "whites" only with difficulty. Indeed, red and pink effects are frequently produced by taking advantage of the greater resistance of bluish reds to caustic soda. The cloth is dyed with a mixture of blue and red shade Alizarins, and is then discharged with caustic soda just sufficiently strong to dissolve out the yellow Alizarin- or Flavopurpurin-lake.

Indigo Dyeing (*for Printing Purposes*).

The method of dyeing Indigo on vegetable fibres is based upon its property of being converted by reducing agents into indigo-white, which is readily soluble in alkaline solutions. When cotton is impregnated with these solutions and then exposed to the air in the wet state, the indigo-white is re-oxidised to insoluble indigotine, and as this is precipitated in the fibres themselves the resulting colour is fast. The alkaline solution of indigo-white constitutes the Indigo Vat.

The reducing agents used in practice are ferrous sulphate or copperas, zinc powder, zinc foil, and hydrosulphite of soda, and the alkaline solvents are for the most part confined to lime and caustic soda. The ingredients composing the vat give it its distinguishing name.

The "Ferrous Sulphate or Copperas Vat" is rarely ever employed nowadays for dyeing Indigo-blue intended for calico printing purposes. The white given by discharging is not so pure as that obtained on a blue dyed in a zinc, or in a hydrosulphite vat, besides which a large amount of sediment is always present in the copperas vat, and as this contains a good deal of Indigo, it entails considerable loss unless steps are taken to recover the Indigo. In any case a certain quantity of dyestuff is always lying useless at the bottom of the vat in the form of a bulky flocculent precipitate of a compound of ferrous oxide and indigotine. In view of the fact that the Copperas vat has been replaced by more suitable methods, it is not considered necessary to go further into the details of its manipulation.

The "Zinc-Lime Vat."—Zinc powder in presence of Indigo and lime rapidly reduces indigotine to indigo white. Thus—

$$C_{16}H_{10}N_2O_2 + Ca(OH)_2 + Zn = C_{16}H_{12}N_2O_2 + ZnO_2Ca.$$

The indigo white dissolves in the excess of lime present, and the solution forms the "dye vat."

The proportions of the ingredients employed in setting the Zinc-Lime Vat vary according to their quality, and, when natural Indigo is used, according to the percentage of indigotine that it contains. Taking the synthetic products, Indigo M.L.B., or Indigo pure B.A.S.F., as pure indigotine, the following proportions will represent approximately the relative amounts used on the large scale:

STOCK INDIGO WHITE.

20 kilos. Indigo pure (or 100 kilos. 20 per cent. paste).
40 ,, slaked lime.
80 litres water at 45° C.

Mix well together and add

12 kilos. zinc powder.

Stir well, and maintain at a temperature of 40°–45° C. for 6–8 hours, stirring up well from time to time. While the reduction of the indigotine is proceeding the rest of the vat may be set as follows:—

4000 litres water.
1 kilo. zinc powder.
4 kilos. slaked lime.

Stir well to thoroughly deoxidise the water, and then add as much of the stock solution of indigo white as is required. Rake up frequently, and then allow the precipitate to settle. If the vat is in good working order, it ought to be sufficiently clear to use in about an hour or an hour and a half after the stock solution has been added.

If desired, the same vat may be made by mixing all the ingredients together in the first instance with about 12 kilogrammes of coarse iron filings and borings, which act mechanically, and promote the more rapid reduction.

A good Zinc-Lime Vat has a substantial blue scum or "flurry" on its surface, is of a clear amber colour, and when stirred up shows broad blue veins all over its surface.

Another zinc powder vat is made by replacing lime with caustic soda thus:—

$$C_{16}H_{10}N_2O_2 + Zn + 2NaOH = C_{16}H_{12}N_2O_2 + ZnNa_2O_2.$$

The indigo white dissolves in the excess of caustic soda present in the vat. Zinc hydrate is soluble in excess of alkali, with which it combines to form zincate of soda ($ZnNa_2O_2$), as shown in the above equation; and as an excess of caustic soda is essential to dissolve the reduced Indigo, it follows that a portion of the zinc is always in solution. The alkalinity of the vat must not be pushed too far, however, otherwise both the shade of blue and the cloth itself are liable to suffer.

Both the Zinc-Lime and the Zinc-Soda vats are liable to the defects of "muddiness" and "frothing," due to the slight but continuous evolution of hydrogen. If these defects are slight, it is usually sufficient to stir up the vat for a short time and then allow it to settle again before use; but if they persist after this treatment, an addition of Indigo must be made, since the evolution of free hydrogen (giving rise to froth, and keeping the sediment in constant motion) only takes place in presence of excess of zinc, and after the Indigo has been fully reduced. In these circumstances, the longer the vat is allowed to stand the worse it becomes, and nothing will improve it but the addition of further Indigo, followed by a vigorous "raking up." After standing for 1½ hours the vat should then be settled sufficiently to allow of the dyeing operations being resumed.

Although the initial cost of Zinc Powder Vats is greater than that of Copperas Vats, they offer counterbalancing advantages which render their use more economical. In the first place they are very simple to set, and then, again, the absence of ferrous hydrate reduces the loss of available Indigo by at least half, that is, from about 20 per cent. to 10 per cent.; and even this loss is not due to the formation of an insoluble compound of Indigo, but to the fact that a good deal of the reduced Indigo remains as such in the useless sediment at the bottom of the vat.[1] As the vat is exhausted, this Indigo can be brought into use again by stirring it up with more water and a little alkali, in which case it serves as a weaker vat for light shades. Little by little, therefore, the sediment can be washed almost free from indigo white; or, conversely, the amount of indigo white it absorbs can be kept almost constant by reducing the quantity of stock solution added to replenish the vat. Another great advantage of the zinc-lime vat is that the precipitate it contains is, at most, only about one-sixth of that in a copperas vat of the same strength. Moreover, this precipitate is much denser, and consequently settles more rapidly, so that the vat is ready for dyeing

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[1] A part of the loss has been shown to be due to the formation of isatin in the vat (Crowther, *Jour. Soc. Dyers and Colourists*, p. 146, 1911).

in a shorter time, especially if iron borings be added. In the case of the Zinc-Soda vat, the precipitate is still further reduced, but the vat is rather more difficult to manage. On the whole, the Zinc-Lime vat is very easy to work. It yields even shades; and as it contains comparatively little sediment, it can be used for a much longer time than the Lime and Copperas vat, which requires cleaning out five or six times as often. Any Indigo remaining in the sediments can be recovered by boiling them with a cheap reducing agent, filtering off, or settling what zinc or lime is undissolved, and then oxidising the solution of indigo white by exposing it to the air in shallow tanks, or by pumping it through spray pipes or a perforated trough arranged at some height above the containing tank, into which it is allowed to fall again through the air. In this way, by constant circulation, the indigo white is thoroughly aerated and oxidised, and the precipitated indigotine only requires to be washed and filtered to a paste of known percentage to be again available for use.

The Zinc-Lime and the Zinc-Soda vats are chiefly employed for dyeing calico in continuous dyeing machines, but the former is also eminently adapted for "dipping vats," and is largely used both in England and on the Continent for the production of the "Indigo Resist or Reserve" style.

The "Hydrosulphite Vat."—The reducing agent employed in this vat is hydrosulphite of soda, a salt which is prepared in practice by acting on bisulphite of soda with metallic zinc. (See "Reducing Agents.")

In presence of caustic soda or milk of lime, this salt reduces indigotine to indigo white, which dissolves in the excess of alkali present, forming a vat—

$$C_{16}H_{10}N_2O_2 + Na_2S_2O_4 + 2NaOH = C_{16}H_{12}N_2O_2 + 2Na_2SO_3.$$

On the large scale, caustic soda is generally replaced by *milk of lime*. Lime vats are said to dye more evenly than those made up with caustic soda, and to keep in good working condition longer, owing to the fact that a thin film of calcium carbonate forms over the entire surface of the liquor and protects it from the oxidising action of the air. At the same time, caustic soda is employed largely in some works, and with excellent results.

The presence or absence of sediment in "hydrosulphite vats" depends upon the method adopted for setting them. If a sediment is not objectionable, it is cheaper and quicker to make a strong stock solution of indigo-white, by mixing together, in a cask, all the ingredients of the "vat," in proper sequence, and then, when the Indigo is fully reduced, to add the whole mixture to the requisite quantity of water in the dye vat or beck. The vat is then allowed to settle in the usual way before it is used for dyeing.

When the dye vessels are too shallow to permit of working in this manner, or when, for any other reason, it is desired to have a perfectly clear vat, the alkaline hydrosulphite must be prepared separately, and filtered from zinc hydrate, etc., before it is added to the Indigo. This occupies some time, and entails the use of a special but cheap apparatus for the manufacture of the alkaline hydrosulphite. If, however, a high yield of a concentrated solution of the salt is required, a filter press will be necessary to extract as much liquor as possible from the useless precipitate thrown down by the alkali used for neutralising the acid salt.

Hydrosulphite vats are "set" in three different ways:—

(1) With zinc powder, bisulphite of soda, lime or caustic soda, and Indigo.

(2) With specially prepared sodium hydrosulphite, Indigo, and caustic soda or milk of lime.

(3) With commercial solid hydrosulphite of soda, Indigo, and caustic soda or lime.

The two latter methods are practically identical, save that in the one the reducing agent is prepared by the dyer himself, while in the other it is bought ready made. As prepared in the dyehouse, the "hydrosulphite," if not used at once, must be stored in well-corked carboys, and kept in a dark, cool place, otherwise it rapidly oxidises, but even if air be excluded it deteriorates.

The Zinc-Bisulphite-Soda Vat.

This "hydrosulphite vat" is largely used in practice; it contains some sediment, but otherwise is as suitable for most kinds of Indigo dyeing as the clearer vats.

(*a*) STOCK SOLUTION.
25 kilos. bisulphite of soda 76° Tw.
25 ,, water.
Add gradually, whilst stirring,
5 kilos. zinc powder.
Stir ½ hour, allow to stand ½–¾ hour, and then add—
25 litres caustic soda 77° Tw.
50 kilos. Indigo 20 per cent. paste.

Stir well, and then add water at 45° C. to bring the whole up to 200 litres. Stir again for ¼ hour, and set aside in a warm place until the solution becomes a golden yellow; the Indigo is then completely reduced, and ready for adding to the vat.

(*b*) THE DYE VAT.
A vat holding about 2500 litres is almost filled with water (say 1700 litres) at a temperature of 40° C.; the following solution is then added to it to deprive it of its free oxygen before the stock solution of reduced Indigo is put in,—

$$\left\{\begin{array}{lll} 500 & \text{grms.} & \text{bisulphite of soda 76° Tw.} \\ 1500 & ,, & \text{water.} \\ 75 & ,, & \text{zinc powder.} \end{array}\right.$$

Mix well, allow to react for ½ hour, and then pour into—
1700 litres water at 40° C.
¼ ,, caustic soda 77° Tw.
Stir up well, and add
200 litres above stock solution of Indigo.

Make the whole to 2000–2250 litres with water, rake up well, and allow to settle, when the vat is ready for dyeing. The vat thus made contains about 5 grms. of Indigo per litre, and is suitable for dyeing dark shades.

Lime (in the proportion of 650 grms. of slaked lime to every litre of caustic soda) may be used in place of caustic soda in the preparation of the foregoing vat. It gives more sediment, however, but in other respects the lime vat is quite as good as the above soda vat.

The Clear Hydrosulphite Vat.

In preparing this vat, which is merely a modification of the preceding, the reducing agent is freed from zinc salts before it is allowed to act on the Indigo. This is effected in the following way:—

Mix in a cask 50 litres of bisulphite of soda 76° Tw. with 80 litres of water at not above 30° C., and then add gradually 7½ kilos. of zinc powder beaten up with 7½ litres of cold water. Stir until the mixture becomes nearly white, then allow to settle. Decant the clear liquor, and add to it 7½ to 8 litres of caustic soda 76° Tw., or a corresponding quantity of milk of lime. Allow to settle again; filter off the precipitate after decanting the clear liquor, pass it through a filter press, and add the filtrate to the rest of the solution. Finally, set at 36° Tw. and use at once.

The vat is made up as follows:—

(*a*) Stock Solution 5 per cent.

25	kilos.	Indigo 20 per cent paste.
30	,,	milk of lime (20 per cent. quicklime).
20	,,	hydrosulphite of soda 36° Tw. as above.
25–30	,,	water.

100 litres.

Heat to 55° C., at which temperature the Indigo is completely and rapidly reduced, forming a clear yellow solution. If the solution is of a decided green colour the reduction is incomplete, and more hydrosulphite of soda must be added; and if, on the other hand, a dense white precipitate settles out, it indicates a deficiency of lime. The precipitate is undissolved indigo white, and disappears on the addition of lime or caustic soda.

(*b*) The Dye Vat ½ per cent.

1790 litres water at 45° C.
10 ,, hydrosulphite of soda 36° Tw.

Stir ¼ hour and then add
200 litres stock solution of Indigo 5 per cent.

2000 litres.

The dye liquor should always contain a slight excess of hydrosulphite, otherwise it oxidises quickly, and becomes both green and turbid. It contains no sediment, and consequently the dyeing can be proceeded with immediately the vat is set.

The continuous running of cloth through the liquor has the effect of churning it up; and if, from this or any other cause, the vat becomes green owing to excessive oxidation, the dyeing must be stopped at once, a little fresh hydrosulphite added to the vat, and the whole warmed to 50° C. In this way the Indigo is reduced again and the vat is immediately available for further work. Excessive alkalinity may be corrected by the careful addition of dilute hydrochloric acid; or if caustic soda is the alkali employed, dilute sulphuric acid will answer the same purpose.

A more convenient method of setting the clear hydrosulphite vat is to employ one of the specially manufactured solid sodium hydrosulphites, but, apart from convenience, these salts offer no other advantage over those prepared by the dyer himself, and as they are expensive, they have not been universally adopted in practice.

For most calico printing purposes the various hydrosulphite vats have proved themselves to be suitable, and especially may that be claimed for the clear vats. The absence of sediment ensures the production of brighter and more regular shades; further, the loss of dyestuff is very small, and, as the vat is stable, it is always ready for dyeing, and can be used for a long time without cleaning out.

The Dyeing of the Cloth.—The dyeing of piece goods is effected either (1) by immersing them for a certain time in the clear solution of reduced Indigo, followed by draining and exposure to the air, or (2) by passing them through the solution in a continuous manner, and then, after squeezing out the excess of liquor, running them over a system of rollers arranged above the dye vats. This exposure to the air varies with the amount of indigo white absorbed by the cloth, and must always be sufficiently prolonged to ensure the complete re-oxidation of the indigo white to indigotine, otherwise the shade will be uneven, owing to the partial removal from the fibre of the unoxidised indigo white during the subsequent processes of washing and souring.

In dyeing by the first or *Dipping Method*, the dried goods are hooked by the selvedges to a rectangular wooden frame furnished with small brass hooks at the top and bottom; each fold is separate, and the cloth is stretched fairly tightly, but not too much so, lest its contraction in the liquor should tear it from the hooks, and not only damage the cloth, but result in uneven dyeing where two folds come in contact. The frame filled with white calico is then lowered into the vat, where it is allowed to remain below the surface of the liquid for 15 or more minutes. At the expiration of this period it is withdrawn and slung above the vat so as to expose the cloth to the air, whereby the reduced Indigo is re-oxidised into insoluble indigotine. The alternate "dips" and airings are repeated as often as is necessary to obtain the requisite depth of shade.

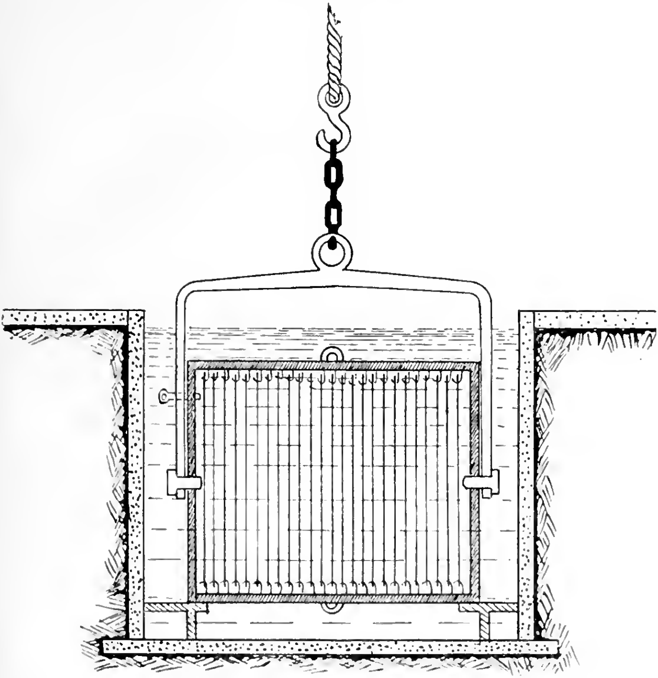


FIG. 72.—Indigo dipping vat.

A "dipping vat" is shown in fig. 72.

In the "Dipping" method it is obviously impossible to dye a level shade with one dip: the liquor drains off the lower selvedge during the exposure to the air, leaving the lower part of the cloth much darker than the upper. Hence, when the cloth is "dipped" a second time, the frame upon which it is hooked is reversed, so that what was the top selvedge becomes the bottom one. In this way the liquor drains off from each in turn, and the ultimate shade is quite even. The frame is reversed at every fresh dip.

Other forms of dipping vats are in use, but they are worked on a similar principle, and call for no special mention. The chief use of all dipping vats is in the dyeing of the Indigo Resist Styles, to be described later.

In the second or *Continuous Method* of dyeing Indigo, the goods are passed through the liquor over a system of guide rollers arranged on an iron frame, which fits into the vat in such a way that the rollers are completely immersed. The frame is removable, so as to allow of the vats being cleaned out or re-set as required. At the exit end of the vat a pair of squeezing bowls are fixed to express the excess of liquor from the cloth as it passes into the air to oxidise before entering a second similar vat. The number of vats through which the cloth passes is regulated by the depth of blue desired, and by the concentration of the dye liquor itself. The continuous Indigo dyeing machine made by Messrs Mather & Platt is shown in fig. 73. From this it will be seen that the cloth passes through several vats in succession, and that between each immersion it is exposed to the air to regenerate the indigotine before it enters the next vat. The "airing" arrangements are simple, effective, do not pull the cloth, occupy but little space, and are not liable to get out of order. They consist of a wince (C) placed high above the vat and a travelling apron or "creeper" (D). The cloth, on leaving the vat, is drawn upwards by the wince, which then plaits it down on the "creeper." This latter, moving slowly forward, and carrying a long length of cloth, in short loose pleats, allows of a large quantity of material being oxidised at once and in a very convenient manner. When the first pleat reaches the end of the "creeper," the cloth is again drawn up and down through the air by a roller placed above the second vat, through which it is then drawn by the action of the squeezing bowls at the point of exit. The exposure to air is then repeated exactly as before, and so on for every succeeding vat through which the goods pass, the whole process being continuous. Each vat is also provided with mechanical agitators to facilitate the setting, and with a supply tank at the side for replenishing the vat with fresh indigo white solution.

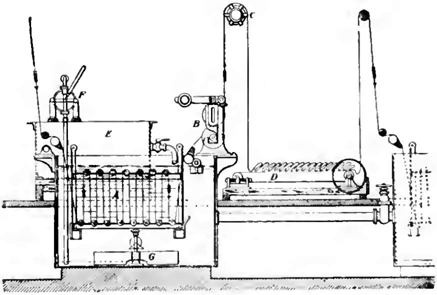


Fig. 73.—Continuous Indigo dyeing machine.

When Indigo is dyed continuously as above it is customary to set the vats at different strengths. The first vat may contain anything between $\frac{1}{10}$ per cent. and $\frac{1}{4}$ per cent. of indigotine, while the stronger succeeding vats contain from $\frac{1}{2}$ per cent. to 1 per cent. of indigotine, reckoned on the weight of their liquid content.

Light blues or "Sky blues" are frequently dyed in a single run, but no attempt to dye a dark blue at a single operation, in a strong vat, ought to be made, since it is practically impossible to obtain a regular shade by this means. The best method is to pass the goods through a series of vats of increasing concentration, and to fully oxidise them between each operation.

After dyeing, the material is allowed to lie a while, then washed lightly, and passed through dilute sulphuric acid (1°–2° Tw.) to remove any alkaline carbonates it may contain, and to brighten the shade. When natural Indigo is employed, the tone of blue is improved by a light soaping, which probably removes the greater part of the brown and yellow colouring matters always present in natural Indigo.

The successful dyeing of Indigo is as much a question of practical experience as of theoretical knowledge—perhaps more so. The setting of the vats, their manipulation, and their maintenance in good working condition are comparatively simple matters when once understood; but to understand them properly, and to recognise the characteristic features and the causes of the various defects they are liable to develop during the course of dyeing, requires a long practical acquaintance with dyehouse work. The condition of the cloth to be dyed, the speed at which it is passed through the vats, and the quantity dyed at a time, are one and all important factors in the production of satisfactory work. The strength of the vats, too, calls for careful attention, and altogether the whole process of Indigo dyeing demands constant and close observation from start to finish. Further information on the details of Indigo dyeing will be found in the *Manual of Dyeing*, by Knecht, Rawson and Loewenthal.

(3) THE INSOLUBLE AZO COLOURS.

GENERAL.—Unlike most artificial colouring matters, the "Insoluble Azo colours"—or, as they are sometimes called, the "Ice colours"—do not come into the market as dyestuffs ready for application, but are produced on the fibre directly, by the combination of their constituents.

When certain aromatic amines are diazotised and combined with suitable naphthols they give brightly coloured precipitates which are insoluble in water, acids, alkalies, and soap solutions, and are, for the most part, tolerably fast to light. In this state the precipitates are used as pigments, and may be fixed upon cloth, like other pigments, by means of albumen, caseïn, and other coagulable bodies. But by far the most valuable property of the insoluble Azo colours is that they can be precipitated on and in the fibre, just as easily as in a liquid medium. For this purpose the cloth is first prepared in an alkaline naphtholate, and, after carefully drying, is either printed with, or passed through, a solution of the requisite diazo compound. The colour is produced almost instantaneously, and is, practically speaking, quite fast; it is very bright in most instances, and being deposited in the body of the material instead of on the surface, as is the case with pigment colours, it resists the usual energetic rubbing processes to which prints are subjected in the domestic laundry. Altogether the Azo colours, when properly dyed, may be classed among the fastest of colours, leaving out of consideration such as the Madder colours in general, Turkey red, Aniline black, and the Indanthrene, Helindone, Algol and Ciba colours, with none of which can any ordinary colour be compared for all-round excellency.

Pre-eminent amongst the Azo colours are what are known technically as "Para red" and "Naphthylamine bordeaux" or "claret." Their beauty and fastness, combined with their cheapness, their simplicity of production, and their adaptability to a great variety of styles, have gained for them a place of such importance that, at the present time, they are indispensable adjuncts to the colour shops of all up-to-date printworks. Para red is as bright as Turkey red, and Naphthylamine claret is brighter and purer in shade than any madder-dyed claret; but neither are so fast as their older competitors, especially to light; and although they have displaced the latter to a great extent in many styles, the Alizarin colours are still unrivalled for the production of the highest class of work —work which is required to possess the utmost possible degree of permanency.

In addition to red and claret, the insoluble Azo colours include various shades of orange, brown, chocolate, puce, blue, and black. A fine pink has also been introduced lately, but, so far, a bright yellow, blue, and green are still absent from the list. These different shades and colours are obtained by using different amines in combination with different naphthols; and as both these classes of compounds can be mixed with others of their own class, it is possible to obtain a great variety of effects.

As a rule, only two naphthols are used in practice,—α-naphthol and β-naphthol. Of these, β-naphthol is far and away the more important on account of the superior fastness of the colours it yields.

Many of the Azo colours are volatile, and gradually disappear, by sublimation, from the cloth. Those prepared from β-naphthol are not only almost entirely free from this defect, but possess also the further, and inestimable, advantage of being insoluble in caustic soda, whereas those developed on α-naphthol (and phenols) are more or less soluble. Hence, wherever possible, β-naphthol is invariably employed: α-naphthol is only used for shading purposes, and then only when other means are not available.

The insolubility in caustic soda of the β-naphthol colours renders them particularly suitable for printing along with strongly alkaline colours like Indigo, other vat dyestuffs, and the sulphide colours; and by working in this way an immense number of very fast colour combinations can be produced both cheaply and rapidly.

The colours obtained by combining the diazo compounds of some of the commoner primary amines with α- and β-naphthols respectively are given in the following table:—

AMINE.	α-NAPHTHOL.	β-NAPHTHOL.
Aniline	Catechu brown	Orange.
* Paranitraniline	Reddish brown	Turkey red.
Metanitraniline	,,	Bright orange.
Paratoluidine	Warm brown	Yellowish ,,
Nitro-paratoluidine	Rich ,,	Orange.
* α-Naphthylamine	Chocolate or Puce	Claret.
β- ,,	,, ,,	Red.
Amidoazobenzene	,,	,,
Ortho-amidoazotoluene	,,	Dull claret.
* Benzidine	Deep chocolate brown	Chocolate.
* Tolidine	,,	,,
* Ortho-nitroparaphenetidine	Not used	Fine bluish red.
* Chloranisidine	,,	Scarlet.
* Ortho-nitrotoluidine	,,	Fine orange.
* Dianisidine	,,	Violet.
* ,, with copper	,,	Navy blue.
* Paranitro-orthoanisidine	,,	Bright red.

The amines marked with an * are those chiefly used in practice.

The above colours all stand a short (very short) steaming. This allows of them being used in combination with certain mordant dyestuffs, Diphenyl black, basic dyestuffs, and pigment colours, as well as with those already mentioned.

The process of producing Azo colours on the fibre consists of three separate and distinct operations:—

(1) The impregnation of the cloth with naphthol.

(2) The diazotising of the amine or diamine.

(3) The development of the colour.

1. Preparation of the Cloth.

For this purpose the cloth is padded in an alkaline solution of the naphthol to be used; generally a solution of β-naphthol in caustic soda.

Various other substances are usually added to the naphthol solution in order either to improve the shade of the colour or to preserve the prepared material from becoming brown on drying, or on standing for a day or two. Turkey-red oil, para soap P.N. (ammonium ricinoleate), antimony compounds, and aluminate of soda are all employed to these ends.

According to Lauber and Caberti, the addition of an alkaline solution of antimony oxide prevents the browning of the naphtholated goods during their drying over copper cylinders; and furthermore, it preserves them in good condition for dyeing or printing for two or three days if they are stored in a dark, cool place. These statements have been verified in practice, for whereas goods padded in simple naphtholate of soda require to be printed or dyed at once with the diazo solutions, those containing antimony oxide yield satisfactory results after having been kept for two and sometimes three days. The other additions chiefly enhance the beauty of the colour, and besides this, Turkey-red oil keeps the cloth soft and tends to give the colour a more transparent quality.

The drying of naphtholated material should always be conducted at as low a temperature as possible: α- and β-naphthols are volatile, and if dried too hard they sublime, leaving the cloth unevenly impregnated, with the obvious result that in dyeing the colour develops irregularly.

For plain dyed shades it is usually unnecessary to make any of the above additions, though, of course, they exercise no detrimental influence on the shades obtained. But plain shades are dyed chiefly for discharge printing, and it is an axiom in this style of work that the freer the cloth is of unnecessary bodies, the cleaner, sharper, and brighter are the patterns discharged upon it; so that, apart from the extra expense, the presence of oil, soap, etc., is apt to be injurious.

β-naphthol itself gives a yellow shade of red with Paranitraniline, which is not suitable for all markets. To correct this it is mixed with a small quantity of "Shading salt" R. (M., L. & B.), or is replaced altogether by Naphthol R., of the same firm, which is really a mixture of ordinary β-naphthol with the shading salt (the sodium salt of β-naphthol-mono-sulphonic acid F.). Still bluer shades of red and pink are obtained from Nitrophenetidine and β-naphthol. Particulars of naphthol solutions will be found further on.

2. Diazotising.

Primary amines, when treated under suitable conditions with nitrous acid, are converted into diazo compounds, the distinguishing feature of which is that the chlorides contain the group Ar—N : N—Cl. Diazo-benzene chloride is the simplest, and will serve as a type of all the various bodies. It is obtained from aniline thus—

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5NH_2.HCl} \quad + \quad \underset{\text{Nitrous acid.}}{HNO_2} \quad = \quad \underset{\text{Diazo-benzene chloride.}}{C_6H_5N:N.Cl} \quad + \quad 2H_2O.$$

When combined with naphthol this body gives a bright orange precipitate of benzene azo naphthol,

$$C_6H_5N:N.Cl + \underset{\text{(Naphtholate of soda.)}}{C_{10}H_7ONa} = \underset{\text{(Benzene azo-naphthol.)}}{C_6H_5N:NC_{10}H_6.OH} + NaCl.$$

From the above it will be seen that one equivalent of aniline hydrochloride requires one equivalent of nitrous acid for its complete diazotisation: or using nitrite of soda and hydrochloric acid, one equivalent of each. Thus—

$$C_6H_5NH_2.HCl + NaNO_2 + HCl = C_6H_5N : N.Cl + NaCl + 2H_2O.$$

In the same way all monamines require one equivalent of nitrous acid, and therefore the same chemical equation will serve for each if aniline is replaced by quantities which are in the case of monamines identical with their molecular weights. Benzidine and Tolidine are both di-amines, and consequently their equivalents are *half* their molecular weights. Thus—

93	parts	by weight of	Aniline	Mol. W.	93	requires	69 parts	$NaNO_2$.
138	,,	,,	p Nitraniline	,,	138	,,	,,	,,
197	,,	,,	Amidoazobenzene	,,	197	,,	,,	,,
225	,,	,,	Toluene	,,	225	,,	,,	,,
92	,,	,,	Benzidine	,,	184	,,	,,	,,
106	,,	,,	Tolidine	,,	212	,,	,,	,,

and so on for all other mon- and di-amines.

If the free bases are taken in the first instance, an extra equivalent of hydrochloric acid will be required to convert them into soluble salts,

$$\underset{\substack{\text{Aniline.}\\ 93.}}{C_6H_5NH_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid}\\ 2\,(36\cdot5).}}{2HCl} + \underset{\substack{\text{Nitrite}\\ \text{of soda.}}}{NaNO_2} = \underset{\substack{\text{Diazo-benzene}\\ \text{chloride.}}}{C_6H_5N : N.Cl} + NaCl + 2H_2O.$$

It is found that the bulk of the aromatic amines are most easily diazotised in presence of excess of acid and of nitrite. The excess of hydrochloric or sulphuric acids usually amounts to 50 per cent., while the excess of nitrite of soda ought not to exceed 10 per cent. of the theoretical quantity, lest the printing rollers should be attacked by the free nitrous acid. Excess of mineral acid hinders, or prevents altogether, the combination of the diazo bodies with naphthols, but the presence of free organic acids has scarcely any effect: hence, when the diazotisation is complete, the excess of mineral acid is neutralised by the addition of sodium acetate.

Diazo solutions are extremely unstable, and must, in general, be prepared at a temperature not above 5° C.—better at 0° C. In order to keep the temperature down, lumps of ice are freely added to the solution, and also to the finished printing colour or dye liquor. A few amines, such as Amidoazobenzene, Amidoazotoluene, and the Nitrophenetidines may be diazotised at 20°–30° C., but for the most part it is safer to work as near the freezing point as possible, otherwise the diazo compound decomposes into a tarry mass that is absolutely useless.

Perfect diazotisation is best effected when the salts of the bases are in solution, or in an extremely fine state of division. Some salts, *e.g.* naphthylamine hydrochloride, are only sparingly soluble, and in such cases they can only be used in dilute solution, or when ground up into a perfectly smooth cream: others, like aniline and p-nitraniline, are soluble as hydrochlorides, and if pure, yield clear diazo solutions without any trouble. As a rule, however, it is safer to filter the solution after diazotising, especially if it be intended for printing.

Not only are diazo solutions susceptible to elevations of temperature, but they may also decompose spontaneously on standing a few hours. Indeed, the whole process of producing the insoluble Azo colours on the fibre must be got through as quickly as possible if good results are to be obtained.

3. The Development of the Colour.

The development of Azo colours is brought about either by printing a thickened diazo solution on the naphtholated cloth, or by passing the latter at the full open width through a solution of the diazo body contained in a padding mangle. If the goods are printed, they are dried lightly and at once washed, sometimes soured, and soaped; if dyed, they are washed and soaped at once, the dyeing, washing, etc., being carried out, as a rule, in a continuous machine. They are then dried and finished as usual. If goods printed in diazo solutions on a naphthol ground are allowed to lie exposed to the air and light, the white unprinted parts become brown, and the whole print is irrevocably spoiled.

Two important features of the insoluble Azo colours are that they can be both "resisted" and discharged by strong reducing agents. In the first case the diazo solution is destroyed by a resist printed on the naphthol-prepared cloth; while, in the second, the fully developed colour is discharged by a reducing agent printed on in a suitable pattern. Details of these processes will be found in the section on "Resists and Discharges."

The Application of the Azo Colours.

According to the class of work in hand, its style, requirements, and the conditions under which it is to be executed, the Azo colours may be applied by any of the following methods:—

A.—By printing a pattern in a thickened solution of naphthol and afterwards dyeing in diazo solutions.

B.—By printing a thickened diazo solution on cloth prepared in naphthol.

C.—By padding the cloth in naphthol for plain shades, and then dyeing it up in diazo solutions.

D.—By coupling diazo compounds with certain other compounds containing free amido groups.

E.—By printing on naphtholated cloth certain reducing agents capable of reducing the diazo compounds before they can unite with the naphthol.

F.—By discharging Azo colour grounds with reducing agents acting under the influence of hot dry steam. The grounds for this process are dyed by method C.

Each of these methods has its special uses, and although similar, almost identical, effects can be obtained from A and B on the one hand, and from E and F on the other, each one will be found to possess certain advantages over the others for certain styles of work.

(A) Printing of thickened Naphthol solutions on plain cloth followed by development in Diazo solutions.

This simple method is largely used for imitating the "Red, Black, and White Madder Style," and gives very good results with Paranitraniline and one or two other amines which do not stain the white too much.

The "colours" given below are printed on white cloth and then thoroughly dried, but at a comparatively low temperature to avoid unevenness in the ultimate colour,—an unevenness due to the fact that at too high a temperature the naphthols sublimate.

I. NAPHTHOL PRINTING COLOUR FOR FULL SHADES OF RED, ETC.

470	grms.	β-naphthol.
30	,,	shading salt R. (M., L. & B.).
1,000	,,	water.
850	,,	caustic soda 50° Tw.
300	,,	Alizarin oil 25 per cent.
7,350	,,	gum tragacanth 5 per cent.
10,000		

II. Printing Colour for light reds or pinks, etc.

46	grms.	β-naphthol.
4	,,	shading salt R. (M., L. & B.).
100	,,	water.
85	,,	caustic soda 50° Tw.
30	,,	Alizarin oil 25 per cent
9,735	,,	gum tragacanth 4 per cent.
10,000		

After printing and drying, develop at once in diazo solutions of any suitable amine, such as—

Paranitraniline for red and pink,
α-naphthylamine for claret,
Chloranisidine for scarlet,
Ortho-nitrotoluidine for orange,

and various mixtures for browns. Recipes for these diazo solutions will be found on pages 405 and 406.

For the Black and Red style, another naphthol sold under the name of Nigrophor is thickened and printed as above. It yields a good black with Paranitraniline, but is not very suitable for use with other diazotised amines.

300	grms.	Nigrophor.
1,500	,,	water.
350	,,	caustic soda 64° Tw.
500	,,	Alizarin oil 40 per cent.
7,350	,,	gum tragacanth 6 per cent.
10,000		

Various shades of chocolate may be produced by adding different amounts of α-naphthol to the β-naphthol printing colours. Thus—

	Medium Chocolate.	Dark Chocolate.
β-naphthol	40 grms.	25
α- ,,	8 ,,	25
caustic soda 70° Tw.	80 ,,	80
water	152 ,,	150
gum tragacanth 6 per cent.	720 ,,	720
	1000	1000

Both these chocolates are developed in diazotised p-nitraniline.

After the development of the colour all goods are well washed and soaped. The addition of a little sodium hypochlorite ("soda chemick") to the soap baths improves the "whites" and imparts a bluer tone to the red.

The foregoing process is extensively practised for the production of red and white kerchiefs, turban cloths, and other dress goods peculiar to the East and the Tropics. The "colours" thoroughly penetrate the thin soft cloth used for these fabrics, giving an exceedingly good "two-side" or reversible print. Although not much used for "sarrie printing," the same process would undoubtedly give satisfactory results with that class of work.

(B) Printing of thickened Diazo solutions on cloth previously prepared in Naphthol solutions.

This method (the exact reverse of the preceding) is perhaps more largely employed than any other, for the simple reason that it is applicable to so many multicolour styles, and that, therefore, it increases the scope of those styles. It allows of the insoluble Azo colours being printed with any "steam colours" that are sufficiently fixed by a short steaming process of 3–4 minutes, and it further allows of a Para red, etc., being employed in combination with some of the raised colours like Iron buff, Chrome yellow, and some of the vegetable colours that are fixed by a run through a solution of bichromate of soda, or, for Iron buff and Manganese bronze, through caustic soda.

In brief, the process is as follows:—(1) The goods are mangle-padded in one or other of the naphthol prepares given below; (2) dried in hot air or over steam heated cylinders; (3) cooled and printed with the thickened diazo solutions; (4) dried and, if required for other colours in the pattern, steamed for 2 to 4 minutes in the rapid ager, and then fixed in tartar emetic, etc.; (5) well washed, soaped, and dried.

(*a*) Preparing with Naphthol.—Each maker of naphthols recommends certain formulæ for the application of his particular products. Most of these formulæ require to be modified for use on the large scale; and as they differ from each other in detail only, it would be neither interesting nor profitable to discuss their relative merits. The only suggestions of any real value that have been made with a view to improving the shades obtained, and to increasing the stability of the naphthol solutions, are those which concern the addition of Turkey-red oil or castor-oil soap and antimony compounds to the prepares. These substances certainly exert a beneficial effect, and are used whenever there is any doubt as to whether the naphtholated cloth can be printed with the diazo solution at once; and also when the naphtholated cloth has to be dried over metal cylinders or printed by machine.

The following naphthol prepares or groundings have all yielded good results in practice:—

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
β-Naphthol . .	30	...	47	25	30	26½
β-Naphthol R. .	...	30	...	...	...	..
α-Naphthol . .	...	...	...	...	...	3½
Shading salt R. .	...	...	3	...	...	...
Caustic soda 36° Tw.	45	60	85	40–50	60–75	60
Turkey-red oil . .	25	25	...	...	25	...
Tartar emetic . .	6	6	10	...	...	...
Tartaric acid . .	7½	7½	12	...	...	...
Boiling water to .	1000	1000	1000	1000	1000	1000

In some instances it is advisable to replace a portion of the water with gum tragacanth in order to ensure an even impregnation of the cloth. The quantity used varies from 70–80 grms. per litre of a 6 per cent. tragacanth thickening.

No. 1 Prepare.—For all ordinary printed Azo reds, clarets, scarlets, and oranges.

No. 2 Prepare.—For very blue shades of "Para red," and reds and pinks, from o-nitroparaphenetidine and paranitro-orthoanisidine.

No. 3 Prepare.—Same as No. 2, but for stronger colours or on thin cloth.

No. 4 Prepare.—An ordinary prepare for Naphthylamine clarets, and Benzidine and Tolidine chocolates.

No. 5 Prepare.—For same purposes as No. 4. Darker shades.

No. 6. Prepare.—For dull reds with p-nitraniline, and dark Naphthylamine clarets.

For light shades of any of the above colours, the prepare is reduced in strength by the addition of extra water. This is, of course, only possible when light shades alone are printed; dark shades require the full quantity of naphthol (3–5 per cent. solutions). An excess of naphthol, however, does not injure the tone of the lighter colours, but is merely wasted when these alone are printed.

It is almost needless to point out that, if desired, any diazo solution can be printed on any of the above prepares. In fact, Nos. 2 and 3 are largely used for multicolour combinations of the insoluble Azo colours, and are, on the whole, the most important of the series.

After drying, the naphthol-prepared pieces are cooled by passing over a system of rollers, wound on wooden or iron shells or centres into rolls, and are then ready for printing with the diazotised amines.

(*b*) Diazo Printing Colours.—Under proper conditions, the printing of diazo solutions is a comparatively simple matter, requiring no more than a reasonable amount of care; but, as already noted, all such solutions are liable to decompose at the ordinary temperature, or when kept too long before use; and therefore, in order to obtain successful results, it is well to observe the following precautions, which reduce the tendency of the colours to decompose spontaneously:—

(1) All colour should be sent to the printer in copper or earthenware vessels standing in a wooden tub filled with ice, or better, with crushed ice and coarse salt.

(2) No more colour should be made than is necessary for the time being; and, as diazo solutions keep longer in presence of free mineral acid, the acetate of soda which is required to neutralise the mineral acid must only be added to the printing colour a few minutes before it is sent in to the printer.

(3) The colour boxes in the printing machine ought to be as small as possible, so that the colour can be constantly renewed with a minimum of loss. They ought, moreover, to be of copper and double cased, or "jacketed," so that the colour can be kept cool by the circulation of cold water between the two casings. A better plan is to have a small box with a double bottom and one double side, sufficiently capacious to allow of broken ice being introduced beneath and around the colour box proper.

(4) For finely engraved and small patterns which take but little colour, or when the particular colour used happens to froth badly, it is advisable to use a "doctor box" in place of the usual colour box. The advantage of this is that the colour can be renewed at very frequent intervals; and as doctor boxes hold very little, they can be washed out and charged with perfectly fresh colour without any great loss of material. The presence of decomposition products not merely gives a poor, dirty shade, but, worse still, accelerates the rate of decomposition of any fresh colour that is added to replenish the colour box. With large heavy patterns or blotches, the colour is printed before it has time to decompose, but with fine patterns there is always a danger of the decomposition products accumulating in a large colour box.

(5) If decomposed particles of colour are found to adhere to the printing roller, they may be removed by using a "brush furnisher." This should be a last resort, however, since thickened diazo solutions are sufficiently prone to froth without any aid from the churning action of a revolving brush furnisher.

(6) To prevent the soiling of the "whites" by an excess of diazo solution which comes off in the subsequent washing operations, the naphthol grounding or prepare must be a little stronger than is absolutely necessary for the full development of the colour, and it should also be made tolerably alkaline. By these means the diazo compound is completely absorbed, and all danger of dirty "whites" arising during washing is avoided.

After printing, the pieces should be well dried, but on no account allowed to stand on the drying cylinders, or in the hot-air chamber, otherwise the naphthol on the white unprinted parts of the cloth turns brown.

After-Treatment of Printed Azo Colours.—The printed goods, if they contain none but Azo colours, are passed quickly through a warm bath of dilute sulphuric acid to remove any surplus diazo compounds that may exist. They are then well washed and soaped, washed again, and dried. If more convenient, a boiling soap bath may replace the acid bath; a hot $\frac{1}{2}$–1 per cent. solution of naphtholate of soda may also be employed instead of the acid. The whites are improved by a light "chemicking" in the chloring machine, or by the addition of "soda chemick" to the last soap bath. A better method, however, is to pad the printed and washed goods in a weak solution of Hyraldite, then dry and steam.

Goods printed both with Azo colours and others fixed by steaming are first passed through the rapid ager and then (if basic colours are present) fixed in tartar emetic, well washed and soaped, the operations being conducted in an "Open Soaper" such as that of Messrs Mather & Platt, or Sir James Farmer & Co.

For blotches and all heavy patterns embodying large masses of colour, gum tragacanth is the best thickening to use with diazo solutions. Smaller patterns, spots, stripes, checks, and parts of multicolour designs, are best printed with mixtures of flour and tragacanth, or of starch and tragacanth (see "thickenings" for proportions) which give a sharper, cleaner impression of the pattern, and are, withal, cheaper. The natural gums, Senegal, Arabic, etc., and the British gums, are rarely used, since they exert a destructive influence on diazo compounds, due to their reducing properties.

The following recipes are taken from practice, and they represent all the more important Azo colours used on the large scale:—

RED P.N. (Paranitraniline).

36 grms. Paranitraniline.
100 ,, ice.
100 ,, hydrochloric acid 30° Tw.
70 ,, water.

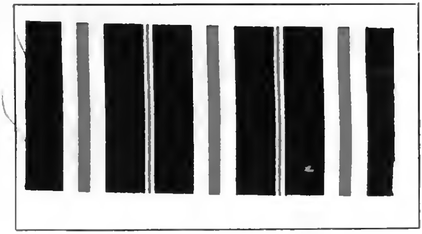
Mix and add quickly

24 grms. nitrite of soda 93 per cent.
70 ,, water.

Stir well, allow to stand 5–10 minutes, and then filter into—

400 grms. 12 per cent. gum tragacanth thickening.
100 ,, ice (lump).
100 ,, acetate of soda.

1000



Para red and Fast printing green (Bayer).

Print on prepares 1, 2, or 3.

The above red is reduced 2 : 1 for heavy engraving, *e.g.* Red P.N. $\frac{1}{2}$.

RED P.N. $\frac{1}{2}$.

2 parts of Red P.N.
1 part of 5 per cent. tragacanth thickening.

On Prep. 1 a Yellow red is obtained.
,, ,, 2 and 3 a Bluish red is obtained.
,, ,, 6 a Brown orange ,, ,, (dull Terra-cotta).

BLUE RED O. (o-nitroparaphenetidine).

73 ,, Blue red O. 25 per cent. (M., L. & B.).
66 ,, nitrite of soda solution $14\frac{1}{2}$ per cent.
20 ,, water. Mix, and then add gradually at 20°–25° C. to—
40 ,, hydrochloric acid 36° Tw.
200 ,, water. Allow to stand 5 minutes and then filter into—
550 ,, flour-tragacanth paste.
51 ,, acetate of soda.

1000 Print on prepares 1, 2, and 3.

Light Pink O.

100 parts by weight Blue red O.
260 ,, ,, ,, 4 per cent. tragacanth thickening.
40 ,, ,, ,, acetic acid 9° Tw.
———
400

The acetic acid is only added to neutralise the excess of alkali in the prepare when this pink is printed along with full strength Azo colours on a strong naphthol ground. Too much alkali is apt to cause irregularities in the colour.

The above red and pink are very stable, as is proved by the fact that ortho-nitroparaphenetidine can be diazotised at 25° C.

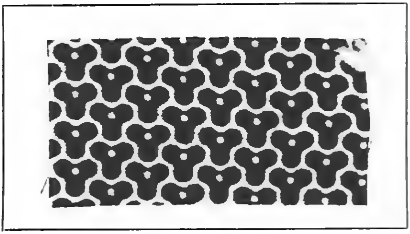
α-Naphthylamine Claret (Claret A.N.)

Stock Naphthylamine Paste:—

36 grms. α-Naphthylamine.
93 ,, hydrochloric acid 30° Tw.
171 ,, 6 per cent. tragacanth thickening.
———
300

Grind to a smooth cream.

For use take
300 grms. Naphthylamine paste.
Add gradually
20 grms. sodium nitrite 93 per cent.
50 ,, water.
100 ,, finely broken ice.
Allow to stand and filter into
425 grms. 4 per cent. tragacanth thickening.
30 ,, benzine.
75 ,, acetate of soda.
———
1000



α-Naphthylamine Claret.

Print on prepares 1, 2, 3, 4, 5, or 6 according to circumstances. For the 3 per cent. prepares, Naphthylamine claret 1/3 may be used for ordinary work.

Naphthylamine hydrochloride and Naphthylamine salt S. are both articles of commerce, and may replace the base in the preparation of the printing colour if the proportions are altered in accordance with the makers' (M., L. & B.) instructions.

Scarlet C.A. (Chloranisidine).

25 grms. Chloranisidine salt M. (M., L. & B.).
150 ,, water.
200 ,, ice.
25 ,, hydrochloric acid 36° Tw. Add gradually, whilst stirring—
8·25 ,, nitrite of soda 93 per cent.
50 ,, water. Allow to stand 15 minutes and then filter into—
506·75 ,, 6 per cent. tragacanth thickening.
35 ,, acetate of soda.
———
1000

Print on prepare 1.

Orange N.T. (Ortho-nitrotoluidine).

30 grms. Ortho-nitrotoluidine.
200 ,, hot water.
56 ,, sulphuric acid 61½° Tw. Dissolve, cool, and add—
100 ,, ice, and then at 0°–5° C.—
60 ,, nitrite solution 29 per cent.

Stir well, allow to stand 20 minutes, and then filter into—

54 grms. water.
40 ,, acetate of soda.
460 ,, 6 per cent. tragacanth thickening.
1000

This colour, reduced to contain 20–25 grammes of nitrotoluidine per kilo., is printed on naphthol prepares 1, 2, or 3.

Orange M.N. (Metanitraniline).

28 grms. Metanitraniline.
200 ,, boiling water.
53 ,, hydrochloric acid 30° Tw. Dissolve, cool, add first—
150 ,, ice, and gradually—
52 ,, nitrite solution 29 per cent.

Allow to stand 20 minutes, then add water to make up to 500 grms.

For use take 500 grms. diazo solution.
460 ,, 6 per cent. tragacanth thickening.
40 ,, acetate of soda.
1000

Print on any 3–5 per cent. naphthol prepare. For the weaker prepare, the colour used is generally Orange M.N. ¼.

Azo Pink B.B.

A { 13 grms. Azo Pink 2 B. (M., L. & B.).
36 ,, water.
16 ,, hydrochloric acid 30° Tw.

B { 50 ,, ice.
100 ,, cold water.
30 ,, 13 per cent. nitrite solution.

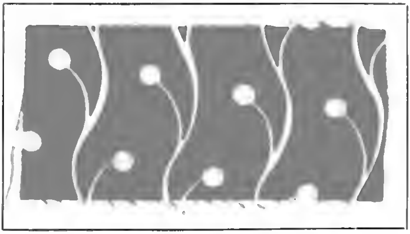
Add B to A gradually, allow to stand 10 minutes, and then filter into—

715 grms. 6 per cent. tragacanth thickening.
20 ,, benzene.
20 ,, sodium acetate.
1000

For red take 26 grms. per kilo. For paler pink take 5–10 grms. per kilo.

Print on prepares 1, 2, 3, or 5. In reducing strong shades to pinks add a little acetic acid (say 8–10 per cent.) to the reducing paste.

Azo orange N.A. (M., L. & B.) is a similar colour prepared from m-nitraniline and is applied similarly.



Azo Orange N.A. (M., L. & B.).

Chocolate T. (Tolidine).

17 grms. Tolidine base.
200 „ water.
52 „ hydrochloric acid 30° Tw.
Boil till dissolved, cool, and add first—
150 grms. ice, and then gradually at 0° C.—
92·8 grms. nitrite solution 13 per cent.
Allow to stand 10–15 minutes and then filter into—
440 grms. 8 per cent. tragacanth.
48·2 grms. acetate of soda.
———
1000

Print on any naphthol prepare of suitable strength (3 per cent.).

Chocolate B. (Benzidine).

Benzidine chocolate is prepared exactly like Tolidine chocolate, except that 14·5 grms. of Benzidine base are taken in place of the 17 grams of Tolidine; the quantities of acid and nitrite of soda remain the same in both cases.

The shades given by Tolidine and Benzidine are almost identical. The former is generally preferred on account of its slightly greater fastness to light.

Red N.A. (Paranitro-orthoanisidine).

26 grms. Paranitro-orthoanisidine.
150 „ water.
35 „ hydrochloric acid 30° Tw. Add gradually at 0° C.—
60 „ nitrite solution 13 per cent.
100 „ cold water.
84 „ ice. Allow to stand 10 minutes, then filter into—
500 „ 6 per cent. tragacanth thickening.
45 „ acetate of soda.
———
1000

Print on prepares 1, 2, or 3.

Red N.A. gives a fine red with a beautiful bluish "reflet"; but it is not so blue in tone as Blue red O., nor so yellow as Para red. For high-class prints on mercerised sateen it is a most useful colour, because it withstands the action of hot steam much better than "Para red," which is always more or less "dulled" if steamed before the naphthol is washed out of the cloth,—an operation that it is impossible to perform before steaming when mordant or basic colours or Indigo, etc., are printed in combination with Azo colours produced on the fibre. At the same time Para red yields excellent results if properly handled, but its shade is generally too yellow for the requirements of the home trade markets of Western Europe.

Blue A.N. (Dianisidine).

12·5 grms. Dianisidine base.
50 „ hot water.
18 „ hydrochloric acid 30° Tw.
Beat into a paste, and then add first
357 grms. cold water (melted ice), and then at 0° C.—
62·5 „ nitrite solution 13 per cent. $NaNO_2$.
Allow to stand 5 minutes, and then filter into—
465 grms. 6 per cent. gum tragacanth thickening.
35 „ copper chloride.
———
1000

Instead of Dianisidine base (12·5 grms.) there may be used—

16·5 grms. Dianisidine salt and 12 grms. HCl in place of 18 grms.
20·5 ,, ,, ,, 80 per cent. paste and 12 grms. HCl in place of 18 grms.

Blue A.N. is printed on a naphthol prepare containing the requisite quantity of acetate of soda to neutralise the free mineral acid in the colour. Thus:—

3 per cent. NAPHTHOL PREPARE.

30	grms.	β-naphthol (or Naphthol D. (M., L. & B.)).
700	,,	water.
60	,,	caustic soda 36° Tw.
20	,,	sodium acetate.
50	,,	Turkey oil 40 per cent.
140	,,	2 per cent. tragacanth thickening.
1000		

Without chloride of copper, Dianisidine gives a dull violet shade of no practical value.

Mixtures of the diazo compounds of Benzidine or Tolidine with Dianisidine blue (without copper) give various tones of deep black on β-naphthol-prepared cloth. Many of the Azo blacks of commerce consist of such mixtures.

The preparation of diazo printing colours can be effected without the use of ice if the amido base and the acid are thickened together and mixed with a second paste containing the nitrite. One example will suffice to illustrate this method of working.

α-NAPHTHYLAMINE CLARET (without ice).

I.	36	grms.	Naphthylamine base.
	171	,,	6 per cent. gum tragacanth thickening.
	93	,,	hydrochloric acid 30° Tw.

Grind to a smooth paste in a mill.

II.	20	grms.	sodium nitrite cryst. 93 per cent.
	50	,,	water.
	525	,,	4 per cent. tragacanth.

Mix I. and II. together, and just before printing add—

30	grms.	benzine.
75	,,	acetate of soda.
1000		

Print on any "naphthol prepare." The presence of the thickening material retards the rate of diazotisation, and the reaction takes place regularly and evenly. At the same time it is not advisable to dispense with ice in warm weather, since all diazo compounds are very sensitive to heat,—that is to say, all diazo compounds prepared according to any of the foregoing directions.

The introduction of the Azophor colours has rendered unnecessary the observance of any particular precautions in the printing of insoluble Azo colours. The Azophor colours (Meister, Lucius & Brüning) consist of *stable* diazo compounds of various aromatic amines, such as paranitraniline, metanitraniline, dianisidine, benzidine, tolidine, and paranitro-orthoanisidine. These come into the market as Azophor red P.N., Azophor orange M.N., Azophor blue D., Azophor blacks S. and D.P., and Azophor rose A. No ice is required at any stage of the preparation of the printing colours, or in their application to the fibre; the colours are simply dissolved in water and added to the thickening, together with a little caustic soda or sodium acetate for neutralising the free mineral acid that may be present.

	RED.	ORANGE.	BLUE.	BLACK.	PINK.
	grms.	grms.	grms.	grms.	grms.
Azophor red P.N.	90	...	...	...	...
,, orange M.N.	...	90	...	...	...
,, blue D.	...	...	36	...	...
,, black S.	...	..	...	120	..
,, rose A.	...	...	...	...	20
Cold water	350	350	300	250	400
Acetic acid 9° Tw.	...	...	...	80	50
Cold water	100	100	...	...	...
Caustic soda 36° Tw.	40	40	...	...	...
6 per cent. tragacanth	500	500	...	...	500
Flour-tragacanth paste	...	...	600	500	...
Acetate of soda	...	...	...	50	20
Copper chloride 77° Tw.	...	...	50	...	...
Chromic acid (cryst.)	...	...	4	...	...
Make up to	1 litre	1 litre	1 litre	1 litre	1 litre

In this table the ingredients above the centre line are first mixed together; then, when the solution has stood for ½–1½ hours, it is filtered into the thickening and caustic soda, well stirred in, and finally made up to 1 litre with water. The acetate of soda, chloride of copper, and chromic acid are best left out of the colours until immediately before printing.

Properly prepared, the Azophor colours are, for diazo compounds, remarkably stable. They may be printed on any of the prepares suitable for the corresponding ordinary Azo colours, and without any specially constructed "colour-boxes" for cooling. In hot weather, however, or in hot machine rooms, it is safer to take some measures to keep them as cool as possible. Brighter colours are obtained, and it is preferable to incur a little expenditure on ice than risk spoiled work.

With Azophor black S., the best results are obtained when the naphthol prepare is slightly thickened with tragacanth and contains little or no Turkey-red oil. If the colour is too concentrated it gives brownish blacks, especially with heavily engraved patterns. Azophor black D.P. is better in this respect; and both products give fuller and better colours when strongly thickened with starch or flour-tragacanth pastes, instead of tragacanth alone.

For many purposes the Azophor blacks are exceedingly useful, but they lack the velvety richness of good Aniline and Logwood blacks, and hence these latter are usually employed whenever the conditions of process will allow.

As is well known, it is impossible to obtain a black when any of the ordinary Aniline blacks are printed on naphthol prepares, even when they are made sufficiently acid to more than neutralise the caustic soda in the prepare. M. Richard, however, found that a mixture of aniline and para-amidodiphenylamine (Diphenyl black), when printed on naphtholate of soda and steamed for 2–3 minutes in the rapid ager, gave a rich, full black, very deep, and much faster than any other black.

The only difficulty with this black is that it is apt to have a light-coloured edge wherever it fits closely to a printed Azo colour, or when it is printed alone on naphtholated cloth which is afterwards dyed in diazo solutions. This light edge, or aureole, is due to the "running" of the acids in the colour, and may be avoided by reducing the acidity, and by adding a little China clay to the thickening.

ANILINE BLACKS ON NAPHTHOL PREPARES.

	I.	II.
	grms.	grms.
Diphenyl black oil D.O.	45	...
,, ,, base I.	...	16
Aniline salt	45	56
,, oil	..	12
Paraphenylenediamine	...	5
Acetic acid 9° Tw.	50	56
Lactic acid 50 per cent.	50	...
Hydrochloric acid 34° Tw.	14	...
Thick acid starch tragacanth paste	612	...
6 per cent. gum tragacanth	...	560
China clay paste 50 per cent.	...	100
Sodium chlorate	35	30
Water	90	70
Copper sulphide 30 per cent. paste	15	20
Water	15	40
Aluminium chloride 52° Tw.	19	20
Vanadium solution 1 per cent.	10	15
	1000	1000

Print, along with any Azo colour, on Naphthol prepares 1, 2, or 3; pass through the rapid ager; wash well and soap. Black II. (Noelting and Lehne) gives a fine, deep colour, free from white edges, and may be used for either printed or dyed styles.

The Logwood blacks printed on naphthol-prepared goods are limited to such as are readily fixed by a short steaming, or even on drying in hot air—*e.g.* the Logwood iron blacks. Any Logwood iron black that is suitable for "Turkey-red discharge" work is well adapted to printing in combination with Azo colours on naphthol prepares. The one given below has been worked out specially for this class of work; it yields a very good black, gives a sharp, clean impression of the pattern, and requires no steaming for its fixation. A run through bichromate of potash improves both its shade and fastness to soaping when the goods are not steamed; but when steamed, it is sufficiently fast without any after-treatment beyond soaping and washing.

One great advantage of this Logwood black over the Azophor and other Azo blacks is, that it gives excellent results with rollers engraved in stipple, a quality which can scarcely be claimed for any other black on naphtholate of soda.

BLACK J. (on Naphthol Prepares).

90 grms. Hematine (dry Logwood extract).
300 ,, water.
100 ,, acetic acid 9° Tw. Dissolve and add—
100 ,, starch.
40 ,, British gum.
100 ,, water.
105 ,, potassium sulphite 90° Tw.
20 ,, olive oil. Boil and add—
105 ,, copperas.
140 ,, water (boiling). Boil for 10 minutes longer and then cool.

1100 = 1000 after boiling.

Print on any naphthol prepare. Goods printed with Azo colours and Black J. alone are not steamed, but passed immediately through a ½ per cent.–1 per cent. solution of bichromate at 40°–50° C.; well washed, soaped, washed, and dried. If "mordant" and "basic" colours are added to the colour combination, the goods are steamed for 2–4 minutes, fixed in tartar emetic, washed, soaped, and washed, the chroming being omitted. All operations of chroming, fixing, washing, and soaping are best and most conveniently carried out in the continuous "Open Soaper."

Direct production of Para red on the fibre.—The production of Para red on the fibre without the necessity of previously preparing the cloth in β-naphthol has been the subject of many investigations; and the problem has, to some extent, been solved successfully, though the processes suggested are but little used.

"Nitrosamine red" supplies one of the solutions. It comes into the market in the form of a paste containing the sodium compound of the nitrosamine $\left(C_6H_4\left\{\begin{matrix}NO_2\\ N:NONa\end{matrix}\right.\right)$ obtained by adding diazotised paranitraniline to excess of caustic soda, and as such is incapable of coupling with β-naphthol. The printing colour is made by mixing caustic soda, β-naphthol, nitrosamine red, acetate of soda, and tragacanth thickening, and it is printed on white unprepared cloth. After printing, the goods are gently dried and exposed to the air for a few hours, and then passed through a bath of dilute sulphuric acid, washed, and dried. The combined action of the carbonic acid of the air and the sulphuric acid results in the formation of Para red, so that the process is capable of varied application in combination with suitable colours.

One of the best contributions to the study of Nitrosamines is cited in the *Journal of the Society of Dyers and Colourists*, August 1909, from which the following particulars are taken. The nitrosamine there mentioned will serve to illustrate the principles of the direct production of Azo colours on the fibre. It consists of a comparatively stable diazo derivative of paranitro-orthoanisidine, and is prepared as under:—

5000	grms.	boiling water.
2530	,,	paranitro-orthoanisidine.
6000	,,	hydrochloric acid 30° Tw. Dissolve, cool, and add—
7000	,,	ice, and then rapidly—
1125	,,	nitrite of soda, dissolved in a small quantity of water.

The diazo solution is allowed to stand 2–3 hours, and is then mixed with 16 litres of caustic soda 36° Tw.; the voluminous microcrystalline green mass of the nitrosamine compound is collected and pressed so as to yield 8500 grms. of paste. It does not undergo decomposition for some days, especially in presence of a little caustic soda; it is easily soluble in water, from which it may be obtained in a crystallised form by salting out; and it does not combine with phenols in presence of alkali. This nitrosamine of p-nitro-o-anisidine is applied to cotton fabrics in exactly the same manner as the older nitrosamines and yields a brighter red, especially with aluminate of soda, which protects it from the action of acids in the atmosphere. The printing paste recommended by Dziewonski, the author of the paper from which the above information is derived, is made up as follows:—

RED FROM NITROSAMINE.

30	grms.	β-naphthol.
25	,,	caustic soda 76° Tw.
35	,,	sulphoricinoleate of soda 50 per cent.
75	,,	aluminate of soda 15° Tw.
50	,,	warm water.
75	,,	Nitrosamine paste.
206	,,	tepid water.
10	,,	acetate of soda.
460	,,	neutral tragacanth thickening 8 per cent.
1020		

Print on white unprepared cloth, dry, expose to the air for a few hours, pass through sulphuric acid (20 grms. H_2SO_4, 168° Tw. per litre) at 65° C., wash well, soap, and dry. A treatment in boiling water may replace the acid bath.

For resist effects under Aniline black a similar paste is used, but containing an extra amount of acetate of soda. It is printed on white cloth, and the red is developed by a 6 hours' exposure in a warm hanging room at a temperature of 30°–40° C. The Aniline black is then printed over it in a cover pattern, or with a pad roller, and the black is developed in the usual way by a run through the rapid ager, followed by chroming, washing, soaping, and drying.

As a discharge on Indigo, the nitrosamine of paranitro-orthoanisidine is particularly suitable, since it gives a first-rate red by the direct application of nitrosamine, naphthol, and chromate of soda. The presence of zinc, aluminium, and chromium salts or hydroxides exerts a beneficial influence on the brightness and fastness of the red. No more caustic soda should be employed than is sufficient to neutralise the chromic acid in the bichromate of soda, and to prevent the coupling of the nitrosamine with the naphthol. The indigo-dyed cloth is prepared with a solution containing 2 per cent. boric acid and 3 per cent. acetate of ammonia. After printing, the goods are steamed 2–6 minutes in the rapid ager, then passed through the ordinary "cutting bath" of oxalic and sulphuric acids at 70°–75° C., and finally well washed and dried.

Although not noted in the original paper, it is probable, in view of the fact that zinc compounds improve the red, that the above nitrosamine would lend itself admirably to the production of red resists under Aniline black covers and pads by Pluzanski's process, and therefore, in combination with Basic colours, Chrome yellow and Prussian blue.

Another process relying on the use of the ordinary nitrosamine of paranitraniline was patented by The Calico Printers' Association and by E. A. Fourneaux in 1907 (No. 704, 1907). In this process the calico is printed with a mixture of β-naphtholate of soda, castor-oil soap, nitrosamine, and an "acid ether" such as acetin or monochlorethyl-alcohol, which splits up by hydrolysis, and by thus yielding free acid probably converts the nitrosamine into the diazo compound, which at once combines with the naphthol to form Para red. The following is one of the examples given:—

PRINTING COLOUR.

25	grms.	β-naphthol.
25	,,	castor-oil soap (60 per cent. fatty acid).
50	,,	caustic soda 36° Tw
120	,,	water.
550	,,	gum tragacanth thickening.
60	,,	Glauber salt. Before use add—
15	,,	chlorethyl-alcohol.
15	,,	neutral acetin (42 per cent. $C_2H_4O_2$).
125	,,	Nitrosamine paste 25 per cent.
1005		

Print on plain bleached cloth, allow to lie 24 hours, and then age or wash according to the necessities of the case.

Further improvements relating to the production of Paranitraniline red on the fibre in one operation formed the subject-matter of a second patent taken out by the Calico Printers' Association and E. A. Fourneaux. (Eng. Pat. No. 765, 1907.)

These improvements consist essentially in printing a thickened mixture of Nitrosamine red and the Magnesium salt of 2-naphthol 1-sulphonic acid (β-naphthyl sulphate), with or without the addition of Turkey-red oil, etc., on white bleached calico, and then, after drying, steaming the goods for 1 minute without pressure.

During the steaming, the nitrosamine reacts with the 2-naphthol 1-sulphonic acid, with the formation of Para red, the sulpho group being eliminated.

This process allows of Para red being associated with almost any class of colouring matter, including Aniline black, Indigo, and mordant dyestuffs like Alizarin blue, Modern blue, violet, and yellow, and others that can be fixed by a short steaming. No previous preparation of the cloth with naphthol is necessary, since the printing colour contains all the elements essential to the production of the red, and thus a considerable economy is effected in time, labour, and material.

The following is an example of the above process:—

Red Printing Colour.

A	36	grms.	magnesium sulphate.
	100	,,	tragacanth thickening.
	125	,,	Nitrosamine red paste.
	181	,,	water.
B	400	,,	tragacanth thickening.
	20	,,	ricinoleic acid.
	20	,,	turpentine.
	15	,,	neutral acetin.
	103	,,	basic magnesium 2-naphthol 1-sulphonate (obtained by stirring the normal salt with excess of magnesium hydrate until the solution contains about 364 grms. of the basic salt per litre).
	1000		

Shortly before printing, mix A and B together, print on plain white calico, dry, steam for one minute without pressure, wash, soap, and dry.

The addition of 1 grm. of urea per kilogramme of printing colour is stated to improve the fastness to steaming.

Azo Colours with Steam Colours.

The use of "steam colours" with the insoluble Azo colours is of special interest, since it permits of an immense variety of multicolour effects being obtained, and thus extends the resources of the calico printer. The colours most frequently employed for this purpose are the basic aniline colours fixed with tannin, and mixed with citric and tartaric acids to neutralise the alkalinity of the naphtholate of soda, as well as to preserve the brightness of the shades. But certain mordant colours are also applicable, and these are most useful for the production of dark olives, myrtles, navy blues, and greys. Amongst the most important may be mentioned—Blue 1900 (of Durand and Huguenin), Chrome violet blue (Geigy), the bisulphite compounds of Alizarin blue, Cœruleïn, Philochromine (M., L. & B), and Chromoglaucine (M., L. & B), Gallo purple and Gallo navy blue (Bayer), and also Persian berries extract, with chromium or tin mordants. All these can be fixed by a short steaming in the rapid ager, and are remarkably fast to soaping.

Chrome yellow and Iron buff are occasionally associated with Azo colours, but they are not in much demand, and are never used with "steam colours."

The following recipes will illustrate the general methods of work in the combined Azo and steam colour styles.

Basic Colours.

With the exception of adding more acid and a small quantity of stannous chloride to preserve the colour from being soiled by the "scumming" of the diazo solution, the basic colours are made up in the same way as for the ordinary steam style. The following may serve as examples:—

	PINK.	YELLOW.	GREEN.	BLUE.
	grms.	grms.	grms.	grms.
Rhodamine 6 G. (100 per cent.)	10	..	...	...
Thioflavine T.	...	20	20	...
Brilliant green	...	..	10	...
New methylene blue N.	...	...	...	25
Acetic acid 9° Tw.	200	200	200	200
Citric acid	25	25	25	25
Starch	120	100	100	100
4 per cent. tragacanth thickening	340	300	300	300
Water	105	155	145	190
Boil, cool, and add—				
Tannin 50 per cent. solution	200	200	200	160
Tin crystals (optional)	5–10	5–10	5–10	5–10
	1000	1000	1000	1000

Print on prepares 1, 2, or 3; steam 2–3 minutes; fix in tartar emetic and chalk; wash well, soap, wash, and dry.

MORDANT COLOURS.

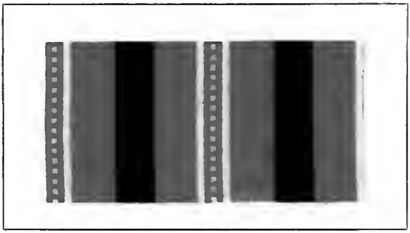
For quiet, fast colours, more suited to the home trade markets, the mordant colours are both the best and the simplest to apply on naphthol-prepared cloth. Their range is limited to navy blues, dark myrtle green, olives, greys, and yellows; the Alizarin pinks, etc., are altogether useless, since they require prolonged steaming for their full development and fixation. Moreover, they are unnecessary, as bright pinks, salmons, scarlets, reds, etc., all occupy an important position in the list of Azo colours themselves.

Typical examples of mordant colours used on the large scale for printing in combination with "Para red" and other Azo colours are given below. They may be, and are, used for ordinary steam styles without any modification whatever.

YELLOW	75	grms.	Persian berries extract 48° Tw.
	75	,,	Quercitron bark extract 48° Tw.
	775	,,	acid starch tragacanth paste.
	75	,,	acetate of chrome 30° Tw.
	1000		
BLUE 1900	30	grms.	Blue 1900 T.C. (Durand & Huguenin).
	820	,,	acid starch paste.
	150	,,	acetate of chrome 23° Tw. (pure).
	1000		
OLIVE	4		Yellow.
	1		Blue 1900.
GREY	1		Yellow.
	4		Blue 1900.
NAVY BLUE	30	grms.	Chrome violet blue (Geigy).
	4	,,	Setoglaucine.
	100	,,	acetic acid 9° Tw.
	300	,,	3 per cent. tragacanth thickening.
	100	,,	starch.
	266	,,	water. Boil, cool, and add—
	150	,,	acetate of chrome 15° Tw.
	50	,,	50 per cent. tannin solution.

Myrtle (DARK BOTTLE GREEN)	60	grms.	starch.
	200	,,	water.
	230	,,	3 per cent. tragacanth water.
	120	,,	Persian berries extract 48° Tw.
	75	,,	Logwood extract 48° Tw.
	30	,,	olive oil.
Boil and add			
	20	,,	Diamond green (B.A.S.F.).
	125	,,	acetic acid 9° Tw.
Boil a little longer; then cool and add—			
	100	grms.	acetate of chrome 15° Tw. (pure).
Stir well and then add			
	40	,,	50 per cent. tannin solution.
	1000		

This Myrtle gives a dark shade of green equal in depth to a Navy blue. In combination with "Para red," Naphthylamine claret, Navy blue, and Black J., it is extensively used for the production of rich plaid checks on flannelettes.



Multicolour Pattern in Para Red, Basic Green, and Mordant Blue.

After printing, the goods are steamed 3–4 minutes in the rapid ager passed at once through tartar emetic, and then washed and soaped.

Reduced with starch paste or tragacanth, the above myrtle gives useful and pleasing shades of a bluish-green, which may be toned to any extent by the addition of yellow.

Colour combinations, containing Navy blue, Myrtle, and any of the brighter colours, always require steaming and fixing in tartar emetic; those containing Azo colour and Black J. only are merely dried after printing, and then passed directly into a chrome bath,—the black fixes perfectly without any steaming, and is, in fact, fast enough to withstand a severe soaping. Diphenyl black must be steamed as is usual for all steam colours.

INSOLUBLE AZO COLOURS PRINTED WITH VAT DYESTUFFS.—The Azo colours may also be printed in conjunction with most of the Vat dyestuffs. In this case the naphthol-prepared goods are printed with the ordinary Indigo, Ciba colour, and Indanthrene colour printing pastes (alkali-hydrosulphite pastes), along with any desired diazo solution; they are then steamed in the rapid ager at 102° C., passed at once into a copious supply of cold running water until the vat dyes are re-oxidised, then soured (if need be) with sulphuric acid at ½° Tw., and finally well washed and soaped (for Ciba colours, at the boil).

AZO COLOURS WITH LEAD YELLOW AND IRON BUFF.—These are simple styles, used only for handkerchiefs, etc., for the Eastern markets. Usually a black is printed at the same time, and, if the style is not very tasteful, the colours are at least very fast.

(*a*) For *Yellow*, the naphthol prepare may contain 2½ per cent. of sulphate of soda. The yellow printed is a thickened solution of basic lead acetate, identical with the "Madder (lead) yellow" already described. After printing, the goods are passed through a warm bath of dilute sulphuric acid ¾°–1¼° Tw., or through an acid solution of sulphate of soda (20 per cent. solution). They are then well washed and raised yellow in bichromate of soda as described for "Madder yellow" (followed by a treatment in lime water if an orange is required), well washed again, soaped, and washed. If Diphenyl black is introduced into the pattern, the goods are steamed in the rapid ager, and the subsequent acid treatment is best carried out with a solution of sulphate of soda, acidulated with acetic acid, or very dilute sulphuric acid. The addition of acid is not absolutely essential, but it improves the whites and helps to remove any excess of diazo solution that has decomposed and formed a dull brownish film over the Azo colour. Catechu brown has also been used with success in combination with Para red, Toluidine orange, etc. In this case, also, the "Catechu madder brown" (*q.v.*) is employed, and the printed goods (after steaming for black) are passed directly into a combined fixing and developing bath.

FIXING AND DEVELOPING BATH.

200	grms.	Glauber salt cryst.
5	,,	bichromate of potash.
1000	,,	water.

Work the goods for 20–30 minutes at 60° C. in this solution, then well wash and soap.

(*b*) *Iron buff* in combination with Diphenyl black and Para red is often used for handkerchiefs. The buff is made by thickening an acetate of iron prepared by the double decomposition of copperas and lead acetate.

BUFF F.

500	grms.	British gum paste.
500	,,	acetate of iron 18° Tw.
1000		

Print Buff F., Red P.N., and Diphenyl black on naphthol prepares 1, 2, or 3; steam 3–4 minutes in the rapid ager; and then raise the Buff by passing the printed pieces through caustic soda 4°–5° Tw. at 60° C.; wash well, and allow the pieces to lie until the dirty olive precipitate of mixed ferrous and ferric hydrates has become fully oxidised to the latter. Wash again and soap.

The chromium lake of Alizarin blue withstands the run through caustic soda, and as it fixes well in the rapid ager, it can be employed, with good effect, as an additional colour in the combination. It gives a pleasing slate-like grey, which goes well with red, black, and buff. For a dark chocolate brown "Manganese bronze" serves admirably. A thickened solution of manganese chloride or sulphate is printed along with the other colours on the naphthol prepare, and the goods are then treated precisely as above. A short run through dilute "chemick" is beneficial after the goods have lain a short time: the chemick completes the oxidation of the manganous hydrate, and brightens the red and white simultaneously.

AZO COLOURS WITH SULPHIDE COLOURS.—The printing of sulphide dyestuffs alongside the insoluble Azo colours calls for no special manipulation of the cloth. After printing, the pieces are steamed in air-free steam for 3–4 minutes, and then passed directly through a series of becks, the first filled with a dilute solution of sulphuric acid (1 part acid 168° Tw. to 100 parts water), and the following ones with water, soap, and water respectively. In other respects the process is identical with that for Azo colours alone.

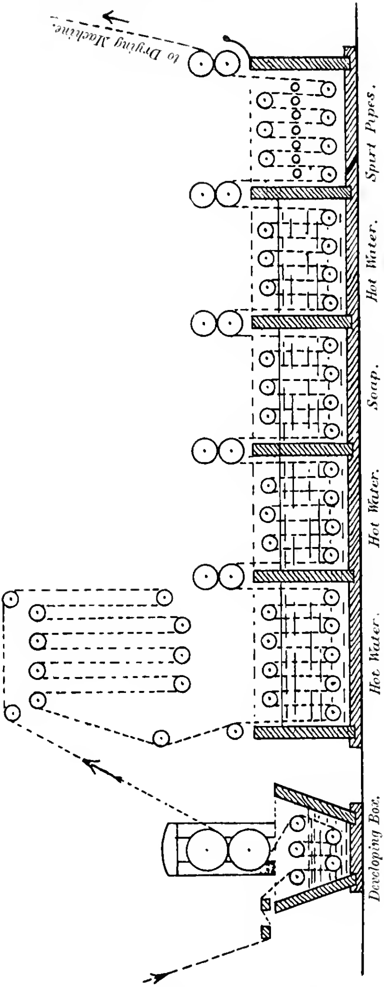


FIG. 74.—Continuous "Para" red dyeing machine.

C. The Dyeing of Plain Shades with the Insoluble Colours.

Plain shades of this description are usually dyed in printworks for subsequently discharging with reducing agents.

The process consists in padding the cloth in one of the "naphthol prepares" already given; and then passing it, after drying, through the necessary diazo solution contained in the liquor box of an ordinary slop-padding machine. The coupling of the diazo compound with the naphthol takes place at once, but, in order to ensure the complete combination of the two bodies, the cloth is given a short run through the air before it enters the washing becks. The whole process is conducted with the cloth in the open width up to the point at which it leaves the washing becks after dyeing in the diazo solution. It may then be washed and soaped in the rope state, since there is no further fear of creases causing unevenness in the shade. A dyeing machine suitable for the purpose is sketched in fig. 74; it is self-explanatory.

The preparation in naphthol is carried out exactly as for printed goods; but, as a rule, it is unnecessary to add any antimony salts to the naphtholate of soda unless the cloth has to be dried over cylinders, or if it cannot be dyed at once. Two suitable prepares for dyed shades are made up as follows—

	FOR REDS.	FOR CLARETS, ETC.
β-naphthol	28	30
Shading salt R.	2	...
Caustic soda 52° Tw.	75	75
Turkey-red oil 40 per cent.	25	...
Water	870	895
	1000	1000

The diazo solutions are prepared in the usual way, but without thickening, and are usually of about two-thirds the strength of the corresponding printing colours. Their concentration varies, however, according to the depth of colour required and the strength of the naphthol solution employed. For most purposes the latter rarely exceeds 3 per cent., but if printing is combined with dyeing for the production of two-colour ground effects, or when strong and weak naphthol "colours" are printed together with the same object, it may reach 5–6 per cent., and in such cases the strength of the diazo solution must be increased proportionately. The dyeing solutions may be made up as under:—

PARANITRANILINE RED.

5,000 grms. Paranitraniline C.
20,000 „ hot water.
25,000 „ hydrochloric acid 30° Tw.

Dissolve, cool, and add

26,000 grms. cold water.
50,000 „ ice.

Then pour in gradually, whilst stirring,

24,000 grms. nitrite solution 13 per cent.

Allow to stand 15 minutes, filter, and add—

74,000 grms. acetate of soda solution 32½ per cent.
1000 „ water or ice.

225 kilos.

α-NAPHTHYLAMINE BORDEAUX.

7,000 grms. α-naphthylamine.
26,000 „ hydrochloric acid 30 per cent.
17,000 „ hot water.
Grind to a smooth paste and cool.
68,000 „ ice.
30,000 „ nitrite solution 13 per cent.
75,000 „ acetate of soda 32½ per cent.
2,000 „ water (or British gum paste).

225 kilos.

The acid in these two mixtures is in a somewhat large excess, but as the acetate of soda is only added immediately before use, and as diazo compounds keep longer in acid solutions, it is an advantage to use a larger quantity, because sometimes the solution has to be prepared some hours before it is actually required.

If desired, the acid can be reduced to 12 kilos. in the red and 13 kilos. in the bordeaux solutions, but the foregoing quantities have been found to give the most regular work in practice.

In a similar way the following dye liquors may be prepared:—

	ORANGE.	SCARLET.	BLUE.	BROWN.	CHOCOLATE.
Ortho-nitrotoluidine	15	...	...	7·5	...
Chloranisidine	...	20	...	...	...
Dianisidine salt	...	...	8·3	...	...
Benzidine	...	...	...	7·5	15
Hydrochloric acid 30 per cent.	...	27	7·2	45	55
Sulphuric acid 123° Tw.	14	...	...	...	...
Water, hot	120	200	50	150	150
Cool, and add—					
Cold water	483	420	645·5	385	340
Ice	200	200	150	200	200
Nitrite solution 13 per cent.	68	58	32	80	90
Acetate of soda solution 32½ per cent.	100	75	...	125	150
Chloride of copper 77° Tw.	...	...	30	...	...
Chromic acid	...	..	2	...	...
6 per cent. tragacanth thickening	...	...	75	...	...
	1000	1000	1000	1000	1000

The blue is dyed on a 3 per cent. naphthol prepare containing 2–3 per cent. acetate of soda (say 30 grms. per litre). In each of the above colours a portion of the water added after cooling is left out until the diazotising is finished. Then, after the diazo solution has stood for some time, the acetate of soda and the rest of the water are added to make up the litre.

After dyeing, the pieces are well washed and soaped in the open width; then washed and soaped again in the rope form. For reds fast to rubbing, the goods, after the last soaping and washing, are passed through a boiling *dilute* solution of phenol, containing 0·2 grms. of phenol per litre. Para reds are soluble in phenol, and consequently their treatment under the above conditions results in the removal of the surface colour, which only adheres loosely to the cloth and is easily rubbed off in use. Incidentally, too, both the red and the "white" are improved.

D. The Coupling of the Diazo Compounds with Colours of the Chrysoïdine Group.

Certain members of the Amido-azo group of dyestuffs combine with diazo compounds to form insoluble, dark brown precipitates. If this reaction takes place on the fibre, the colour obtained is similar to Catechu brown in shade, is very full and rich, and of excellent fastness to light and soap.

In practice, the finest, and therefore the most important, colours of this class are produced by the action of diazotised p-nitraniline (paranitro-diazo-benzene chloride) on Chrysoïdine and Bismarck brown (Vesuvine). These two dyestuffs are put on the market by the Farbwerke Höchst, as Parabrown salt G. (Vesuvine) and Parabrown salt R. (Chrysoïdine)—names which have been given to them because they are specially adapted to coupling with diazotised paranitraniline.

The method of producing Para browns on the fibre is practically the same as that employed for the production of Para reds, the only difference being that the cloth, instead of being prepared in naphthol, is printed or padded with solutions of one or other of the Brown salts R. and G. The Brown salt R. gives a redder shade than the G. mark; both are equally suitable for either printing or padding, and both are developed in the ordinary diazo solution used for Para reds. Moreover, the Brown salts can be printed on naphthol-prepared goods, so that when dyed, a brown pattern on a red ground is obtained; and further, as the brown and red are both discharged by the same reducing agents (hydrosulphites), it is possible to obtain white and coloured patterns on a two-colour background.

Printing of "Para Brown."—The best thickening to use for this purpose is a gum tragacanth starch paste, or a starch paste alone, according as a blotch or a "peg" pattern is to be printed.

DARK BROWN PRINTING COLOUR 2½ per cent.

25	grms.	Brown salt R. or G.
150	,,	acetic acid 6° Tw.
300	,,	water.
50	,,	starch (dry).
475	,,	4 per cent. gum tragacanth thickening.
1000		

Boil and cool.

This colour is too strong for ordinary use and must be reduced 4 : 1 (Brown ¼), but for lightly engraved or stippled patterns it is quite suitable. Print on white cloth, dry, and develop in diazotised paranitraniline (1·5 to 2 grms. paranitraniline per litre).

Printed thus on plain white cloth, brown and white effects are obtained; while if printed on naphthol-prepared cloth, brown and red effects are produced. After dyeing, the goods are simply washed, soaped, and dried.

Dyeing of "Para Brown."—The cloth is first padded in a 1½–2 per cent. solution of Brown salt R. or G.; then dried and developed in diazotised p-nitraniline; well washed, soaped, and dried.

The Brown salt padding liquor is usually thickened slightly with tragacanth in order to facilitate the even impregnation of the cloth.

A padding solution, used in practice for dark browns, is made up as follows:—

2 per cent. BROWN SALT FOR PADDING.

20	grms.	Brown salt R. or G.
50	,,	acetic acid 9° Tw.
450	,,	boiling water.
Dissolve, and add		
100	,,	3 per cent tragacanth thickening.
380	,,	cold water.
1000		

Pad in any type of padding mangle; dry in hot air or over cylinders, the first few of which are preferably wrapped with calico; and then develop as before in p-nitraniline, wash, soap, and dry.

For "two-brown" styles, pad the cloth in a ⅓ per cent. solution of Brown salt, then print on a stronger colour (say 2–2½ per cent.), dry and develop as usual.

The "coupling," *i.e.* the combination of paranitro-diazo-benzene with Brown salt takes place much more slowly than with naphthols. After development, therefore, the pieces must be well squeezed between the mangle bowls to express excess of liquor, and then allowed to lie in pile or batch until the reaction is complete. This usually occupies from 15–20 minutes, after which period the pieces may be washed and soaped without any fear of irregularities arising. If washed too soon, the colour is not only weak, but it is apt to be uneven, and in any case full advantage is not taken of the possibilities of the materials used.

Compared with the browns obtained from benzidine and tolidine in combination with metanitraniline, etc., the Para browns possess several advantages. In the first place, they are faster to light; (secondly) they are not volatile, even when hot calendered or embossed, and therefore they can be ironed in the laundry without "marking off"; and thirdly, they yield a pure white with hydrosulphite discharges. These valuable qualities, combined with their rich, "bloomy" appearance, their ease of production, and their adaptability to many styles hitherto only possible to produce by roundabout methods, have rendered the "Para browns" of the utmost importance to the calico printer, and have enabled him not only to introduce many new effects, but also to simplify some of his older processes, and to turn out, at a cheaper rate, a larger quantity and a more varied assortment of high-class goods than he could formerly.

(E *and* F) **Resist and Discharge Effects on Insoluble Azo Colour Grounds.**

In addition to direct printing, there are two methods of producing white and coloured designs on grounds dyed with Azo colours: (1) by printing, on the naphthol-prepared cloth, some substance which is capable of chemically changing the diazo compound when the goods are dyed, and thus preventing the formation of colour on the printed parts; and (2) by printing on the dyed cloth certain reducing agents which, under the influence of steam, bleach out the colour from those parts of the dyed cloth upon which they are printed. The first of these methods is known as the "Reserve or Resist Style," and the second as the "Discharge Style." They both form part of a special branch of calico printing; and as the processes and materials involved in their production are common to other and quite different classes of colouring matters, their description will be deferred to the next section.

(4) DISCHARGE AND RESERVE (RESIST) STYLES.

Perhaps the most important of the many valuable features of "Discharge" and "Reserve or Resist" styles of printing is that they allow of white and coloured patterns being produced on *dyed* grounds.

As is well known, it is possible to obtain by dyeing a depth, fulness, and richness of colour altogether unapproachable by any process of printing. It is a very great advantage, therefore, to be able to print upon white cloth a reserving or resisting substance which will prevent the fixation of colour during the dyeing operation; or to print upon dyed cloth a substance which will discharge the colour from the printed parts. But these styles are not restricted to dyed work; they may be, and are, applied equally well to all sorts of printed patterns, so that it is possible to obtain a vast variety of effects on figured backgrounds. Any colour that can be dyed and printed can be "discharged" or "reserved," irrespective of the method by which it has been applied, provided always that it is suited to this class of work. Mordants also can be treated in the same way, as has already been noted in the description of the "Madder Style."

Another advantage, which relates more particularly to discharge printing, is that fine, delicate patterns can be discharged on dark grounds with a perfection and crispness of definition quite impossible in printing with a blotch roller. In the latter case, the colour always runs to a slight extent, and this, with delicate line or spot patterns, is almost invariably sufficient to spoil the sharpness of the impression: the colour swells, and fills up the finer details of the design. Some improvement may be effected in the impression of a blotch roller by using thicker colour, but then the ground colour suffers, and is very apt to become thin and weak in appearance, or "clothy" or "bare," as it is termed technically. On the whole, therefore, it is safer and better in all respects to employ the discharge or the resist methods whenever circumstances permit.

"Discharging" agents always act chemically. "Resisting" or "Reserving" agents may act either chemically or mechanically; very often they do both. It is needless to give a detailed list of the numerous substances that go to make up the various "discharges" and "resists"; but it may be noted that both classes of bodies include oxidising and reducing agents, acids and alkalies, various salts, China clay, and, in the case of "resists," fats, wax, resin, and solid matter like lead or barium sulphate.

The chemical action of these substances will be touched upon here only in so far as it relates to their suitability for producing patterns on dyed and printed grounds; but further information on the nature and properties of oxidising and reducing agents will be found in the special chapter on these bodies.

DISCHARGE STYLES.

The Discharging of Indigo by Oxidation.

Although Indigo may be discharged either by oxidising or reducing processes, the former are the ones in most general use, since the latter, though yielding good results, are at present somewhat difficult to manipulate on the large scale.

Oxidising agents convert Indigo into isatin, which dissolves out of the cloth during the process, leaving a white pattern wherever the cloth was printed. The most important substances used for this purpose are—(1) Chromates; (2) Chlorates (and sometimes Bromates); and (3) Red prussiate of potash in combination with caustic soda. The methods depending on the use of these reagents are distinguished as—

(1) The Chromate Discharge.
(2) The Chlorate Discharge.
(3) The Prussiate Discharge.
(4) The Nitrate Discharge (Freyberger).

Each possesses certain advantages in special cases, but the first is by far the most generally useful and finds the most extensive application.

(1) The Chromate Discharge.

In this process the Indigo-dyed cloth, printed with a pattern in a chromate, is passed through a hot bath of sulphuric acid; chromic acid is liberated and destroys the Indigo. At the same time, however, the cloth is liable to be tendered by the formation of oxycellulose, especially if an excess of chromate be used in the discharge. Under the most favourable conditions a slight tendering always takes place, as it is impossible to gauge exactly the quantity of chromate required for a given shade of blue; and if too little is taken, the white is poor. Hence it is advisable to use a small excess of chromate in order to obtain a clear, sparkling white. To some extent the formation of oxycellulose can be regulated by the addition of reducing agents to the acid or "cutting liquor"; the addition of glucose, glycerin, brown sugar, and dextrin have been recommended for this purpose, but hitherto they do not seem to have exercised any particularly beneficial effect. Oxalic acid acts in much the same way, and is perhaps the best, as it is certainly the most commonly used, substance to counteract the energetic oxidising action of chromic acid. It tends to regulate the discharging, and simultaneously it renders the excess of chromic acid in the bath innocuous by reason of its reducing properties. If the chromic acid were allowed to accumulate, it would soon become sufficiently concentrated to affect the colour on the unprinted parts of the cloth; indeed, with light Indigoes it not infrequently happens that the colour is partially destroyed over the whole surface of the cloth, owing to an excess of chromic acid in the "cutting liquor."

One of the most important advantages of the Chromate discharge is that it allows of bright and fast colour effects being obtained on an Indigo blue ground of any depth. The pigment colours—Chrome yellow, Chrome orange, Guignet's green, Yellow ochre, Sienna, Lamp black, Vermilion, and various lakes and Prussian blue—are used for this purpose. They are fixed with albumen, which is coagulated during the run through the acid bath. Steaming is both impossible and unnecessary, the hot acid effecting the coagulation quite as well, and in a manner sufficiently complete to fix the pigments permanently.

For a discharge white, the bichromates of soda or potash may be used as such; they are simply dissolved in water and added to starch paste or British gum thickening. For colours, however, they must be neutralised with caustic soda, soda ash, or ammonia, otherwise the acidity of the bichromates would coagulate the albumen before the colour was printed. Excess of ammonia is not detrimental, except to colours containing Prussian blue; and in the case of Chrome yellows, and the various oxides of iron, and the earths, an excess of soda ash even may be allowed. A little free alkali improves the working qualities of printing colours containing albumen, but care should be taken not to add too much, lest the coagulation be retarded.

The general directions, given elsewhere (Preparation of Printing Colours), for the grinding and straining of pigment colours must be strictly followed in discharge printing if good results are to be secured. A brush furnisher must also be used; and it is advisable at the outset to add a little turpentine, benzene, or oil to the printing colours to prevent any undue frothing.

The percentage of bichromate in the printing pastes varies with the depth of the Indigo blue to be discharged, and with the strength of the engraving. Coloured discharges usually require less than white discharges, as the opaque pigments mask the slight under-tint of blue.

The following examples of Chromate discharges are taken from practice:—

White 160 I.

810	grms.	British gum paste.
160	,,	bichromate of soda.
30	,,	turpentine.
1000		

Yellow 120 I.

320	grms.	Chrome yellow.
60	,,	6 per cent. tragacanth thickening.
20	,,	rape seed oil.
20	,,	turpentine.
300	,,	40 per cent. albumen solution.
120	,,	bichromate of soda.
100	,,	caustic soda 70°–71° Tw.
60	,,	water.
1000		

Grey 120 I.

250	grms.	Lampblack.
280	,,	6 per cent. tragacanth thickening.
200	,,	40 per cent. albumen.
120	,,	bichromate of soda.
50	,,	water.
100	,,	caustic soda 70° Tw.
1000		

Green 120 l.

200	grms.	Guignet's green.
100	,,	Chrome lemon yellow.
100	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
50	,,	water.
30	,,	turpentine.
1000		

Straw 120 l.

300	grms.	Chrome yellow.
10	,,	Prussian blue 25 per cent.
70	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent. albumen.
40	,,	rape seed oil.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
60	,,	water.
1000		

Red 90 I.

200	grms.	Vermilion.
100	,,	Vermilion substitute.
140	,,	6 per cent. tragacanth thickening.
90	,,	bichromate of soda.

Grind together, and add in turn—

145	grms.	6 per cent. ammonia.
20	,,	rape seed oil.
30	,,	turpentine.
275	,,	50 per cent. egg albumen.
1000		

Brown 120 l.

250	grms.	Burnt Sienna paste.
100	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent. albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
90	,,	water.
40	,,	rape seed oil.
1000		

Chamois 120 I.

60	grms.	Chrome yellow (lemon).
20	,,	,, ,, (maize).
150	,,	China clay.
150	,,	water.
300	,,	6 per cent. tragacanth thickening.
100	,,	50 per cent. egg albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
1000		

Various shades of olive can be obtained by mixing yellow, green, and grey, or from some of the many colour lakes of all descriptions put on the market for discharge styles by different makers.

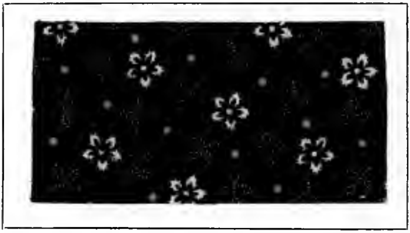
The numbers in the foregoing recipes denote the amount of bichromate per kilogramme of colour, and those given are suitable for the ordinary dark shade of Indigo blue.

After printing the above colours, the Indigo-dyed cloth is dried and then passed through the following bath at 60° C.:—

Acid or "Cutting" Bath.

60	grms.	sulphuric acid 168° Tw.
20– 30	,,	oxalic acid.
920–910	,,	water.
1000		

The speed of the cloth is arranged so that it takes about ½ minute to pass through the acid bath; that is, the time of immersion is ½ minute. From time to time the bath is replenished by the addition of fresh liquor. The goods are finally well washed and dried.



Discharge White and Yellow on Indigo (Chromate).

The concentration of the cutting liquor varies in different works: the above has been found to give excellent results on the large scale, but the proportions of the two acids may be varied considerably without appreciably affecting the ultimate effect.

A modification of the Chromate discharge, first suggested by Prud'homme, and later worked out by others, is in use in Russia. It consists in dispensing with oxalic acid in the "cutting liquor," and adding the oxalates of potassium or calcium to the printing colour. Good results are said to be obtained with both white and colours, and it is claimed for the process that it effects a considerable economy in oxalic acid. This is not unlikely, but, so far, the new process has not been shown to possess any conspicuous advantage over the older one, and has not come into general use.

Chromate Discharge White with Oxalate.

180	grms.	bichromate of soda.
80	,,	20 per cent. ammonia.
540	,,	British gum paste.
200	,,	calcium oxalate 50 per cent. paste.
1000		

Print on dark Indigo, dry, and discharge in—

80	grms.	sulphuric acid 168° Tw.	at 60° C.
920	,,	water	
1000			

Wash well and dry.

Cheap dark shades of blue are obtained by first dyeing the cloth a light Indigo blue and then padding it in a weak Aniline black bath. The same principle is applied differently in the production of discharge effects on a two-colour ground of Indigo blue and Aniline black. The light blue goods are printed in Chromate discharges containing acetate of soda, or better, an excess of soda ash; they are then covered with a pattern in Aniline black, dried, passed through the rapid ager to develop the black, and finally "cut," as described above, in sulphuric and oxalic acids. The presence of free alkali prevents the development of the black on the printed parts, so that a clear cut pattern in discharge colours appears on a blue and black ground. Some of the styles produced in this way are very effective, and they had a great run some years ago.

The following two colours will illustrate the preparation of Chromate discharges to resist a black cover or pad:—

CHROMATE WHITE TO RESIST BLACK COVER.

60	grms.	bichromate of soda.
150	,,	soda ash.
200	,,	water.
590	,,	British gum paste.
1000		

YELLOW TO RESIST BLACK COVER.

40	grms.	bichromate of soda.
100	,,	soda ash.
120	,,	British gum (dry).
10	,,	olive oil.

Heat until the gum is dissolved, then cool and grind in—

260	grms.	Chrome yellow (paste).
160	,,	40 per cent. albumen.
1000		

Print on light Indigo-dyed cloth; dry; cover in a prussiate Aniline black, pass through the rapid ager, discharge in acid, wash well and dry. A red may be obtained by replacing Chrome yellow with Vermilion, or one of the Vermilion substitutes.

Azo Colour Discharges on Indigo.—The fact that certain diazo compounds withstand the action of chromic acid has been utilised by Elbers, Frey, Kurz, and Grosheintz for the production of red and orange discharges on Indigo. For this purpose the most suitable amido bases to use are Amido-azo-benzene, p-Nitraniline, and m-Nitraniline; most of the others are more or less acted upon by chromic acid, and some of them are entirely destroyed—a property which makes it possible to obtain effects similar to those last described, namely, coloured discharges on a blue and black ground.

A very convenient way of working the insoluble Azo colour discharge process is to employ the stable diazo compounds of the para- and meta-nitranilines—Azophor red P.N. and Azophor orange M.N. respectively—but the ordinary diazo printing colours may be used with equally good results.

The discharge colours are made up as usual for Azo colours plus the required amount of bichromate of soda, and are then printed on Indigo-dyed cloth prepared in β-naphtholate of soda. After drying, the printed goods are discharged by running through the acid "cutting bath," as used for Indigo, at a temperature of 50°–60° C. They are then well washed and dried.

DISCHARGE RED OR ORANGE A.Z.

	RED.	ORANGE.
Azophor red	112 grms.	...
,, orange	...	112 grms.
Water	300 c.c.	300 c.c.
Caustic soda 36° Tw.	50 ,,	50 ,,
Water	150 ,,	150 ,,
Gum tragacanth 6 per cent.	400 grms.	400 grms.
Bichromate of soda	150 ,,	150 ,,
Make up the whole to	1 litre	1 litre

Print on Indigo blue cloth previously padded in naphthol prepares 1, 2, 3, 4, or 5 (page 389); dry, and pass through the ordinary cutting liquor; wash well and dry.

The insoluble Azo colours can be printed along with all the ordinary chromate discharges except white, which is difficult to obtain pure, as the chromic acid acts on β-naphthol, producing a dirty brownish coloration. The only way of overcoming this disadvantage is to wash the goods free from naphthol before they are passed into the acid bath. With soluble chromates this is impossible, so that insoluble chromates have to be used. These are either produced upon the fibre directly or added to the printing colour in paste form.

Kurz and Kunert have worked out a method based upon the employment of a naphthol prepare containing sodium bichromate, and printing colours containing lead acetate. Chromate of lead is deposited on the fibre, and the goods are then rinsed in water to remove the naphthol grounding before being treated in the acid bath. The lead chromate resists the washing, and is subsequently decomposed, with the liberation of chromic acid during the "cutting" operation. To avoid the deposition of lead sulphate on the cloth, the "cutting liquor" may be composed of hydrochloric and oxalic acids in place of the usual sulphuric acid liquor.

Messrs Meister, Lucius & Brüning recommend the addition of barium chromate to the diazo discharge colours, which can then be printed on naphtholate of soda prepares, pure and simple. Thus—

CHROMATE DISCHARGE RED B.C.

90 grms.	Azophor red P.N.
250 ,,	water.

Allow to stand ½ hour, then add—

50 grms.	caustic soda 36° Tw.
50 ,,	water.
260 ,,	thick tragacanth 8 per cent.
300 ,,	Barium chromate 85 per cent. paste.
1000	

Print on naphthol-prepared Indigo-dyed cloth; dry, and then pass in the open width through dilute ammonia to remove the superfluous naphthol; squeeze out the excess of ammonia, and pass through a "cutting liquor" composed of 60 parts hydrochloric acid at 33° Tw. and 20 parts oxalic acid per 1000 of water; wash well, soap, and dry. The washing in dilute ammonia previous to "cutting" requires the greatest care, otherwise a portion of the mechanically adhering barium chromate will be detached, with the result that the Indigo will be incompletely discharged.

An ingenious suggestion has been made recently for obtaining a pure white with chromate on naphthol-prepared Indigo-dyed material without the necessity of washing the naphthol out of the cloth before "cutting." It consists in adding to the chromate discharge some substance capable of combining with the naphthol to form an easily soluble colouring matter. For this purpose the diazo compound of sulphanilic acid has been recommended, since it forms with β-naphthol a readily soluble yellow azo dye which does not dye cotton in colours fast to washing. Probably many of the other diazo compounds obtained from the sulphonic acids of the primary aromatic amines would behave in the same way.

To obtain red and white patterns discharged on a two-colour ground of light Indigo and black, Bloch and Zeidler (*Bull. Soc. Ind. Mulhouse*, 1906, p. 229) make use of the fact that chromic acid destroys the blacks produced from mixtures of Dianisidine blue and Benzidine puce, or from Azophor black and various other Diazo blacks.

They prepare the Indigo-dyed cloth, as usual, in a solution of naphthol, then print on it Paranitraniline or Azophor red mixed with bichromate of soda, and an ordinary chromate discharge white. After gently drying, a second or cover pattern is printed over the first in a Diazo black, and the cloth is then passed through the "cutting liquor" at 50°–60° C. The chromic acid destroys both the blue bottom and the black cover wherever the first pattern was printed, thus producing a two-colour pattern on a two-colour figured ground of blue and black. The best results have been obtained by using a red about half as strong again as that used for ordinary printing. The following proportions have given satisfactory work in practice:—

Red A.Z.B.

120 grms. Azophor red.
400 ,, cold water.

Dissolve, allow to stand ½ hour, filter, and add—

55 grms. caustic soda 36° Tw.
45 ,, water.
500 ,, thickening C.; then make up to—

1 litre.

Thickening C.

(1)
400 grms. 8 per cent. tragacanth.
80 ,, starch.
220 ,, water.
100 ,, acetic acid 9° Tw.

Boil, cool, and add

(2)
200 grms. bichromate of soda.
100 ,, water.

1 kilo. after boiling.

The discharge Red A.Z.B. contains 100 grms. bichromate per litre, a quantity greatly in excess of what is required to discharge the light Indigo blue, but which is necessary to "cut away" the black over-print or "cover." Print the red (and white) on light Indigo-dyed cloth previously prepared in a 3 per cent. solution of naphtholate of soda; dry and cover with Azophor black; dry and pass into the ordinary "cutting" liquor of sulphuric and oxalic acids; and finally wash well and soap.

A discharge orange is obtained in exactly the same way by substituting Azophor orange M.N. for the red in the above recipe.

Although the diazo compounds of the para- and meta-nitranilines and amidoazo-benzene all resist the action of chromic acid sufficiently long to allow of their being utilised for coloured discharges, they are, nevertheless, slowly acted upon by it, and therefore it is advisable to prepare the colours in small quantities as required. The sodium bichromate ought to be added immediately before printing, and the colour ought to be printed at once. Even then it is difficult to obtain regular results if the colour is not renewed at frequent intervals. On the whole, the Azo colour discharge style on Indigo is somewhat unreliable, and for that reason it finds but little application in practice.

Another method of discharging Indigo may be noted here, as it bears a close resemblance, in some respects, to the Chromate process. It was worked out and patented by Dydynksi and the Calico Printers' Association in 1906, and is based upon the oxidising action of bromine. The process consists in printing the Indigo-dyed calico with a mixture of bromide and bromate of sodium, and then in passing the goods through a "cutting liquor" of dilute sulphuric acid (12 per cent.) at 85°–93° C. The liberated bromine oxidises the indigotine to isatin, producing a white discharge,

$$5NaBr + NaBrO_3 + 3H_2SO_4 = 3Na_2SO_4 + 3H_2O + 3Br_2$$

In practice, an excess of bromate is found to yield better results. Instead of the 22·7 per cent. of bromate in the mixture, it is better to employ a quantity between 25 per cent. and 30 per cent. The cutting liquor may be used at 40°–50° C., but better and cleaner discharges are obtained at the temperature mentioned above (85°–93° C.). The speed at which the cloth is run through the cutting liquor is regulated so as to allow of a 7–20 seconds' immersion, according to the class of work in hand. All chance of bromine vapour escaping into the air is avoided by adding a little ferrous sulphate to the "cutting liquor." Most of the bromine accumulates in the bath as sodium bromide, and may be recovered from the cutting liquor by distillation with bichromate of soda and acid.

For discharging a dark shade of Indigo the following is a suitable paste for a fairly fine pattern:—

WHITE DISCHARGE B.R.

180 grms. bromate of soda.
420 ,, bromide ,,
1 litre British gum paste.

Print, dry, pass through 12 per cent. sulphuric acid at 85°–90° C.: wash well and dry.

(2) The Chlorate Discharge.

This process is chiefly used for the production of white effects only, since it cannot be applied along with colours which are comparable with Indigo for fastness, and at the same time as bright as those obtained by the Chromate method. In some cases, however, Chlorate discharges are combined with pigment colours, but goods so printed cannot afterwards be passed through caustic soda, in order to improve the white.

The Indigo is discharged by steaming in the rapid ager for 1–3 minutes, and the discharge printing pastes contain, besides chlorate of soda, a certain amount of red or yellow prussiate of potash or vanadium salts, both of which act as oxygen carriers. The addition of citric acid or citrates of soda or ammonia also improves the discharge, but care should be taken to avoid an excess of acid, as the fibre is easily tendered thereby. For fine patterns which require a more energetic oxidising agent to discharge the Indigo properly, the chlorate of soda is replaced by chlorate of alumina. The chief defect of chlorate discharges is, that they are liable to "run" in steaming. To minimise this, it is usual to add a plastic substance, like China clay, to the printing pastes, and to steam the goods in dry steam as hot as possible.

Chlorate discharges are especially suitable for heavy patterns, since they are less apt to form oxycellulose than chromate discharges; and for very heavy patterns their oxidising action is often still further moderated by replacing part of the chlorate with bromate of soda or ammonia. Bromine and its oxy-acids do not attack the fibre so energetically as chlorine and its oxides.

To obtain a good white on Indigo, the dyed cloth must be well soured and washed after dyeing in order to remove all traces of lime or alkali. If these are allowed to remain, the discharge will be irregular and the white poor. The rollers, too, must be strongly engraved, so that the discharge may be effected completely in one steaming operation of from 1–3 minutes; a longer steaming increases the risk of running.

To prevent "doctor streaks" from discharging the blue ground where not required, the cloth may be prepared before printing in dilute solutions of sulphites, thiosulphates, or sulphocyanides. These salts act as effective resists to the action of the small quantity of chlorate transferred to the cloth through a defective doctor, but do not, at the strength used, affect to any appreciable extent the discharge of the Indigo in the properly printed parts.

The following chlorate discharges are suitable for dark shades of Indigo; lighter shades require reducing according to their intensity.

CHLORATE DISCHARGE WHITE I. 20 per cent.

250 grms. British gum powder.
470 ,, water.
200 ,, chlorate of soda.

Boil, cool to 30° C., and add

50 ,, yellow prussiate of potash (finely ground) and—
30 ,, citrate of ammonia 50° Tw.

1000

CHLORATE WHITE II. 15 per cent.

A
50 grms. starch (dry).
250 ,, water.
200 ,, 50 per cent. China clay paste.
150 ,, chlorate of soda. Boil and cool.

B
30 ,, yellow prussiate of potash.
245 ,, 6 per cent. tragacanth thickening.
75 ,, citric acid (powder).

1000

Mix A and B.

CHLORATE WHITE III. 15 per cent.

80 grms. China clay.
70 ,, water.
530 ,, 40–50 per cent. gum Senegal.
150 ,, chlorate of soda.

Dissolve, cool to 30° C., and add

90 tartaric acid in powder.

Cool, and add

75 ammonium ferricyanide 36° Tw.

1000

Chlorate White IV. 20 per cent.

250 grms. British gum powder.
400 ,, water.
100 ,, 50 per cent. China clay paste.
200 ,, chlorate of soda.

Dissolve, cool to 30° C., and add—

20 grms. red prussiate of potash (ground).

Cool, and add

20 ,, ground citric acid.
10 ,, vanadium solution 1 per cent. (see Mordants).

1000

Aluminium Chlorate White I.

200 grms. British gum powder.
60 ,, water.
550 ,, chlorate of alumina 42° Tw.
150 ,, chlorate of soda.

Boil, cool, and add

40 ,, red prussiate of potash.

1000

Aluminium Chlorate White II.

45 grms. flour.
250 ,, water.
150 ,, chlorate of soda.
200 ,, ,, barium.

Boil, cool to 50° C., and add

130 grms. sulphate of alumina.
130 ,, boiling water.

Cool, and add

40 ,, red prussiate of potash (powder).
55 ,, 8 per cent. tragacanth thickening.

1000

Chlorate Discharge Yellow A.

250 grms. Chrome yellow paste.
200 ,, 40 per cent. albumen.
150 ,, chlorate of soda.
280 ,, 8 per cent. tragacanth thickening.

Grind well together in a mill.

30 ,, red prussiate of potash (ground).
50 ,, citrate of soda 40° Tw. (neutral).
20 ,, olive oil.
20 ,, turpentine.

1000

All the foregoing chlorate discharges are printed on cloth dyed dark Indigo. After printing, the goods are dried and steamed for 1–3 minutes in the rapid ager with dry steam at 95°–100° C.; then washed in water for 2–4 minutes at 60°–80° C., and, if they contain no yellow, passed in the open width through caustic soda at 4° Tw., or through a bath composed of equal parts of caustic soda and silicate of soda made up as under :—

10 litres caustic soda 66° Tw.
10 ,, silicate of soda 66° Tw.
1000 ,, water.

If the pattern contains yellow, the goods are simply washed and lightly soaped after steaming.

Another method of producing a Chrome yellow discharge on Indigo is sometimes employed for certain African styles. The yellow is produced on the fibre after the discharging has been effected by the chlorate. For this purpose the following paste is printed on a medium shade of indigo:—

CHLORATE DISCHARGE YELLOW B.

450 grms. water.
155 ,, British gum.
100 ,, chlorate of soda.
175 ,, lead nitrate.
Dissolve with heat, cool a little, and add
50 grms. citric acid.
Cool, and add
20 ,, red prussiate of potash.
50 ,, water.

Print; steam 3 minutes; pass through a hot solution of sulphate of soda, and then directly into a hot ½ per cent. solution of bichromate of potash (neutralised with ammonia) to raise the lead yellow. A slight excess of ammonia is beneficial in giving a warmer tone to the lead chromate. Finally, wash well and dry.

The above discharge yellow is principally used in the production of the bizarre mixed-up effects so popular in the West Coast of Africa trade. An example of these curious effects is produced by the following series of operations:—

On white cloth prepared in oleine 2½–4 per cent.

(1) Print a stripe pattern (or any other) in Alizarin red and pink, Pigment yellow, Pigment green. Steam and wash.

(2) Dip the printed goods to a medium shade of Indigo, corresponding to say about 1 per cent. of Indigo on the cloth. Wash well in water and soap lightly.

(3) Print a two-colour scroll pattern in Chlorate white III. 10 per cent. and Chlorate discharge yellow B. Steam for 3 minutes in the rapid ager; wash off in sulphate of soda; wash well in water; develop the Chrome yellow by a run through a 1 per cent. solution of neutral chromate of soda at 60° C.; wash well again and soap lightly to clear the white and colours.

The ultimate result is a scroll pattern in white, yellow, red, pink, scarlet, orange, and two shades of green, on a striped ground of pure Indigo blue, a purplish shade of blue, a greenish blue, a chocolate, and a green. The chlorate discharges cut away the Indigo, allowing the pattern first printed to show through, and the shades of orange, scarlet, and yellowish green are obtained from the superposition of the discharge yellow on red, pink, and green. The strength of the discharges is arranged so that they "cut" the Indigo without affecting the colours underneath it; and care must be taken to avoid using them at a greater strength than is necessary for this purpose, as if too strong they will discharge, or at least partially discharge, the steam Alizarin pink and reduce the depth of the Alizarin red. The parti-coloured ground is, of course, the result of dyeing Indigo over the pattern first printed.

Various other motley effects of a similar nature are obtained by combinations of the "Madder Style" with Indigo dyeing and chlorate discharges.

The chlorate of alumina discharges can be applied to the production of an Alizarin red discharge on Indigo. The dyed goods, after printing and steaming, are passed at once through any of the usual "dunging liquors" to fix the alumina, and then dyed up in Alizarin as usual for the Madder styles (F. Brandt. See also Prud'homme, *Teinture et Impression*, p. 154.)

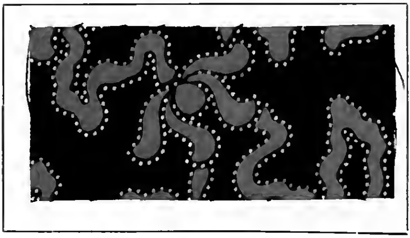
Another method of producing fast-coloured discharges on an Indigo ground is based upon the fact that certain Azo colours are unaffected by the oxidising action of chlorate discharges. Of these colours, the most valuable is the red obtained from the diazo-compound of para-nitro-ortho-anisidine coupled with β-naphthol. The process is as follows:—The Indigo-dyed cloth is first padded in a 2½–3 per cent. β-naphthol prepare according to the methods already mentioned in connection with the production of the insoluble Azo colours; it is then printed with the red and white discharges given below, and, after drying, steamed for 4 minutes in the rapid ager. Finally it is worked for 10–15 minutes in a 1 per cent. solution of silicate of soda at 60° C., washed well, soaped, washed again, and dried.

	Discharge Red.	Discharge White.
{ Thick flour paste	400 grms.	550 grms.
{ Chlorate of soda	250 ,,	250 ,,
Dissolve, cool, and add—		
Chlorate of aluminium 42° Tw.	45 ,,	50 ,,
{ Red prussiate of potash (powdered),	25 ,,	25 ,,
{ Water	80 ,,	100 ,,
Cool completely and add—		
Citric acid	25 ,,	25 ,,
Acetate of soda.	25 ,,	...
Diazo solution A.Z.P. . . .	150 ,,	...
	1000	1000

Diazo Solution A.Z.P.

168 grms. p-nitro-o-anisidine (Azo pink N.A. (M., L. & B.)
300 ,, hydrochloric acid 36° Tw.
300 ,, water.
Mix to a fine paste and add—
500 grms. ice water.
And then slowly—
260 grms. nitrite of soda, 29 per cent. solution.

Make up to 1500 with water.



Chlorate White and Azo Pink N.A. (M., L. & B.).

The Azo colours discharged on Indigo in this manner give bright fast colours, but, owing to their liability to unevenness, they require very careful handling on the large scale, and consequently they are not employed to any great extent.

(3) Prussiate Discharge.

This process is founded on the oxidising action of red prussiate of potash ($K_3Fe(CN)_6$) in presence of caustic soda. It is only applicable to light and medium shades of Indigo, as "red prussiate" cannot be kept in solution at a strength sufficient to discharge dark shades. The cloth is printed with a thickened solution of "red prussiate," and, after drying, is passed through a warm bath of caustic soda, then well washed and, if necessary, soaped. In combination with the diazo compounds of para- and meta-nitraniline, nitrotoluidine, α-naphthylamine, chloranisidine, and o-anisidine, very fine, fast, and brilliant discharge effects are obtained on Indigo-dyed cloth previously prepared in β-naphthol. The nature of the process allows of a fine white being obtained, since the caustic soda removes all excess of naphthol (or diazo compound in the colours).

PRUSSIATE WHITE.

200 grms. red prussiate of potash.
500 ,, water.
60 ,, starch.
240 ,, 4 per cent. tragacanth thickening.
1000

Boil and cool.

DISCHARGE RED P.

15 grms. Paranitraniline.
75 ,, hot water.
24 ,, hydrochloric acid 36° Tw.
Dissolve, and add
75 grms. ice.
82·5 ,, ice water.
And at 0° C.,
28·5 grms. nitrite solution 29 per cent.
510 ,, flour-tragacanth paste.
160 ,, red prussiate (finely ground).
30 ,, sodium acetate.
1000

Other diazo solutions may be applied similarly. Print on Indigo-dyed cloth prepared in a 2½–3 per cent. solution of β-naphthol; dry and discharge the blue by a 10 to 20 seconds' run through the discharging bath given below.

DISCHARGING BATH.

100 litres caustic soda 20° Tw.
750 grms. soda ash.

Used at 20–25° C.

For white alone, the temperature of the discharging bath may be raised to 50° C. Wash well (and soap lightly for colours) after discharging. A run through dilute sulphuric acid in the cold acts favourably on both ground and discharges; this should be given before soaping.

The prussiate discharge finds only a limited application in practice at the present time.

(4) Freyberger's Nitrate Discharge.[1]

This process consists in printing on the Indigo-dyed fabric a nitrate and then running the pieces through fairly strong sulphuric acid. If the acid is weak, practically no action takes place.

A 12 per cent. solution of nitric acid acts very slowly on Indigo-dyed goods, but the same strength of acid, if diluted with sulphuric acid of 50 per cent. strength, instead of with water, instantly destroys the Indigo. If the concentration of sulphuric acid is increased to 70 per cent., even 6 per cent. nitric acid is sufficient to discharge the Indigo.

The presence of a small proportion of nitrite in the nitrate discharge renders the process more effective.

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[1] *Journ. Soc. of Dyers and Colourists*, 1910, p. 253; *Färb. Ztg*, 1910, p. 239.

WHITE DISCHARGE.

275 grms. nitrate of soda.
50 ,, nitrite of soda.
675 ,, British gum thickening.
1000

Print, dry, and pass through sulphuric acid 100° Tw. at 75° C.

Coloured effects may be obtained by adding diazotised amines to the white discharge paste and printing on Indigo-dyed fabrics previously prepared in β-naphthol. By the addition of lead nitrate to the discharge paste and subsequent chroming a yellow discharge is obtained, and if the paste is not sufficiently strong to destroy all the Indigo, a green discharge results.

If the process is suitably conducted, neither hydrocellulose nor oxycellulose are formed, and there is therefore no tendering of the fibre. The sulphuric acid may be chosen of such a strength that mercerisation of the fabric is brought about simultaneously with the discharge.

The nitrate process is cheaper than any other, and is specially adapted for discharging very dark blues.

(5) Reduction Discharges on Indigo.

According to Aubert, Frossard, and Fleischer (*Revue générale des matières colorantes*, 1907, pp. 419, 422), perfect whites can be obtained on Indigo and Thio-indigo by means of the hydrosulphite formaldehydes. These compounds are thickened and printed on the dyed material, which, after drying, is steamed for 3–5 minutes at 102° C. in dry air-free steam, and then passed at once through a hot bath of caustic soda; then soured, washed, and soaped. Another method is to pass the steamed goods through a hot bath of bisulphite of soda before the treatment in alkali. Soda ash may also be used.

Aubert recommends the following proportions for the white discharges:—

WHITE DISCHARGE I.

600 grms. hydrosulphite N.F.
400 ,, 50 per cent. gum Senegal.
1000

Print, dry, steam as described; pass one minute through a bath at 75° C. containing 10 per cent. bisulphite of soda, and then directly afterwards, for 50–60 seconds, through a bath at 75° C. containing 10 per cent. caustic soda. Finally, sour, wash, and soap.

WHITE DISCHARGE II.

200 grms. hydrosulphite N.F. conc.
200 ,, gum Senegal 50 per cent.
420 ,, 50 per cent. China clay paste.
180 ,, saturated solution of bisulphite-acetone.
1000

Print, dry, steam in the "hydrosulphite ager" for 3–4 minutes, and then run through a boiling bath containing 10 grms. soda ash per litre. Wash, sour, wash, and soap lightly. The bisulphite acetone may be replaced by a mixture of 10 grms. ferrous sulphate or ferric chloride and 10 grms. nitrite of soda, but the resulting white is not so pure.

It is imperative, with these discharges, to wash the goods in alkali immediately after steaming, as otherwise the Indigo begins to re-oxidise. The rapidity with which this re-oxidation takes place renders the process a delicate one, and one difficult to control on the large scale, and it was, at first, the main obstacle to the general adoption of the hydrosulphite discharges on Indigo. It is evident that to secure regular results from hydrosulphite alone special arrangements are necessary in order to ensure that the printed cloth has an uninterrupted run through the whole process. If, after steaming, the printed goods are allowed to lie before washing-off in alkali, the purity of the whites is either impaired or destroyed altogether according to the length of time the goods are exposed to the air; hence any breakdown in the continuity of the process results in considerable loss. Fortunately these drawbacks were soon overcome, and the hydrosulphite process is now in general use.

The first improvement (suggested by the Farbwerke Höchst) consisted in the addition of anthraquinone to the discharge pastes,—an addition which, along with zinc oxide and neutral acetin, made it possible to allow the goods to lie for about half an hour between the steaming and washing-off operations. The presence of anthraquinone improves the whites and renders them more stable in the air by retarding the re-oxidation of the indigo-white, its action being due probably to the formation of oxyanthranol, which, by becoming oxidised, first protects the indigo-white for a certain time.

If the printed goods cannot be washed off immediately after steaming, it is advisable to wrap them up and store them in a warm dry place. Whenever possible, however, the washing-off in alkali should be proceeded with at once. The following recipe will serve to illustrate the composition of a discharge white:—

DISCHARGE WHITE H.A.
200 grms. hydrosulphite N.F. concentrated.
580 „ British gum thickening.
Heat to dissolve, cool, and add—
75 grms. zinc oxide.
75 „ water.
50 „ anthraquinone paste 30 per cent.
20 „ acetin (neutralised with soda).
1000

Print on dark Indigo blue, dry, steam 4 minutes at 102°–104° C. in air-free and fairly dry steam, run at full width through a boiling 1 per cent. solution of silicate of soda, and finally wash and dry.

Notwithstanding the great improvement effected by the use of anthraquinone, the hydrosulphite process still left much to be desired, and it was not until the introduction of the Leukotropes that it was finally put on a thoroughly practical basis.

THE LEUKOTROPE PROCESS.—The Leukotrope process of discharging Indigo differs from the earlier hydrosulphite processes in that the indigo-white produced on the fibre is at once converted into stable yellow compounds, which are soluble or insoluble in alkalies according to circumstances. The means whereby these results are brought about were patented by the Badische Anilin und Soda Fabrik, who, in January 1910, put on the market the two products most suitable for the purpose, namely Leukotrope W. and Leukotrope O. These two products belong to a class of bodies which consist of compounds of certain tertiary bases with benzyl chloride, and its substitution products.

The principle of the Leukotrope process is, briefly, as follows:—When compounds of benzyl chloride with dimethylaniline, methylethylaniline, methylphenylaniline, dimethylmetamidophenol, etc., are brought into contact, in presence of zinc oxide, with indigo-white, first produced on the fibre by the hydrosulphite discharge, they form brilliant reddish-yellow dyestuffs, which, being fast to acids, alkalies, air, and soap, are suitable for the production of yellow discharge effects on Indigo-dyed cloth. Leukotrope O. is a member of this series.[1]

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[1] K. Reinking, *Jour. of Soc. of Dyers and Colourists*, Dec. 1910.

On the other hand, if the benzyl radicle in the above compounds is replaced by benzyl chloride with a sulphonic group substituted in the nucleus, a second series of Leukotropes is obtained; and these bodies—of which Leukotrope W. is one—also combine with indigo-white to form yellow dyestuffs which, while unaffected by air and moisture, are very soluble in alkalies, and are therefore well suited to the production of white discharges on Indigo.[1]

The stability, in moist or dry air, of both the soluble and insoluble yellow derivatives of indigo-white dispenses with the necessity of washing the printed goods in alkali immediately after steaming, a great practical advantage over the older hydrosulphite discharges.

As compared with the oxidation discharges (chromate and chlorate), the Leukotrope-hydrosulphite discharge possesses a still greater advantage, viz. that the deepest shades of Indigo can be discharged to a pure white, in either the heaviest or lightest of patterns, without any fear of "tendering" the cloth in the slightest degree.

Rongalite C.L., hydrosulphite C.L., and Hyraldite C.L. are mixtures of Leukotrope W. with Rongalite C., hydrosulphite N.F. conc., and Hyraldite A. respectively. They may be applied in exactly the same way as for an ordinary hydrosulphite discharge.

In applying the Leukotropes, the Indigo-dyed cloth is printed with any of the following discharge pastes, all of which are suitable for ordinary dark shades of blue.

STRONG DISCHARGE WHITE (for fine patterns).

160	grms.	zinc oxide paste 50 per cent.
100	,,	Leukotrope W.
240	,,	Rongalite C.
40	,,	anthraquinone paste 30 per cent.
460	,,	British gum thickening.
1000		

For heavier patterns and lighter shades of Indigo, the above may be reduced with thickening as required.

WHITE DISCHARGE with Rongalite, C.L.

160	grms.	zinc oxide paste 50 per cent.
40	,,	anthraquinone paste 30 per cent.
200	,,	Rongalite C.L.
600	,,	British gum thickening.
1000		

YELLOW DISCHARGE.

460	grms.	British gum thickening.
200	,,	Rongalite C.

Dissolve, cool, and add—

100	grms.	Leukotrope O.
40	,,	anthraquinone paste 30 per cent.
200	,,	zinc oxide paste 50 per cent.
1000		

BLUE DISCHARGE.

100	grms.	Indanthrene blue G.C.D. paste.
200	,,	alkaline thickening (for Indigo). Mix, and add—
200	,,	Rongalite C.
500	,,	alkaline thickening (for Indigo).
1000		

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[1] Germ. Patent B. 56,300 (Dr Holt), B.A.S.F.

All the above printing pastes are very stable; they will keep in good condition for a fortnight at least.

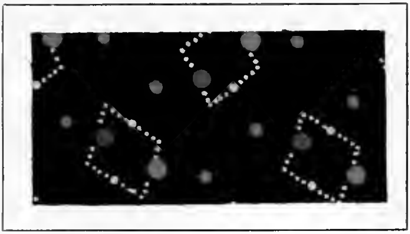
After printing, the goods are dried, and then steamed for 4–5 minutes in the rapid ager at 102°–104° C. They are then run, at full width, through a boiling 1–2 per cent. solution of silicate of soda, well washed, and finally dried.

If a blue discharge is printed together with white and yellow discharges, it is advisable to treat the goods in alkali immediately after steaming, since the blue contains no Leukotrope.

In place of silicate of soda, corresponding quantities of soda ash, caustic soda, or milk of lime may be employed in the stripping bath.

Red discharges, in combination with white, yellow, and blue, may be obtained by printing a chlorate discharge containing Tuscaline red base B. (B.A.S.F.) along with the Leukotrope discharges and Indanthrene blue. Other coloured discharges can be obtained by using various vat dyestuffs, such as Indanthrene yellow, and several of the Algole colours, etc. Except in very few works, however, the Leukotrope process is restricted to the production of white effects on Indigo. The yellow given by Leukotrope O., while fast to washing, is extremely loose to light,—a disadvantage which renders it unfit for the highest class of work.

Perrotine Print.



White—Leukotrope W.
Yellow—Leukotrope O.
Blue—Indanthrene blue, G.C.D.

Titanium Discharges on Indigo.—The application of the powerful reducing action of titanous salts to the discharging of Indigo has been patented by E. Knecht and Peter Spence & Sons, Ltd.

On medium shades of Indigo good results have been obtained by this method, but hitherto practical difficulties have prevented its employment for dark shades.

All the titanous salts reduce Indigo rapidly, even on drying, but, with the exception of the sulphocyanide, they all either tender the cloth, or are too unstable for use as printing pastes.

The sulphocyanide is made directly by the double decomposition of titanous sulphate and barium sulphocyanide; and as the precipitated barium sulphate is in an extremely fine state of division, and has no action on the reducing powers of the titanous salt, it is allowed to remain, the whole mixture being simply thickened with British gum and printed.

Discharge White T.

1000	grms.	titanous sulphate solution [15 per cent. $Ti_2(SO_4)_3$].
500	,,	barium sulphocyanide.
150	,,	British gum.
1650		

Boil till smooth.

Print on a medium shade of Indigo, dry, and strip off the reduced Indigo by passing at once through a boiling solution of caustic soda 2° Tw. Wash well and dry.

A short steaming may be given before stripping if desired, but it affects the ultimate result very slightly, and is, moreover, apt to tender the cloth. The addition of glucose is an advantage in this latter connection.

The fact that titanic hydrate is deposited on the discharged parts of the cloth renders possible the production of white and coloured discharge effects. For this purpose a Leukotrope white is printed alongside white discharge T, the goods are steamed and stripped in the usual way, and then washed well and dyed up in mordant colours such as Alizarin, Alizarin orange, Persian berries, Quercitron bark, etc. The titanic hydrate acts as a mordant for these dyestuffs, yielding red, orange, yellow, and gold respectively, whereas the parts upon which the Leukotrope discharge is printed remain white.

CONVERSION EFFECTS ON INDIGO.—A conversion effect depending on the discharging of both dyed and printed Indigo is obtained in the following way. A green composed of Indanthrene yellow G. and Indigo in combination with caustic soda and hydro-sulphite-formaldehyde is printed on a light Indigo-dyed ground. The goods are steamed for 3 minutes at 102° C., and then well washed in cold water to develop the mixed green. This gives a green pattern on a light blue ground. If a Chromate white discharge is now printed over the green and blue, it discharges the blue completely and converts the green into a yellow by destroying its blue element. If the pattern printed in green be a check and the pattern in white a large spot, the effect produced is that of a yellow and white check spot on a blue and green check ground, the check being continuous all over. A similar effect is produced by printing Indanthrene yellow alone, but in that case the green is too weak to contrast well with the blue ground.

Thio-indigo red, Indigo, and Indanthrene yellow may be used in the same way to give a red and white spot on a blue and chocolate ground. In fact, the various modifications of the different Indigo discharge processes are so numerous that it is impossible to enumerate more than one or two in a work of this size.

Discharging of Turkey Red.

The production of white and coloured patterns on dyed Turkey-red grounds is effected in two totally distinct ways, namely, (1) by the Acid or Chloride of Lime process, and (2) by the Glucose-Alkali process.

Both these methods are in general use, and are of the utmost practical value for the printing of the well-known "Turkey-red chintzes."

(I) The Acid Process.

The acid process derives its name from the fact that the dyed material is printed with strongly acid solutions, though the real discharging agent is bleaching powder, through a solution of which the cloth is passed after printing. The acids liberate hypochlorous acid from the bleaching powder, and this acid destroys the Turkey red on the printed parts of the cloth.

For a white discharge either citric, tartaric, or arsenic acids may be used with equally good effect, but for colours the organic acids only are employed. Yellow is obtained from citric acid and lead salts; blue from a solution of Prussian blue in oxalic and tartaric acids; and green from a mixture of blue and yellow. The black printed on Turkey red in the acid discharge process is generally a Logwood and iron black, which fixes itself on drying, and which is made sufficiently strong to resist the bleaching action of the "chemick" bath. Aniline black is out of the question, since it requires either steaming or a few hours' ageing for its development, and both these processes give rise to defective work. Steaming causes the strong acids to attack and tender the fibre, and ageing gives them both the time and the chance of absorbing moisture, which causes them to "run," and thus give clumsy impressions with "woolly" edges.

After printing, the goods are carefully dried (in hot air if possible), and are then run in a continuous manner, and at the full open width, through a series of tanks or "becks" fitted with top and bottom guide rollers and squeezer bowls, in much the same way as an "open soaper." The first of these becks contains a solution of bleaching powder 12° Tw., and a little chalk to prevent it from becoming too acid; the second and third are supplied with running water; the fourth contains a slightly warm $\frac{1}{2}$–1 per cent. solution of bichromate of potash to precipitate the lead salts as Chrome yellow; and the rest consist of washing becks, through each of which fresh water flows continuously.

The object of the "chemick bath" is twofold: (1) to discharge the Turkey red from the printed parts of the cloth, and (2) to precipitate the lead salts as chloride, which, being insoluble in cold water, adheres to the cloth during the following operation of washing in the second and third becks, and is finally fixed as the quite insoluble Chrome yellow in the bichromate or "chrome" bath.

Blue shades of Turkey red are more difficult to discharge than the yellow shades, and in practice the latter are almost invariably used, as they are both easier to manipulate and yield more brilliant effects. The bluer shades can, however, be discharged satisfactorily, and are occasionally employed for "home trade" chintzes. Another point to observe in the discharging of Turkey red is to avoid an excess of oily compounds on the fibre: they resist the penetration of the acid printing colours, and therefore prevent the bleaching liquor from acting anywhere but on the surface of the material, with the result that an incomplete discharge is obtained.

The various discharge colours may be made up as follows:—

Discharge White I.

600	grms.	water.
115	,,	flour. Boil, cool, and add whilst cooling—
250	,,	citric acid.
30	,,	oxalic acid.
5	,,	Indigo extract (for sightening).
1000		

Discharge White II.

435	grms.	water.
80	,,	acetic acid 9° Tw.
100	,,	flour. Boil, cool, and add—
380	,,	arsenic acid 173° Tw.
5	,,	Blue standard 15 per cent.
1000		

Discharge Blue I.

300	grms.	water.
25	,,	starch.
15	,,	olive oil. Boil, cool, and add—
15	,,	turpentine.
250	,,	Blue standard 15 per cent
145	,,	arsenic acid 175° Tw.
300	,,	White discharge II.
1000 when cooled.		

Discharge Blue II.

450	grms.	water.
50	,,	starch.
50	,,	flour.
25	,,	olive oil. Boil, and whilst cooling add—
200	,,	tartaric acid (pulverised). Cool, and add—
250	,,	Blue standard 15 per cent.
1000 when finished.		

Blue Standard 15 per cent.

300	grms.	Prussian blue 50 per cent. paste.
50	,,	oxalic acid.

Allow to stand over-night, then add—

650	grms.	boiling water, and stir till dissolved.
1000		

Discharge Yellow.

350	grms.	water.
250	,,	lime juice 48° Tw.
100	,,	flour.
200	,,	lead nitrate. Boil, cool a little, and add—
100	,,	tartaric acid. Cool.
1000		

Discharge Green, 8/I.

8	grms.	Discharge yellow.
1	,,	Discharge blue I. or II.

A somewhat brighter green is obtained by replacing a portion of the lead nitrate in the yellow with lead acetate. About equal parts of each give a good result.

Print the above colours on Turkey-red dyed cloth; dry and pass through bleaching powder solution 12° Tw.; wash and pass through a $\frac{1}{2}$ per cent. solution of sodium bichromate at 30°–40° C.; wash well and dry.

If the rollers are lightly engraved or worn down, the percentage of acid will require to be increased; as a rule, however, it is better to strengthen the engraving, since the strengthened colours are apt to crystallise out.

Almost any Logwood and iron black is suitable for printing alongside the chintz colours given above. The only condition to be observed is to make it strong enough to withstand the oxidising action of the bleaching powder bath. The addition of a little Prussian blue improves the shade; the blue may be added either as such or formed in the colour during its preparation. Both the following blacks are used on the large scale:—

Black I.

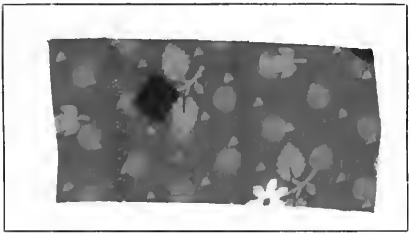
475	grms.	Logwood extract 18° Tw.
32·5	,,	acetic acid 9° Tw.
225	,,	pyrolignite of iron 28° Tw.
75	,,	starch
25	,,	British gum.
23·75	,,	nitrate of soda.
12·5	,,	olive oil. Boil, cool, and add—
37·5	,,	acetate of copper 40° Tw.
93·75	,,	nitrate of iron 54° Tw.
1000		

BLACK II.

12·5	litres	Logwood extract 48° Tw.
32·5	,,	water.
20	,,	acetic acid 9° Tw.
5	,,	olive oil.
10	kilos.	starch. Boil, and add—
5·5	,,	ferrous sulphate.
10	litres	water.
2	kilos.	yellow prussiate of potash.
10	litres	water.
1·25	,,	red liquor 8° Tw., and when cold—
1·25	,,	nitric acid 60° Tw.
100		litres when finished.

Both these blacks are fixed on the fibre by the mere operation of drying after printing. Black II. after fixing contains Prussian blue.

In all the Logwood blacks used for Turkey-red chintzes the Logwood is present in the form of a finely divided precipitate, and this makes them difficult to work in the ordinary way, as they stick in the engraving. In order to prevent this as much as possible a brush furnisher must be used; and in some works a strip of "wire card" fixed on a bar of wood is used instead of a "lint doctor." The "card" scratches the smooth surface of the roller considerably and wears down the engraving rapidly, but it answers its purpose admirably, and, apart from the cost of engraving, it is really an economical arrangement, since it ensures a good, full impression of the pattern (of the black roller). The black roller certainly "scums" badly owing to the rough state of its unengraved surface, but in reality this "scum" consists of so thin a film of black that it is entirely removed in the subsequent operations, and hence it has no detrimental influence on the ultimate effect. As a matter of fact, it is owing to the energetic action of bleaching powder on Logwood that it is essential to print the cloth heavily with very strong blacks. A good part of the black is removed in the discharging beck, and if it is at all weak to commence with, or has been printed with a worn or a too lightly engraved roller, it is quite impossible to obtain a full, rich black.



Turkey Red—Acid Discharge.

Many recipes for discharge colours are in general use, but they are based upon the same principle as, and consist of so many modifications of, those given above. The only exception of any note is the use of lactic acid, patented by C. F. Boehringer & Sons, of Nieder Ingelheim a/Rh. It is claimed by them that lactic acid possesses advantages over other organic acids, but so far it has not displaced these latter to any great extent.

(2) The Glucose-Alkali Process. (Alkaline Discharges.)

This process is based upon the fact that Alizarin alumina lakes (Turkey red, etc.) are soluble in concentrated caustic soda, and, when associated with the glucose process of Indigo printing, it affords an exceedingly valuable means of producing very fast Turkey-red chintz styles. Indigo is much faster than Prussian blue to soaping, and another great advantage is that Aniline black may be used, so that, taken altogether, alkaline discharges yield the most permanent colours it is possible to apply to Turkey red. As in the acid process, the discharge yellow is produced on the fibre by precipitating a lead salt with bichromate, and the green is a mixture of Indigo and Chrome yellow.

The general method of working is practically identical with the glucose process of Indigo printing. The Turkey-red dyed cloth is first prepared in a 30 per cent. solution of glucose; then dried, printed with the alkaline colours, steamed for 2–3 minutes in the rapid ager, and then passed through a boiling solution of silicate of soda to clear the whites, etc., and finally through an acidified solution of bichromate of soda to develop the Chrome yellow and the green.

Caustic soda alone does not yield a satisfactory white, for, although it dissolves out the Alizarin lake, it always leaves a white, tinged more or less strongly with pink. To obtain a pure white discharge it is necessary to add an alkaline solution of stannous hydrate, silicate of soda, and a trace of Indigo to the thickened caustic soda. These additions enhance the purity of the white enormously, but are not essential in the case of blue, yellow, and green.

ALKALINE DISCHARGE WHITE I.

750 grms. alkaline thickening T.R.
100 ,, stannous chloride.

Mix the stannous chloride very gradually with the thickening at a temperature not exceeding 30° C. When dissolved add—

148 grms. silicate of soda 77° Tw. and—
2 ,, Indigo L. (Badische) 25 per cent. paste.

1000

ALKALINE DISCHARGE WHITE II.

758 grms. alkaline thickening T.R.
70 ,, glycerin.
50 ,, stannous chloride.
100 ,, silicate of soda 77° Tw.
20 ,, turpentine.
2 ,, Indigo L. 25 per cent. paste.

1000

ALKALINE DISCHARGE YELLOW I.

625 grms. alkaline thickening T.R.
300 ,, lead hydrate 50 per cent. paste.
75 ,, silicate of soda 77° Tw.

1000

ALKALINE DISCHARGE YELLOW II.

100 grms. lead acetate.
40 ,, lead nitrate.
90 ,, boiling water.
60 ,, glycerin.

Dissolve, and add to

675 grms. alkaline thickening T.R.
35 ,, silicate of soda 77° Tw.

1000

Alkaline Discharge Blue.

730	grms.	alkaline thickening T.R.
20	,,	starch (maize).
50	,,	water.

Heat to 60° C., cool, and add—

150	grms.	Indigo L. 20 per cent. paste (B.A.S.F.).
30	,,	glycerin.
20	,,	turpentine.
1000		

Alkaline Discharge Green I.

560	grms.	alkaline thickening T.R.
240	,,	lead hydrate 50 per cent.
100	,,	Discharge White II.
20	,,	turpentine
80	,,	Indigo L. 25 per cent. paste (B.A.S.F.).
1000		

or

Discharge Green II., 3 parts Yellow II. above.
1 part alkaline Discharge Blue.

Alkaline Thickening T.R.

100	grms.	light British gum.
900	,,	caustic soda 100° Tw.
1000		

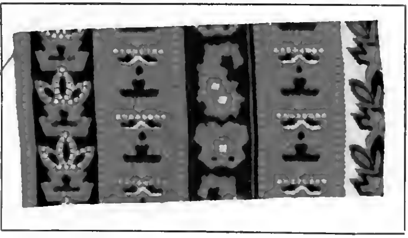
Heat to 60° C. and cool before use.

Indigo L. 25 per cent. Paste.

250	grms.	Indigo L. powder (B.A.S.F.).
700	,,	30 per cent. gum Senegal solution.
50	,,	caustic soda 100° Tw.
1000		

Grind or mix well together.

Any other brand of artificial Indigo—Indigo pure, M., L. & B., etc.—may replace the Indigo L., if desired, without any alteration in the foregoing formulæ.



Turkey Red—Glucose-Alkali Discharge.

Any steam Aniline black or a Diphenyl black may be printed in conjunction with the alkaline discharge colours. As a rule, a strong Vanadium black is preferred, but equally good results are obtained from Copper sulphide blacks; and if the pattern is a heavy one, a Prussiate black yields perfectly satisfactory results, and is, moreover, much safer to use, since it is not nearly so liable to tender the fibre. Recipes for Aniline blacks will be found in the section on "The Steam Style."

After printing, the goods are thoroughly dried, and steamed immediately in the rapid ager for 2–3 minutes. They are then passed through a boiling 2–3 per cent. solution of silicate of soda for 3–5 minutes, well washed in water, chromed in an acidified solution of bichromate of potash or soda, and then washed well and dried. The Chrome bath is made up as follows:—

Chrome Bath ½ per cent.

100 litres		water.
500	grms.	sulphuric acid 168° Tw.
500	,,	bichromate of potash.

Used at 30°–40° C.

In order to secure the best results, the following precautions must be observed after printing:—

(1) The goods must be quite dry before steaming, otherwise the colours will run and the discharge will be imperfect.

(2) Steaming must be proceeded with as soon as possible after printing. If the printed goods are allowed to lie, the colours absorb carbonic acid from the air; and as sodium carbonate is quite useless as a discharging agent, the results are poorer the longer the goods remain unsteamed.

(3) In "chroming," care must be taken to avoid using too strong a bath, lest the blue be impoverished by too energetic an oxidation. In cases where the pattern contains very light blues, the amount of sulphuric acid may be reduced, and sometimes even it is advisable to omit it entirely.

A modification of the alkaline discharge process consists in first printing the glucose prepared Turkey-red cloth with white, blue, green, or yellow, and then, after drying, printing it with a "cover" pattern in Aniline black. The alkalinity of the discharge colours prevents the development of the black during the steaming process, so that a clear-cut coloured pattern appears on a figured ground of black and red. This style is chiefly confined to black, red, and yellow effects.

One of the most important uses of the "Glucose-alkali discharge" is in the production of the well-known Blue and Red Style. This consists for the most part of Indigo blue stripes and blotches on a Turkey-red ground, and is produced by methods identical with those already described. A simpler and quicker method of obtaining the same effect is, print a mixture of Indigo, caustic soda, and hydrosulphite on plain *unprepared* Turkey-red cloth. For this purpose the following colour may be used:—

Indigo Blue H.S.

700	grms.	alkaline thickening T.R.
{ 75	,,	hydrosulphite N.F. conc.
{ 75	,,	water.
150	,,	Indigo M.L.B. 20 per cent. paste.
1000		

Print; dry; steam 2–3 minutes in air-free steam at 102° C.; pass through 1 per cent. solution of silicate of soda, wash well in water and dry.

The Indanthrene colours (B.A.S.F.) and the Ciba colours (Soc. Chem. Ind., Basle) are both suitable for Turkey-red discharge styles by the alkaline process, and neither require the cloth to be previously prepared with glucose, although somewhat better results are obtained if glucose is used. Both Ciba and Indanthrene blues are far faster than Indigo in every respect, and, so far as shade is concerned, they are much brighter and purer in tone. It is surprising that their application to Turkey-red chintz styles has been almost ignored, and that they are practically unused for Turkey-red discharges on the large scale. It is therefore impossible to say how they would work in bulk; but judging from the results obtained in the laboratory from the colours given below, it would appear that they have a future before them in this branch of the industry.

CIBA BLUE DISCHARGE ON TURKEY RED.

120	grms.	Ciba blue 2 B.D. paste.
40	,,	stannous hydrate 50 per cent. paste.
50	,,	glycerin.
40	,,	gum Senegal 30 per cent.
750	,,	alkaline thickening T.R.
1000		

Allow to stand ½ hour before using.

Ciba violet B. or R. may be used in the same way.

INDANTHRENE BLUE DISCHARGE ON TURKEY RED.

150	grms.	Indanthrene blue R.S. paste.
60	,,	stannous hydrate 50 per cent. paste.
50	,,	glycerin.
740	,,	alkaline thickening T.R.
1000		

Allow to stand 1–2 hours before printing.

Indanthrene yellows, oranges, and green are also suitable.

After printing either of the above classes of colours, the goods are well dried and steamed 4–5 minutes in air-free but slightly moist steam at 100°–102° C. They are then rinsed in cold water for a few minutes, run through boiling silicate of soda, chromed for the lead yellows, and finally well washed and soaped to brighten the shades.

Other vat dyestuffs can be applied in an analogous manner.

The Discharging of the Insoluble Azo Colours.

The problem of producing discharge effects on cloth dyed with the insoluble Azo colours has long occupied the attention of chemists, and has only been solved satisfactorily in recent years by the introduction of the hydrosulphite-formaldehyde compounds.

The insoluble Azo colours are destroyed by powerful reducing agents, and the earlier methods of discharging them were based upon the well-known reducing properties of stannous oxide and of glucose-alkali. Stannous oxide alone has not much action on Azo colours produced on the fibre, but H. Schmid, in 1896, succeeded in discharging them to a pure white by adding certain organic solvents to the tin oxide paste. In this connection the use of acetin was patented by the Farbwerke Höchst, and tin oxide discharge colours were put on the market under the names of—

Discharge white P.N. Discharge yellow P.N.
,, blue P.N. ,, green P.N.

These, thickened with starch and British gum, were printed on cloth dyed with colours prepared from para- and meta-nitranilines, nitrotoluidine, amido-azo-benzene, nitrophenitidine, and β-naphthylamine.

The printed goods, well dried, were then steamed for 5–8 minutes in air-free steam at 100° C., and if they contained no colours, were then well washed, soured in hydrochloric acid 1½ Tw., washed again, and passed through a weak solution of bleaching powder, which increased the brilliancy of the white and improved the brightness of the red or orange ground colour.

For blue discharges and Aniline black, the goods, after steaming, were treated successively in the following solutions, through which they passed continuously at the full open width:—

(1) For ½ minute through hydrochloric acid 1° Tw. at 60° C.

(2) Cold water.

(3) Warm ½ per cent. solution of bichromate of potash in hydrochloric acid 1° Tw. at 60° C.

(4) Hydrochloric acid 1° Tw. at 60° C. for 1 minute.

(5) Well washed in water and dried.

For yellow and green discharges, in combination with black, white, and blue, the goods are simply treated in a solution of tartar emetic, followed by a thorough washing in cold running water to re-oxidise the reduced blue and green dyestuffs. The addition of a little peroxide of hydrogen accelerates the oxidation, but neither bleaching powder nor chrome are to be recommended, as they destroy the yellow.

The colours being the tin lakes of basic dyestuffs, are *not* remarkable for their fastness to soap.

The glucose-alkali discharge is carried out in the same way as for Turkey reds, except that the printed goods are treated in a slightly different manner after steaming. Instead of being run through a boiling solution of silicate of soda, they are passed through tepid sulphuric acid at 8° Tw., then washed, soaped, and washed again. If yellow and green are printed, the goods are finally chromed as usual in an acidified chrome bath, washed well and dried.

The ordinary alkaline discharge blue, yellow, and green as used for Turkey red may be employed for the insoluble Azo reds and oranges. The addition of 17–18 per cent. of glycerin is, however, essential to the securing of the most perfect discharges. The colours are very fast, and in this respect the glucose-alkali discharge is superior to the tin-oxide process.

Neither method is, however, applicable to colours prepared from α-naphthylamine, tolidine, benzidine, or dianisidine, none of which can be satisfactorily discharged by any practicable reducing agents except the sulphoxylate compounds (hydrosulphites).

The tin-oxide process of H. Schmid and the alkali-glucose process of Schlæpfer, Wenner & Co. are therefore limited to the discharging of red and orange ground colours only. Moreover, both processes together only include the application of a very small number of dyestuffs, so that, on the whole, it is not surprising that they have been superseded by the hydrosulphite process, which is not merely applicable to almost every insoluble Azo colour, but which is much simpler, safer, reliable, and successful in practice, and is adaptable to the production of coloured discharges in Basic, Sulphide, Mordant, Pigment, and Vat dyestuffs.

The Hydrosulphite Process.

The first hydrosulphite preparations which appeared on the market—hydrosulphite (B.A.S.F.) and hydrosulphite O. (M., L. & B.)—were of little practical value for any kind of calico printing on account of their instability; and an insoluble zinc preparation, hydrosulphite Z., was of scarcely greater use, because, although it was fairly stable, it was exceedingly difficult to print, by reason of the fact that even with a brush furnisher it persistently stuck in the engraving. The discovery of the stable and very soluble hydrosulphite-formaldehyde compounds by Baumann, Thesmar, and Frossard, chemists at Zündel's Works in Moscow, was an important event in the history of calico printing, and has rendered easy the production of discharge effects on insoluble Azo colours—effects altogether novel, and otherwise impossible of attainment.

Thickened solutions of these compounds printed on Para red and Para brown give, on steaming, remarkably pure white discharges. For coloured effects, any dyestuffs which resist the powerful reducing action of the hydrosulphites, and which, at the same time, are capable of being fixed by a process of steaming, are suitable. Of these, certain basic colours are the most important, but others, such as the Vat dyes, Gallocyanine, and Modern violet groups, and the Sulphide colours, are coming more and more into use for fast dark styles.

α-Naphthylamine clarets and Benzidine and Tolidine puces are only discharged by prolonged steaming at a high temperature, such as is obtained in the Simon-Weckerlin apparatus. But by adding certain catalytic agents to the discharge paste, it is possible to produce perfect discharges on these colours in the ordinary "hydrosulphite ager" at a temperature of 102° C. The firm of Meister, Lucius & Brüning observed that the presence of certain compounds derived from the action of formaldehyde on xylidine and other amines had the effect of rendering Naphthylamine clarets capable of being discharged by the usual methods of steaming.

In 1905 they put on the market a product of this kind under the name of Rodogen. The Rodogen could be added either to the printing colour, or the cloth could be prepared in a weak solution of it and then printed with the same discharges as were used for Para red. Both methods gave equally good results, the latter being generally preferred, as it allowed of one set of colours being used for different ground colours. The only objection to it is, that the shade of claret is dulled slightly.

About the same time Wilhelm found that certain colouring matters—Setopaline, Alizarin orange, Rhodamine—increased the dischargeability of Naphthylamine clarets, and a little later (Feb. 1906) the Badische Co. patented a process for the same purpose—a process so simple, elegant, and perfect that it almost immediately displaced all other methods then in use. The Badische Co.'s patent claimed the use of Induline scarlet, of which one-third of a gramme per kilo. of a 20 per cent. hydrosulphite discharge paste is quite sufficient to produce a fine white on claret and chocolate grounds.

Another method, used with great success in practice, was discovered by Sunder, and described by him in the *Bulletin de la Société Industrielle de Mulhouse.* Sunder's method consists in adding a small quantity of anthraquinone to the discharge colours, and while it yields results equal to those obtained by the Badische Co.'s process, it has a slight advantage over the latter, inasmuch as in large patterns the white is entirely free from the faint pinkish tinge imparted by the Induline scarlet. On the other hand, Induline scarlet can be applied in two ways like Rodogen, whereas anthraquinone being insoluble can only be mixed with the printing colour in the form of a finely ground paste. The quantity of anthraquinone required to produce a pure white is from 7–10 grammes per kilo. of printing colour.

The two processes of the Badische Co. and Sunder have superseded those of Baumann and Thesmar (iron salts and nitrite), Meister, Lucius & Brüning (Rodogen), and Wilhelm (Setopaline, etc.) in most printworks, and may be regarded as the most important up to date.

The pinkish appearance of large patterns discharged by the Induline scarlet method may be avoided by using Patent blue in place of the scarlet. In this case 20–30 times more dyestuff must be used, but the discharge takes place more rapidly.

Oxidising agents printed on Para red, Naphthylamine claret, etc., preserve them from being discharged, by counteracting the reducing action of the hydrosulphite discharge "covers" afterwards printed over them. On red and claret the resists consist of citric or tartaric acids, with chlorate of soda under white "covers," and of the same substances with antimony salts under basic colours. On Para brown an alkaline solution of copper gives the best results under white discharges. Recipes for these and other "resists" will be given later.

The most important hydrosulphite-formaldehyde preparations in common use are—

(1) Hydrosulphite N.F. concentrated (Höchst).
(2) Rongalite C. (Badische).
(3) Hyraldite C. extra (Cassella).
(4) Hydrosulphite N.F. conc. special (Höchst).
(5) Rongalite C. special (Badische).
(6) Hyraldite A. special (Cassella).

The first three products consist essentially of the formaldehyde compound of sodium sulphoxylate ($NaHSO_2.CH_2O + 2H_2O$), of which they contain 85–88 per cent. So far as their respective reducing powers are concerned, there is practically nothing to choose between them; all are equally effective, and may replace each other, weight for weight, in any of the recipes given hereafter. The latter three preparations consist also of sulphoxylate-formaldehyde, but contain in addition the requisite quantity of catalytic agents which are necessary for the discharging of Naphthylamine clarets and Benzidine and Tolidine chocolates. The general name for all sodium-sulphoxylate-formaldehyde products is "Hydrosulphite," though, strictly speaking, this term is incorrect, since the true hydrosulphites consist of salts of an acid having the formula $H_2S_2O_4$, whereas the "hydrosulphites" mentioned above correspond to sulphoxylic acid H_2SO_2.

Basic colour discharges contain, in addition to the dyestuff, hydrosulphite and tannin, certain organic substances—*e.g.* aniline, phenol, acetin, alcohol, glycerin, etc.,—which not merely prevent the too rapid precipitation of the colour lake, but which also influence favourably the brightness, keeping qualities and regular working of the colours. Mordant colours of the Gallocyanine and Modern violet group are made up as for the "steam style," but with the addition of a sufficient quantity of "hydrosulphite" to discharge the dyed Azo colour grounds; and the same may be said, in the main, of the Vat dyestuffs, Sulphide colours, and Pigment colours. Any important variation from type will be found by an inspection of the formulæ given below.

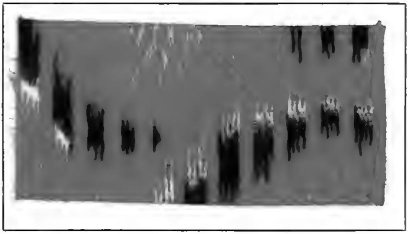
(*a*) Discharges on Para Red, Para Brown, and Nitro-toluidine and m-Nitraniline Oranges.

Discharge White P.

250	grms.	Hyraldite C. extra.
50	,,	glycerin (optional).
250	,,	British gum paste.

Dissolve at 50–60° C. and add to—

450	grms.	starch-tragacanth paste.
1000		



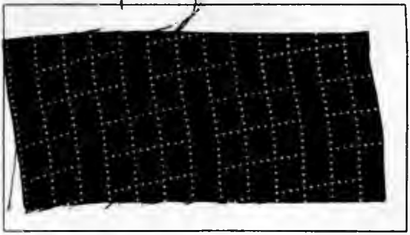
Para Red discharged with Hyraldite C.

Discharge White II. P.

225 grms. hydrosulphite N.F. conc.
200 ,, British gum paste.

Dissolve at 50° C., cool, and add—

10 grms. formaldehyde 40 per cent.
10 ,, hydrochloric acid 33° Tw.
50 ,, water.
505 ,, starch - tragacanth paste.
1000



Para Brown (Brown salt R.) discharged with hydrosulphite N.F. conc.

Discharge White II. P. is especially suitable for Para browns, but White I. is almost equally effective, though the goods require a more complete washing. For flannelettes and other rough cloths it is advantageous to add zinc oxide to both the above discharges. Zinc oxide acts mechanically, preventing the undue absorption of the discharge by the material, and simultaneously improving the white by forming a white covering over the fibres. With a sufficiently strong discharge, however, and a heavily engraved pattern, the use of zinc oxide is unnecessary, and its absence improves the working qualities of the colours.

(1) Basic Colour Discharges.—The fastest colours are obtained with a starch-tragacanth thickening: gum Senegal gives more level shades in large patterns, and can be used for such, but it gives colours which lose a good deal of depth in washing, and should therefore be avoided as much as possible. In a slightly less degree, the same remarks apply to British gums.

Among the basic colours which withstand the reducing influence of hydrosulphites, the following are, perhaps, the most generally employed:—Auramine, Thioflavine T., Rhodamine 6 G. extra, Thionine blue O. or G.O., Methylene yellow H., Flavophosphine R. conc., and fast Marine blue S. extra.

	Yellow P.	Pink P.	Blue P.	Orange P.	Green P.	Dk. Blue P.
Auramine conc.	...	...	...	...	15	...
Thioflavine T.	20	...	...	16	...	...
Rhodamine 6 G. extra	...	10	...	4	...	...
Thionine blue O.	...	...	25	...	5	...
Fast marine blue S. extra	...	...	...	...	...	30
Glycerin	40	40	35	40	40	30
Alcohol	40	40	40	40	40	40
Water	100	100	100	100	100	100
Starch-tragacanth paste	200	210	200	200	200	200
Tannic acid solution 50 per cent.	100	100	100	100	100	100
Discharge paste C.D.	500	500	500	500	500	500
	1000	1000	1000	1000	1000	1000

Discharge Paste C.D.

20 grms. starch.
90 ,, water.
400 ,, 4 per cent. gum tragacanth.
90 ,, aniline oil. Boil, cool to 60° C., and add—
400 grms. hydrosulphite N.F. conc.

Dissolve at 60° C. and maintain at this temperature until the aniline is thoroughly incorporated. Properly made, the paste ought to be homogeneous and of a light yellow colour, and almost as transparent as gum tragacanth thickening.

If desired, the aniline may be replaced by 100 grms. phenol; and acetin may be used instead of alcohol.

Rhodamine pinks require to be exposed to the air for a considerable time before they re-oxidise to their full shade; and as this is a tedious operation, they are often replaced by the bright but more fugitive Phthaleïn colours, fixed with chromium acetate.

Discharge Pink.

40	grms.	Erythrosine A. (or Eosin or Phloxin).
50	,,	glycerin.
60	,,	starch.
350	,,	water. Boil, cool, and add—
100	,,	chromium acetate 32° Tw.
200	,,	Hyraldite C. extra.
200	,,	4 per cent. tragacanth thickening.
1000		

The Phthaleïn pinks are by no means so permanent as Rhodamine (or Irisamine), but they are very bright, pure colours, and require no special treatment for their development after steaming.

(2) Mordant Colour Discharges.—The application of the mordant colours to the production of discharge effects on Para red, etc., is confined almost exclusively to the printing of dark blues, obtained from Modern violet and Modern blue (Durand and Huguenin), Chrome violet blue (Geigy), and the lighter blue, Chromoglaucine (Höchst). Other dyestuffs of the Gallocyanine group may also be employed.

The Phthaleïn colours already given are also, in a sense, mordant colours when fixed with chromium oxide, though, as a rule, they are not included in this category.

Navy Blue C.V.B.

30	grms.	Chrome violet blue.
80	,,	acetic acid 9° Tw.
20	,,	acetin.
265	,,	water.
75	,,	starch.
200	,,	5 per cent. tragacanth thickening.
30	,,	olive oil.

Boil, cool, and add—

100	grms.	chromium acetate 30° Tw.
50	,,	tannin solution 50 per cent.
300	,,	discharge paste R. 60 per cent.
1050 = 1000 when boiled.		

Navy Blue C.G.

50	grms.	Chromoglaucine V.M. 40 per cent. paste.
200	,,	water.
150	,,	starch paste, 20 per cent.
200	,,	6 per cent. tragacanth thickening.
100	,,	chromium acetate 30° Tw.
300	,,	discharge paste R. 60 per cent.
1000		

Discharge Paste R. 60 per cent.

600 grms.	Rongalite C. (Badische).
400 „	6 per cent. tragacanth thickening.
1000	

Blue 1900 and Modern violet 40 per cent. paste may be applied like Navy blue C.V.B. and Navy blue C.G. respectively. The addition of tannin is beneficial in both cases, inasmuch as it increases the fastness of the colour, and gives it a bluer tone than can be obtained from the chrome lake alone.

The mordant-blue discharges find their chief use in the production of the well-known and popular "Blue and Red" style, which was formerly produced either by the alkaline Indigo discharge on Turkey- and Para-reds, or by tannin resists under the latter.

Albumen Discharge Colours.

The albumen discharge colours are of secondary importance, and are only used occasionally. The pigments used consist for the most part of the tannin lakes of the basic colours: the most important pigment colour—lead or chrome yellow—is unreliable, since it is apt to be destroyed by the "hydrosulphite" in steaming; and although it sometimes withstands the reducing action, it is not to be depended upon. The other ordinary pigment colours are either more or less affected in the same way or they offer no advantages over the tannin lakes.

The tannin lakes are prepared by precipitating a mixed solution of dyestuff and tartar emetic with a solution of tannin. The precipitate is washed well with water and then filtered to a consistency corresponding to 50 grammes of the original dyestuff per kilogramme of paste.

The printing colours are prepared as follows:—

	Yellow.	Green.	Blue.
Thionine blue G.O. lake	...	100	400
Thioflavine S. lake	400	300	...
Starch-tragacanth thickening	150	150	150
Blood or egg albumen 50 per cent. solution	150	150	150
Discharge paste R. 60 per cent.	300	300	300
	1000	1000	1000

Treatment of the Goods after Printing.—After printing, the pieces are well but not too hardly dried, and then steamed for 2–3 minutes in the "hydrosulphite ager" at 102–103° C. They are then allowed to lie exposed to the action of the air for a short time in order to re-oxidise the leuco compounds of the colouring matters, and finally fixed, washed, and soaped. Tannin colours are run through 1–2 per cent. solution of tartar emetic, and, when associated with mordant blues, are further passed through a chrome bath, which promotes the re-oxidation of all leuco compounds but that of Rhodamine. The fixing in tartar emetic, the "chroming," and the subsequent washing, soaping, and drying are all done in the open width, and, as a rule, in a continuous manner. In this way all chance of the colours "marking off" is avoided.

Vat and Sulphide Colours on Para Red, etc.

The composition of Vat- and Sulphide-colour discharges on insoluble Azo colour grounds differs only from that of the ordinary printing colours in that the quantity of hydrosulphite is increased sufficiently to discharge the dyed grounds. With the exception of Indigo, very few of the vat dyestuffs are employed for this purpose, but the Sulphide colours are used fairly extensively for some styles, and it is not unlikely that both groups will, in the future, find a wider application for all classes of fast discharge work.

The following recipes are typical of the way in which these colours are made up for discharging Para red, Para brown, and other grounds destroyed by "hydrosulphite."

Indigo Blue Discharge.

150 grms. hydrosulphite N.F. conc.
125 ,, water.
Dissolve at 50° C. and add to —
575 grms. alkaline thickening (for Indigo).
Cool and add—
150 ,, Indigo L. 20 per cent. paste (Badische).

1000

Brom-Indigo may be applied in the same manner; it gives a redder shade than either Indigo L., Indigo pure, or Indigo M.L.B. Lighter shades may be obtained by reducing the proportion of Indigo.

Indanthrene Colour Discharges.

	Blue.	Yellow.	Green.
Indanthrene blue G.C.D. paste	100	...	40
,, yellow G. paste	...	100	60
Glycerin	75	75	75
Zinc oxide 50 per cent. paste	100	100	100
Water	50	50	50
British gum thickening	360	360	360
Rongalite C.	190	190	190
Caustic soda 91° Tw.	50	50	50
Potassium carbonate	75	75	75
	1000	1000	1000

Indanthrene Yellow discharge on Para Red.

Ciba-Colour Discharges.

	Blue.	Violet.
Ciba blue 2 B.D. paste	250	...
Ciba violet B. or R. paste	...	250
Gum Senegal 40 per cent.	120	120
British gum-paste thickening	190	190
China clay 50 per cent. paste	90	90
Glycerin	50	50
Soda ash	100	100
Hydrosulphite N.F. conc.	200	200
	1000	1000

The "hydrosulphite" is added last at 50° C., and then the whole is well stirred until complete solution ensues. The Ciba colours may be toned as desired by mixing them with any dyestuff which can be fixed as a leuco compound (Indigo and the Sulphide and Indanthrene colours, for example), and by this means it is possible to obtain a variety of extremely fast discharge effects.

Sulphide-Colour Discharges.—Most of the Sulphide colours now on the market are more or less capable of yielding satisfactory discharge effects on the insoluble Azo dyes. The Pyrogene, Kyrogene, Thiogene, and Immedial colours, etc., are all suitable for the purpose, but perhaps the most extensively employed are the two specially prepared brands of Meister, Lucius & Brüning, and L. Cassella & Co., namely, the D. brands of the Thiogene colours (M., L. & B.) and the "Immedial" colours "soluble" (Cassella). Both these groups are quite soluble in caustic soda without the addition of sodium sulphide, and their introduction has considerably simplified, and rendered more certain the results of, all processes connected with the application of the "Sulphide colours."

The following directions may be observed in the preparation of colour-discharges on Para red, etc.

Sulphide Blue Discharge.

40 grms.	Thiogene blue B.D. conc.
50 ,,	glycerin.
50 ,,	caustic soda 100° Tw.
100 ,,	China clay 50 per cent. paste.
270 ,,	British gum-starch thickening.
150 ,,	hydrosulphite N.F. conc.

Heat to 50° C., cool, and add gradually—

340 grms.	caustic soda 77° Tw.
1000	

British Gum-Starch Thickening

100 grms.	maize starch.
200 ,,	British gum.
700 ,,	water.
1000	

Boil and cool.

Other Thiogene colours are prepared for discharge work in a similar manner

IMMEDIAL COLOUR DISCHARGE.
40 grms. Immedial colour.
20 ,, caustic soda 77° Tw.
50 ,, glycerin.
100 ,, water.
140 ,, British gum-starch paste (page 441).
Heat to 50° C., cool, and add—
150 grms. alkaline thickening (see Indigo printing).
500 ,, Hyraldite thickening 50 per cent.
1000

HYRALDITE THICKENING 50 per cent.
500 grms. Hyraldite C. extra.
500 ,, British gum paste.

The above will serve as a type of all Immedial colour discharges, equal in strength and suitable for the style.

After printing Indanthrene, Ciba, and Sulphide colours, and also Indigo on Para red, etc., the goods are dried well, steamed 2–3 minutes at 102° C., allowed to air, and then washed well in the open width. A run through a dilute solution of bichromate of potash is beneficial in re-oxidising the reduced dyestuffs, and a treatment in dilute hydrochloric acid improves the brightness of Indigo, Indanthrene, and Ciba colours. The goods are finally washed again, soaped, and dried.

(*b*) Discharges on H. Schmid's Bistre.

We owe to Henri Schmid an elegant process for obtaining white and coloured discharges (including a fine red) on a bistre or chocolate ground, resulting from the superposition of Aniline black on Para red. The red-dyed cloth is first padded in a weak Aniline black, then gently dried to prevent the oxidation of the aniline, and finally printed in the discharge colours. The red is obtained by printing a substance—acetate of soda—which prevents the development of the black during the steaming operation, but which has no effect upon the Para red itself. The other colours and the white must, of course, resist the black, and simultaneously discharge the red beneath it. For this purpose the basic colour discharges given on page 437 are used with the addition of 120–150 grammes acetate of soda per kilogramme of printing colour. The red and white discharges are prepared as follows:—

WHITE DISCHARGE S.B.
250 grms. Hyraldite C. extra.
600 ,, 6 per cent. tragacanth thickening.
Dissolve at 50–60° C., cool, and add—
150 grms. acetate of soda.
1000

RED RESIST S.B.	I.	II.
Sodium acetate (crystals)	150	100
Sulphite of potassium 90° Tw.	...	125
Gum Senegal 30 per cent. (or tragacanth)	850	775
	1000	1000

No. II. gives the brightest red.

The bistre or chocolate ground to be discharged is obtained by padding Para-red dyed cloth in the weak Aniline black given below :—

Black for Bistre.

I. { 75 grms. aniline salt.
1000 ,, water.
II. { 35 ,, chlorate of soda.
750 ,, water.
III. { 40 ,, yellow prussiate of potash.
1000 ,, water.

Mix solutions I., II., and III. when cold, and make the whole to 3½ litres with water. Pad the red cloth in this solution, dry it gently in hot air, and then print on the discharge colours. After steaming, the goods are passed in succession through tartar emetic, water, "chrome," water, soap and water, and then dried.

Another method of obtaining similar results is based upon the fact that ferrocyanide of zinc fixes basic colours. In this instance the colours are mixed with zinc oxide and hydrosulphite, and the Aniline black contains an excess of yellow prussiate. The zinc oxide plays the double rôle of a resist for the black and a fixative for the colours.

Zinc Oxide-Hydrosulphite Resist Discharges on Henri Schmid's Bistre.

	Blue Z.	Yellow Z.	Green Z.
Thionine blue G.O.	30	...	7·5
Thioflavine T.	...	30	22·5
Glycerin	60	60	60
British gum paste	210	210	210
Dissolve, cool, and add—			
Hydrosulphite paste F.	700	700	700
	1000	1000	1000

Hydrosulphite Paste F.

{ 80 grms. zinc oxide.
90 ,, British gum powder.

Beat well into a creamy paste with—

280 grms. water.

Boil, cool to 50–60° C., and add—

250 grms. hydrosulphite N.F. conc.

700

For heavy patterns the amount of hydrosulphite may be reduced to 175 grms. For these colours the quantity of yellow prussiate in the black may be increased to 40 grms. per litre with advantage.

Print the above Blue Z., Yellow Z., and Green Z., together with White S.B. and Red resist S.B., on the bistre ground; steam 2–3 minutes at 102° C. in air-free steam, and pass through a weak chrome bath at 50° C.; wash well and dry.

This process yields very bright discharge effects on a fine chocolate ground. The red is exceedingly rich and brilliant, and is far superior to the red obtained by any other means. The zinc oxide colours are more brilliant than the tannin colours with aniline or phenol, but they are not so fast to soaping, although sufficiently so for most styles.

(c) Discharge Effects on α-Naphthylamine Claret and Benzidine and Tolidine Chocolates.

The production of white and coloured discharges on dyeings of the above three colours, and especially on the most important of them—α-Naphthylamine claret—has occupied the attention of colour chemists ever since the successful discharging of Para red was accomplished.

The "Stannous Oxide" and "Glucose Alkali" processes are absolutely useless for the purpose; and, as previously noted, even the strongest hydrosulphite mixtures give only an imperfect or half discharge on α-Naphthylamine claret, except at the high temperature (130° C.) of the Simon-Weckerlin rapid ageing apparatus. Where the ordinary "hydrosulphite ager" (temp. 102°–104° C.) is employed, white and indeed good coloured discharges can only be obtained by the addition of Induline scarlet, Anthraquinone, Patent blue, Setopaline, etc., to the hydrosulphite discharge paste. In the absence of these and similar substances (which are supposed to act catalytically), it is impossible to obtain satisfactory results under ordinary conditions; and even with Setopaline, Patent blue, and Induline scarlet, the whites are apt to be somewhat impure, owing to the reoxidation of these colours. To some extent this defect can be overcome by a thoroughly drastic steaming, followed by the immediate soaping of the goods; and for white discharges alone, a run through acidulated bleaching powder solution cleans up the whites perfectly. Coloured discharges, however, will not stand the "chloring" operation, and therefore the goods should be well soaped as soon as possible after steaming. Anthraquinone, being almost colourless, is not liable to sully the "whites"; and although a much larger quantity of it is required than of Induline scarlet to obtain the same results, its employment does away with a strong soaping, and consequently allows of some economy being effected in the cost of dyestuffs; for the colours of patterns that have to be heavily soaped must be made darker than is otherwise necessary, in order to allow for loss of depth in process. On the other hand, the actual soiling of the "whites" with Induline scarlet at the strength used is so slight as to be unnoticeable in all but the largest designs; and as it is extremely reliable in work, and can be applied either in the naphthol prepare, the diazo solution, the printing colour, or to the dyed material directly by padding, it is, on the whole, the most useful addition to employ, as it is certainly the most convenient. The impregnation of the fabric during dyeing or after dyeing has the advantage over the addition to the printing colour, in that the same range of colours can then be used indiscriminately for Para red, Para brown, Naphthylamine claret, Tolidine puce, etc. The simplest method is to add the requisite quantity of Induline scarlet (0·25–0·5 grm. per litre) to either the naphthol prepare or to the diazo solution, and dye in the usual way. The dyed goods are then soaped to render the discharging somewhat easier, and, if desired, they may also be brightened by a previous souring to remove the excess of diazo solution, which, if allowed to remain, turns brown and dulls the shade, besides increasing its resistance to the discharge paste. Neither soaping nor souring affect the Induline scarlet prepared pieces.

The duration of the steaming operation is an important factor in the discharging of Naphthylamine claret, and indeed of all insoluble Azo dyes. If the speed of the printed goods is so regulated that they occupy from five to six minutes in passing through the "ager" at 102° C., or if they are steamed twice, it is possible to obtain good whites on claret with reduced quantities of both Induline scarlet and hydrosulphite; in fact, an excellent white has been obtained in this way by printing a paste containing only 120 grammes of hydrosulphite per kilogramme on cloth dyed in a diazo solution containing as little as 0·25 gramme of Induline scarlet per litre. As a rule, however, it is inconvenient to prolong the steaming, and consequently about double the above quantities of scarlet and hydrosulphite are used for the finer patterns usually employed in discharge work on deep clarets. For ordinary shades of claret dyed like Paranitraniline red, on a 2½ per cent. naphthol prepare, but containing Induline scarlet, a satisfactory white is given with rather more than half the quantity of hydrosulphite required to obtain comparable results on Para red.

In general, however, all risk of an imperfect discharge is avoided by using discharge pastes containing from 20–25 per cent. of their weight of hydrosulphite-formaldehyde compounds. The further addition of ammonium oxalate has a beneficial influence on the effectiveness of the discharge; it dissociates in steaming, and the liberated oxalic acid supplements the action of the steam in decomposing the hydrosulphite.

(1) Discharges on α-Naphthylamine Claret dyed with the addition of 0·5 grm. Induline Scarlet per litre of the Diazo Solution or of the Naphthol Prepare.

On cloth prepared and dyed by this method, discharge effects are easily obtained by printing the same colours as are used for Para red and Para brown. The same applies to other difficultly dischargeable Azo colours prepared in the same way. No modification of the printing colours is required, and therefore pieces dyed in red, brown, chocolate, orange, and puce can all be wound on one roll, and printed in succession without intermission, and without the loss of time occasioned by the emptying out and washing up of half a dozen colour boxes and rollers, and perhaps a dozen doctors. A white discharge which has given excellent results on claret in practice is made up as follows:—

WHITE N.F.O.

{ 250 grms. hydrosulphite N.F. conc.
{ 700 „ British gum-starch paste.

Dissolve at 60° C., cool, and add—

50 grms. oxalate of ammonia 5° Tw.

1000

Print white and colours (and if a black is required, a prussiate Aniline black or a Logwood-iron black); dry and steam 2–3 minutes in air-free steam at 102° C.; pass through a 1–2 per cent. solution of tartar emetic; wash well, and pass through a cold ½ solution of bichromate of soda; wash, soap, wash, and dry.

Rodogen may be used instead of Induline scarlet, but is by no means so efficient.

(2) Discharges on α-Naphthylamine Claret, etc., with the addition of the Catalytes to the Printing Colours.

In operating by this method the cloth is dyed exactly as described under insoluble Azo colour styles, and the substances that are necessary to effect the discharge are all contained in the various printing pastes. In general, only three catalytic agents are used, namely, Induline scarlet, Anthraquinone, and Patent blue, and of these, Induline scarlet is the most popular, and perhaps the best, though Anthraquinone is strongly recommended in some quarters, and in the hands of Sunder, who first described its use in this connection, yielded both white and coloured discharges equal to any produced by other means.

(*a*) DISCHARGES WITH INDULINE SCARLET.

WHITE DISCHARGE I.N.

250 grms. hydrosulphite N.F. conc.
50 ,, glycerin.
350 ,, 5 per cent. tragacanth water thickening.

Dissolve at 60° C. and add—

320 grms. starch paste.
30 ,, 1 per cent. solution of Induline scarlet.

1000

Heat gently until the scarlet is reduced.

Hydrosulphite N.F. conc. special, or the corresponding Hyraldite A. special (Cassella) or Rongalite C. special (Badische), may all be used instead of the ordinary formaldehyde compounds of hydrosulphites. They contain the necessary catalytes.

Thus—

WHITE DISCHARGE H.A.

250 grms. Hyraldite A. special.
750 ,, starch tragacanth paste.

Dissolve at 60° C. and cool.

1000

The coloured discharges may be prepared as under:—

	NAVY I.N.	YELLOW I.N.	BLUE I.N.	GREEN I.N.
Auramine conc.	...	20	...	22·5
Thionine blue G.O.	...	...	20	7·5
Fast marine blue S. extra	30	...	...	...
Water	40	40	120	100
Glycerin	40	40	50	50
Acetin	20	20	20	20
Starch-tragacanth paste	350	360	300	320
Alcohol	30	30	...	...
Tannin 50 per cent. solution in water	100	100	90	100
Turkey-red oil 25 per cent.	40	40	50	50
Discharge paste I.N. 50 per cent or Discharge paste S. 50 per cent.	350	350	350	350
	1000	1000	1000	1000

DISCHARGE PASTE I.N. 50 per cent.

500 grms. hydrosulphite N.F. conc.
450 ,, starch-tragacanth paste.
50 ,, 2 per cent. solution of Induline scarlet.

Dissolve at 60° C. and warm until the scarlet is reduced.

DISCHARGE PASTE S. 50 per cent.

500 grms. Hyraldite A. special.
500 ,, starch-tragacanth paste or British gum-starch paste.

1000

The addition of aniline or phenol to the above colours in the proportion of

40–50 grams. per kilo. is beneficial, inasmuch as it prevents the premature precipitation of the colour lake. In such cases the alcohol and a portion of the glycerin may be omitted with advantage.

If anything, phenol is preferable to aniline in all hydrosulphite discharges on the Azo colours developed on the fibre. The aniline colours will keep good for months, especially if formaldehyde be also added, but they yield slightly duller shades than those prepared with phenol.

Another method, patented by the Bayer Co., consists in adding a solution of tannin in glycerin to the discharge pastes containing 2–3 per cent. of phenol. The method resembles the preceding, but is said to yield superior results, the colours being very clear and brilliant. One example will suffice to illustrate the practical application of this process:—

Discharge Blue T.G.
20 grms. Thionine blue G.O.
30 „ glycerin.
10 „ acetin.
140 „ water.
Dissolve, and add hot to—
200 grms. starch tragacanth paste.
Heat until the blue is dissolved completely, then cool, and add, when lukewarm,
30 grms. phenol.
90 „ water.
And when cold,
80 grms. tannin-glycerin.
400 „ 50 per cent. discharge paste I.N.
1000

Other colours are made similarly by replacing the blue with suitable dyestuffs, thus:—

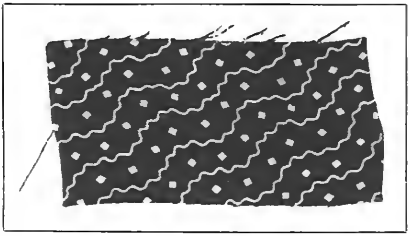
For Yellow:— 20 grms. of either Auramine conc. or Thioflavine T.
For Green:— 3 parts yellow.
1 part blue.
For Pink:— 50 grms. Erythrosine A.
100 „ acetate of chrome 30° Tw. per 1000 grms.
In the pink omit both the tannin-glycerin and the phenol.

Tannin-Glycerin.
100 parts tannic acid.
60 „ glycerin.
Heat together until a perfectly smooth syrup is obtained.

Print, steam, fix, and wash all the foregoing colours in exactly the same manner as for Para reds.

(*b*) Discharges with Anthraquinone in the Printing Colours.

The only essential difference between the formulæ of these colours and those containing Induline scarlet is in the replacement of the scarlet by a larger quantity of Anthraquinone. In all other particulars, the recipes given above will be a sufficient guide to the preparation of Anthraquinone discharges. The simplest method of effecting the necessary modifications is to prepare a standard discharge paste, containing the requisite proportion of Anthraquinone in the form of a finely ground paste.



α-Naphthylamine Claret discharged with Rongalite and Anthraquinone.

Discharge White N.F.A.
250 grms. hydrosulphite N.F. conc.
350 ,, 5 per cent. tragacanth thickening.
Dissolve at 60° C. and add
350 grms. starch paste.
Cool and add
7·5 grms. Anthraquinone ground up in—
42·5 ,, water.
1000

A little glycerin and ammonium oxalate may be added with advantage.

For coloured discharges the proportions given below have yielded good results in practice; all the colours were made on the type of the blue.

Discharge Blue A.N. on Claret.
20 grms. Thionine blue G.O.
30 ,, glycerin.
10 ,, acetin.
100 ,, water.
Dissolve, and add to—
200 grms. thick starch-tragacanth paste.
Heat again, cool a little, and add—
30 grms. phenol in—
80 ,, water.
Cool, and add—
80 ,, tannin-glycerin (see above).
200 ,, hydrosulphite N.F. conc. dissolved in—
200 ,, starch-tragacanth paste.
6 ,, Anthraquinone, ground up in—
44 ,, water.
1000

Yellows:—Auramine or Thioflavine.
Greens:— ,, ,, and blue.
Print, steam, and treat generally as for other discharges on clarets, etc.

A white discharge on Naphthylamine claret with Patent blue may be made according to the following directions:—

White Discharge P.B.
20 grms. Patent blue.
80 ,, glycerin.
50 ,, water.
285 ,, starch-tragacanth paste.
Boil, cool, and add—
40 grms. phenol.
25 ,, formaldehyde 40 per cent.
250 ,, hydrosulphite N.F. conc., dissolved in—
250 ,, British gum paste.
1000

This discharge is only suitable for white patterns, since, in order to obtain pure whites, it must be soaped strongly immediately after steaming, to prevent the leuco compound of the blue from re-oxidising on the fibre.

Any of the Mordant, Sulphide, and Vat colours that are suitable for discharging Para red are equally suitable for discharging Naphthylamine claret when combined with Induline scarlet or Anthraquinone.

When *any* hydrosulphite discharge white is to be covered with Aniline black, an addition of both zinc oxide and acetate of soda is essential to the production of a clear-cut white pattern. The best results, too, are obtained when the two colours are printed and steamed separately; if printed and steamed together, the chlorate of the black is apt to counteract the reducing influence of the hydrosulphite, and thus prevent the perfect discharge of Azo colour ground. Suitable "whites" for this cover style are the following:—

White Discharges to resist Black Covers.

	I.	II.
	grms.	grms.
Zinc oxide	100	100
British gum (light)	100	100
Water	400	370
Boil, cool to 60° C., and add—		
Hydrosulphite N.F. conc. . .	250	250
1 per cent. sol. Induline scarlet .	...	30
Acetate of soda.	150	150
	1000	1000

I. is used for Para red and Nitrotoluidine oranges.
II. „ Naphthylamine clarets.

Print the white on the dyed cloth; steam for 2–3 minutes at 102° C., and then print a prussiate Aniline black cover; steam again to develop the black, and then wash off and soap as usual.

Satisfactory white and coloured discharges can be obtained on Benzidine and Tolidine chocolates, and on Chloranisidine scarlets, by any of the methods employed for Naphthylamine clarets.

Resists under Hydrosulphite Discharges.

As already noted above, oxidising agents neutralise the discharging properties of the hydrosulphites, and on this fact is founded a useful resist style.

The dyed cloth is first printed with a thickened solution of an oxidising agent, and then "covered" with a hydrosulphite discharge paste. On steaming, the hydrosulphite only discharges the colour from those parts of the cloth upon which no oxidising agent has been printed. The presence of organic acids improves the "resist," and for resists under coloured discharges the addition of tartar emetic is essential. Chlorate of soda is the oxidising agent most commonly employed, but in certain cases persulphates, chromates, manganese dioxide, and copper salts may be used with advantage. An alkaline copper solution is especially suitable for reserving Para brown and Benzidine chocolate; it cannot be used for reds and clarets on account of its action on these colours, which it converts into dirty brown shades. Basic colour discharges are resisted with antimony salts; Modern blue, Blue 1900, and other colours of the Gallocyanine series, with antimony salts and chlorate when they contain tannin, and with chlorate alone when they are fixed with chromium oxide without tannin.

Chromoglaucine blue is resisted in the latter way also; and all the various resists contain a certain amount of citric or tartaric acid.

The following recipes are typical of the methods employed for counteracting the reducing action of hydrosulphite discharges on the insoluble Azo colours:—

White Resists.

	I.	II.	III.	IV.	V.
British gum paste	600	550	525	800	650
Citric acid	50	75	75	100	150
Chlorate of soda	150	150	200	100	200
Sodium tartar emetic	...	225	200	...	...
Oxalate of antimony	200	...	...	...	...
	1000	1000	1000	1000	1000

Nos. I., II., and III. are chiefly used under basic colour discharges, but they are equally efficient under two-colour cover prints in white and basic colours. No. IV. is for resisting a white discharge on Para red, Para brown, and other Azo dyes, while No. V. is employed under mordant colours fixed with chromium acetate alone. Such colours as Modern blue, Blue 1900, etc., which contain tannin as well as chromium acetate, may be satisfactorily resisted by Nos. I., II., or III.

Alkaline Copper Resist.

200 grms. dark British gum.
250 ,, water. Mix to a smooth paste and add slowly—
150 ,, caustic soda 100° Tw. Warm to 60°–70° C., then cool, and add—
400 ,, alkaline copper solution.
1000

Used under white discharges on Para brown and Benzidine and Tolidine chocolates.

Alkaline Solution of Copper.

400 c.c. copper chloride 105° Tw.
120 ,, water.
250 grms. tartaric acid.
200 c.c. glycerin. Dissolve, cool, and in the cold mix with—
480 c.c. caustic soda 105° Tw.
100 ,, water.
1550

Another "resist" used in practice with excellent results for the "Para brown cover white style" consists in the main of chlorate and chromate of soda, with the addition of aluminium acetate.

Reserve for Para Brown.

70 grms. chlorate of soda.
50 ,, bichromate of soda.
90 ,, water.
75 ,, British gum
150 ,, acetate of alumina 20° Tw.
20 ,, acetic acid.
50 ,, caustic soda 70° Tw.
15 ,, olive oil.
10 ,, turpentine.
500 Boil and cool.

The caustic soda ought to be added to the solution of bichromate in the gum paste before the aluminium acetate is introduced. Print on the brown-dyed cloth, dry, cover in any suitable hydrosulphite discharge white, steam, etc., as usual. By printing a discharge white along with the reserve, and then throwing a delicate cover pattern in white over the whole, very pretty effects of dark brown and white patterns, standing out clearly on a mixed brown and white ground, are obtained.

Discharge Effects on Dyed Basic Colour Grounds.

White and coloured discharges are obtained on bright basic colour grounds by means of Chlorate discharges similar to, and in some instances identical with, those used for discharging Indigo (which see). The bleached calico is padded in a 2–3 per cent. solution of tannic acid in water, then dried well and passed through a 1 per cent. solution of tartar emetic to fix the tannin as an insoluble tannate of antimony. Thus mordanted, the cloth may be dyed in any basic colour that is dischargeable to a white with chlorate pastes. The most easily dischargeable colours, and those most commonly used, are Auramine, Brilliant green, Malachite green, Victoria blue, Methyl violets, and, in light shades, Rhodamine, Methylene blue, Thionine blue, Safranine and Methylene green. The list might be extended, but these colours furnish a sufficient variety for most purposes, and are capable of yielding a great number of compound shades when mixed in different proportions. The dyeing may be carried out in either a jigger or a spiral dye-beck, whichever is most convenient. Dark shades are dyed with 1–1½ per cent. of dyestuff on the weight of the cloth; light shades with ¼–½ per cent. dyestuff on a correspondingly weaker mordant. After dyeing, the goods are washed well, and are then ready for printing. A light soaping helps considerably in obtaining a good white discharge.

Any of the chlorate white discharges employed for Indigo are equally suitable for basic colours. Usually they will be found to be too strong, and must be reduced by addition of starch paste or British gum solution. For coloured discharges, pigment colours, lakes, and certain basic and direct colours which withstand the oxidising action of the discharge pastes are employed, with albumen as fixing agent.

The strength of the chlorate discharge determines the length of the steaming operation. With strong discharges, containing from 10–15 per cent. of chlorate, a short steaming in the rapid ager is sufficient to effect the destruction of the ground colour; with weaker discharges a more prolonged steaming—*e.g.* 15 minutes to an hour—is necessary to produce a full discharge. Generally speaking, it is preferable to employ strong discharges in conjunction with a short steaming, the reason being that the printed colours are then less liable to "run," owing to the fact that they pass too quickly through the steaming chamber to absorb any appreciable quantity of moisture. At the same time it is to be noted that if the discharge pastes are stronger than is necessary for discharging the ground colour, they will cause the appearance of "running" whether they be steamed rapidly or slowly. Too strong a discharge, also, attacks the fibre; and in order to guard against this defect as much as possible, it is advisable to fix transverse bars of wood on the copper guide rollers in the ager, or at least wrap them with calico. Both these simple precautions prevent the cloth from coming in contact with the hot metal, and reduce its liability to become "tender."

After steaming, the goods are washed well in hot water, and finally soaped and dried. Single white discharges are improved by a run through a bath of dilute caustic soda at 40°–50° C.

The strength of the discharge paste must be regulated according to the depth and dischargeability of colour to be operated upon. A very suitable white discharge for general work, and one which is used extensively on the large scale, is made up as follows:—

White Discharge for Basic Colours.

15 grms. starch.
110 .. British gum.
75 ,, China clay.
75 ,, water.
550 ,, chlorate of alumina 42° Tw.
105 ,, chlorate of soda.

Boil, cool, and add—

25 grms. red prussiate of potash.

1000

For discharging a ground dyed with 1½ per cent. Victoria blue, or with 1 per cent. Malachite green, take—

1 part of the above White discharge.
2 ,, British gum paste.

On a one per cent. Methyl violet grounding take equal parts of Discharge white and British gum paste. For deeper shades, use at full strength.

Below is given another practical recipe for a white discharge:—

White C.S. 150.

120 grms. citric acid.
640 ,, British gum paste.

Dissolve, cool a little, and add—

150 grms. chlorate of soda.
70 .. caustic soda 70° Tw.

Cool, and add—

20 .. red prussiate of potash finely ground, and allow to dissolve in the cold.

1000

Coloured Discharges.

	Blue C.	Pink C.	Yellow C.	Green C.
Methylene blue	20	...	...	...
Rhodamine 6 G. extra 100 per cent.	...	10	...	...
Chrome yellow paste	...	...	300	..
Lemon chrome yellow paste	...	...	...	150
Guignet green paste	...	...	...	150
Glycerin	30	30	20	30
Acetic acid 9° Tw.	50	50	...	...
Water	140	140	...	...
Neutral citrate of soda 46° Tw.	100	100	50	50
Oil (olive or rape seed)	...	...	20	20
Gum tragacanth 8 per cent.	390	400	290	290
Chlorate of soda	100	100	100	100
Albumen solution 40 per cent.	150	150	200	190
Red prussiate of potash	20	20	20	20
	1000	1000	1000	1000

The pigment colours yellow and green must be well ground in a mill before printing.

Print; steam 2–5 minutes in the rapid ager at 90° C.; wash well, and soap to clear the whites and to remove the thickening.

If the amount of chlorate in the above colours is reduced, they may be printed in combination with any ordinary steam colours on light dyed grounds. For example, in an eight-colour floral pattern on a moderately light grey or fawn ground, the pink, white, yellow, light green, and blue parts of the pattern might be discharged, while the dark olive, chocolate, and black were obtained by printing ordinary steam colours. The printed goods would in such a case be steamed for $\frac{3}{4}$–1 hour, and afterwards treated as usual for chlorate discharges.

Certain basic colours are also discharged by reducing agents—*e.g.* sulphite of potash, alkaline stannous oxide pastes, and by the glucose alkali process. Of these, the sulphite discharges alone are of practical interest, and even they are little used on account of the technical difficulties encountered in their application on the large scale. Fairly light shades of Brilliant green, Methylene blue, Azo phosphine, Magenta, Malachite green, and Methylene green are all discharged by sulphite of potash. On the other hand, Auramine, Methyl violet, Victoria blue, Safranine, Rhodamine, and Phosphine resist the action of sulphite, and may therefore be utilised for the production of coloured effects. The addition of caustic soda, however, to the sulphite of potash yields a mixture easily capable of discharging most basic dyestuffs, under the influence of steam.

SULPHITE WHITE.

500	grms.	sulphite of potash 90° Tw.
50	,,	caustic soda 77° Tw.
200	,,	water.
250	,,	British gum powder.
1000		

TYPE OF COLOUR DISCHARGES WITH "SULPHITE."

20	grms.	Auramine conc.
30	,,	glycerin.
250	,,	water.
200	,,	British gum.

Boil, cool, and add—

500	grms.	sulphite of potash.
1000		

Blue = 20 grms. Victoria blue.
Pink = 10 ,, Rhodamine 6 G. extra, or Roseazine.
Green = 3 parts yellow to 1 part blue.

Print on grounds of the dischargeable colours mentioned previously; steam 2–3 minutes; wash and soap.

The great disadvantage of the sulphite process is that the colours are extremely difficult to print without "scumming." To some extent the effect of the "scum" can be counteracted by preparing the pieces in a dilute solution of chlorate of soda ($\frac{1}{2}$ per cent.) previous to printing; but this treatment must not be carried too far, lest the finer parts of the discharge pattern be affected also.

The Discharging of Direct Cotton Colours.

With the exception of certain yellows, oranges, reds, browns, and blacks, almost all the direct-dyeing cotton colours are readily discharged by reducing agents. It would be impossible to give anything like a complete list of the dyestuffs suitable for this purpose—they are far too numerous—but amongst the many that yield good results the following occupy an important place:—Erika, Geranine, Cresotine yellow G., Aurophenine O., Diamine rose, Diamine sky blue F.F., Diamogene blues, Oxydiamine brown G., Diamine brown S., Diamine bronze G., Dianil reds, Dianil blacks B., R., and G., Dianil blues, Oxamine blue, Chicago blue, and Diamine violet. Many others could be mentioned, and are used extensively, but the above will be sufficient to illustrate the style. They comprise a wide range of colours, and vast numbers of compound shades can be produced from them at will.

Undoubtedly the best discharging agent for direct cotton colours is hydrosulphite formaldehyde: it gives a good white in cases where other reducing agents are useless. Nevertheless, the Tin discharges are still employed, and will probably retain their place for some time to come.

HYDROSULPHITE DISCHARGES.

For very dark shades of blue, green, and brown, and for direct blacks, the same discharge colours and whites as are used for Para red may be used for the direct cotton colours. For lighter shades, the amount of hydrosulphite must be reduced from 200 grms. to from 25–75 grms. per kilo. of colour. With this slight alteration in the percentage of hydrosulphite, the same formulæ exactly will serve for the preparation of all white and coloured discharge pastes used in the discharging of direct dyes.

On flannelettes, for which the style is eminently adapted, it is advisable to add zinc oxide to the discharge white. The zinc oxide keeps the paste on the surface of the material, and gives a better local discharge in consequence.

HYDROSULPHITE WHITE F.Z.

150 grms. hydrosulphite N.F. conc.
650 ,, flour-tragacanth paste.

Dissolve at 60° C., cool, and add—

100 grms. zinc oxide.
25 ,, glycerin.
75 ,, water.

1000

REDUCING PASTE (for above).

150 grms. zinc oxide.
150 ,, water.
700 ,, flour paste.

1000

With the above reduced in strength, very fine imitations of light Indigo styles are obtained. The blue ground is dyed with Diaminogene pure blue N. (Cassella), diazotised and developed with β-naphthol. It is faster than light shades of Indigo, and is not subject to the same irregularity in dyeing.

The dyeing is carried out as follows:—

LIGHT BLUE D.

(1) Slop-pad the bleached cloth in—

1000 parts water.
12 ,, Diaminogene pure blue N.
30 ,, sulphate of soda.
10 ,, caustic soda.

Squeeze through the mangle bowls and dry directly over steam cylinders. The goods may now be diazotised at once, or passed through the rapid ager. A short steaming improves the fastness. After cooling, they pass to the next operation.

(2) Diazotising and developing.—Run the goods at full width and in a continuous manner through—

a { 1000 litres water.
4 kilos. nitrite of soda 98 per cent.
8 „ sulphuric acid 168° Tw.

And after a run through water—

b { 1000 litres water.
13 kilos. β-naphthol.
13 „ caustic soda 66° Tw.

Wash well in the rope form and then soap lightly; squeeze and dry up through a ½ per cent. solution of sodium chlorate to counteract any "scumming" that may occur in printing. For a black and white effect on a blue ground, print on Aniline black or Black J. and Hydrosulphite white F.Z. 2 (that is, 2 parts gum paste to 1 part White F.Z.); steam 2–3 minutes; wash and soap, and then dry. Any other hydrosulphite-formaldehyde compound—Hyraldite C. extra, Rongalite C.—will give equally good discharges. If the combination contains basic colour discharges, the goods, after steaming, are passed through tartar emetic (10 grms. per litre) previous to washing, etc.

A fine Navy blue ground suitable for white discharges is obtained in a similar way from Diamine azo blue. The percentages are reckoned on the weight of the cloth:—

NAVY BLUE D.

(1) Dye with—

{ 2½ per cent. Diamine azo blue 6 B.
10 „ Glauber salt.

Wash well.

(2) Diazotise with—

{ ⅝ per cent. nitrite of soda 98 per cent.
1¼ „ sulphuric acid 168° Tw.

in a sufficiency of water. Wash well.

(3) Develop in—

1 per cent. β-naphthol
1 „ caustic soda 66° Tw. } in water.

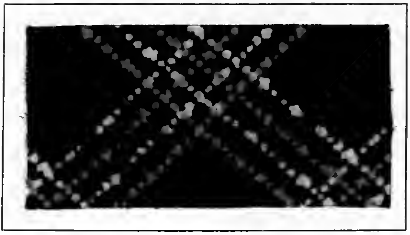
Wash, etc., exactly as for Light blue D. The printing and subsequent operations are identical with those described for the Light blue D. The discharges, however, are stronger, containing from 75–100 grms. hydrosulphite per kilo., according to the style of pattern printed and to the depth of the engraving.

The following light shades of pink, blue, violet, and green, and similar shades, may be easily discharged with 25 grms. (or less) of hydrosulphite per kilo. of colour:—

Pink	dyed with	1½	per cent.	Erika.
Blue	„ „	1	„	Chicago blue or Diamine sky blue F.F.
Violet	„ „	½	„	Chicago blue.
		½	„	Erika.
Green	„ „	1½	„	Aurophenine O.
		½	„	Chicago blue.

Several direct blacks are also suitable for the production of white discharge effects on black or grey grounds. Of these, Dianil black (M., L. & B.) and Diamine nitrazol black (Cassella) may serve as examples. The former is a simple direct colour, while the latter requires coupling with diazotised Paranitraniline.

Discharges which are required to resist an Aniline black "cover" are made as usual by the addition of sodium acetate to the ordinary printing pastes, with a further addition of zinc oxide to the white. (See Para red and Naphthylamine claret Discharges.)



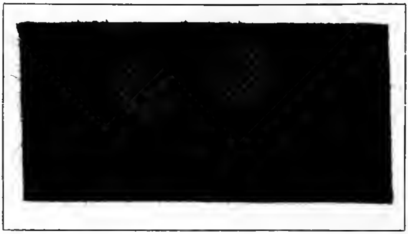
Dianil Black E.S. discharged with Hydrosulphite N.F.

Blacks, reds, and chocolates are now rarely dyed for discharging, as better results are secured by employing the insoluble Azo colours.

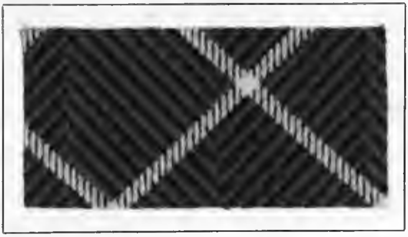
For coloured discharges on Direct colours, the same Basic and Sulphide colour discharges may be used as are employed for Para-red grounds, but with less "hydrosulphite." A good imitation of Para brown is obtained by dyeing the cloth as follows:—

3 per cent. of Diamine brown M.R. } on the weight of the cloth.
0·15 „ „ Oxydiamine black }

Wash well after dyeing, and couple with diazotised Paranitraniline; wash again, dry, and print on a hydrosulphite white and a yellow made up as already described under Para-red discharges; steam 2–3 minutes at 102° C., wash and dry. The following pattern illustrates this method.



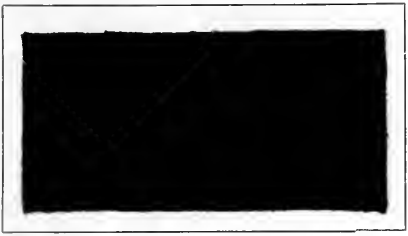
Ground { Diamine brown.
Ground { Oxydiamine black.
White Hyraldite C. extra.
Yellow Immedial orange.



Ground	Diamine catechine G. " " B.Z.
Dark Brown	Diamine catechine G.
White	Hyraldite C. extra.

Discharges on patterned backgrounds may be obtained by printing a Direct colour on the dyed cloth, and subsequently overprinting with the discharges. In this way a great variety of effects, similar to that shown in the pattern opposite, are obtainable.

The application of the Basic colour discharges to Direct colour grounds differs in no way from their application to Para-red grounds, unless it be that they usually contain less "hydrosulphite." The subjoined pattern is dyed with a mixture of Diamine blue C.V., and Diamine blue R., and is discharged with Basic colour and Hyraldite C. extra.



Diamine blues discharged with Basic colour and Hyraldite.

Coloured discharges on grounds of Direct blacks are not often printed, better results being obtained by the Aniline black resist style.

TIN DISCHARGES.

Prior to the introduction of the hydrosulphite-formaldehyde compounds, all really practicable processes for producing discharge effects on ground shades of direct dyes were based on the application of the reducing properties of stannous salts. The "hydrosulphites" are undoubtedly the reducing agents *par excellence* of the calico printer; but in order to take the fullest advantage of their powerful action, they require to be submitted to the influence of air-free steam at a temperature only possible of attainment in specially constructed "agers." On the other hand, the stannous compounds effect the decolourising of direct dyestuffs in ordinary rapid agers, and under the ordinary conditions which obtain in those simple machines—that is, in the presence of moisture and air, and at a comparatively low temperature. In some cases even the mere drying of the printed cloth is sufficient to bring about the decolourising reaction. Hence the tin discharges are valuable alternatives to those prepared from "hydrosulphites," if only because they can be applied, with good results, under circumstances and conditions unfavourable to the latter. Tin discharges do not give so pure a white as do the "hydrosulphites," and, moreover, they are liable to attack the fibre. With care, however, they yield excellent results; and for the flannelette trade, for which they are principally used, the quality of the white is usually sufficiently good to pass unquestioned.

The stannous compounds may be used either as acid salts or in the form of alkaline stannites, the latter chiefly for white discharges which are required to resist a cover print of Aniline black. The acid tin discharges consist for the most part of "tin crystals," tartaric or citric acids, and of acetate of soda or of stannous acetate, together with organic acids, and sometimes with tin crystals in addition. Coloured discharges of the same type are obtained generally by adding tannic acid and basic colours to an acid tin discharge paste.

(*a*) Acid Tin Discharges.

White Discharge A.T. I.

90	grms.	starch.
360	,,	water.
100	,,	acetic acid 6° Tw.
60	,,	6 per cent. tragacanth thickening. Boil, cool, and add—
250	,,	tin crystals.
120	,,	acetate of soda cryst.
1000		

White Discharge A.T. II.

85	grms.	starch.
450	,,	water.
100	,,	6 per cent. tragacanth. Boil, cool, and add—
25	,,	citric acid.
240	,,	tin crystals.
100	,,	ammonium sulphocyanide.
1000		

This gives a very good white.

Both these discharge whites are suitable for a 2–3 minutes' steaming in the rapid ager. The acetate of soda and sulphocyanide of ammonia are introduced to prevent the tendering of the fibre.

Discharges for prolonged steaming may be made from the preceding by reducing the tin crystals content to 5–7½ per cent.

Thus I. 4 parts starch paste.
1 part Discharge white A.T. I.
II. 3 parts starch paste.
1 part Discharge white A.T. II.

Discharge whites for long steaming are also composed of acetate of tin.

Discharge White A.T. III.

50	grms.	starch.
200	,,	dark British gum.
580	,,	acetate of tin 32° Tw.
120	,,	acetic acid 9° Tw.

Boil, and add whilst cooling—

50	grms.	tartaric acid (powdered).
1000		

Coloured discharges to work alongside the above are commonly obtained by adding basic colours and tannic acid to thickened mixtures of acetate of tin and organic acids, or of stannous chloride and acetate of soda. The goods are steamed for an hour to effect the discharge, and then washed in water and soaped lightly. A run through tartar emetic improves both the white and the fastness of the colours, but is not absolutely necessary. Blacks, chocolates, dark olives, etc., are printed in ordinary "steam colours."

The following recipes are typical of those used according to this method:—

BASIC COLOUR DISCHARGES ON DIRECT COLOUR GROUNDS.

Methylene blue, Nile blue, Marine blue, Auramine, Thioflavine T., Brilliant green, Rhodamine, Roseazine, Safranine, Phosphine, etc., are all suitable for coloured discharges.

GENERAL FORMULA.

20– 30 grms. colouring matter.
240–230 ,, acetic acid 6° Tw.
50 ,, tartaric acid. Dissolve, and pour into—
240 grms. starch paste.
Heat for a short time, cool, and add—
100–150 grms. 50 per cent. tannin solution (in acetic acid).
350–300 ,, discharge paste C.

1000–1000

DISCHARGE PASTE C.

400 grms. acetate of tin 32° Tw.
120 ,, British gum.
25 ,, starch.
160 ,, water. Boil, cool, and add whilst still lukewarm—
45 ,, acetate of soda.
200 ,, tin crystals.
Stir till dissolved, and then add—
50 grms. citric acid (ground fine).

1000

Print, steam for $\frac{3}{4}$–1 hour, fix in tartar emetic, wash well, and soap lightly.

In working on the large scale, and especially with heavy patterns, the results obtained in this way leave much to be desired. As pointed out by one of the authors some years ago (*Jour. Soc. Dyers and Colourists*, p. 17, 1899), the process has several disadvantages, of which the following may be cited:—

1. The discharge colour does not always work well in printing—it is apt to stick in the engraving, and consequently gives an unsound print.

2. The shades produced are not so bright as one would expect from basic colours.

3. The colours are not particularly fast to either hot water or soap.

The last, perhaps, is the most objectionable, for if passable colours are desired the pieces ought not to be "hot watered" or "soaped"; and if either of these operations be omitted, the whole of the thickening and tin remains on the cloth. If the goods are merely washed in cold water the colours are "toppy," and extremely liable to "mark off" or smear the ground shade whilst in the wet state.

These defects are due in a large measure to the formation in the printing colour of an insoluble compound colour lake, which has therefore no chance of being fixed on the fibre, and simply adheres to it mechanically like an unfixed pigment colour. With a view to overcoming them, an improved process was suggested, which, while based upon the same principle as the older method, differed from it in the manner of applying the tannic acid. Instead of printing a discharge colour containing tannic acid on the plain dyed cloth, the latter was previously mordanted with tannate of antimony in the usual way; then printed with a discharge consisting only of basic dyestuff, thickening, and any suitable salt of tin; and finally steamed, washed, and soaped.

The results obtained were superior in almost every respect to those yielded by the older process. The colours worked better, were brighter, and, as regards their fastness to soaping, were quite equal to the ordinary basic print-on colours. The only objection to this method is, that the ground colours are very slightly dulled by the presence of tannate of antimony. This difficulty was surmounted at a later date by a modification of the process which consisted in padding the dyed cloth with tannin alone, and in adding the antimony salt to the discharge colour.

In washing, after steaming, the whole of the tannin except that combined with the discharge colour is removed from the cloth, leaving the cloth practically in its original condition before printing.

In carrying out this improved process, the directions given below may be followed:—

(1) Pad the cloth in

20	grms.	tannic acid.
5	,,	chlorate of soda.
1000	,,	water.

Dry in the hot flue if possible; if not, over cylinders, the first half dozen of which are wrapped with calico.

(2) Print with any of the colours given below. Dry.

(3) Steam 2–3 minutes in the rapid ager.

(4) Wash well and soap.

It is advantageous to pass the printed goods through *ammonia vapour* before steaming; and though not absolutely essential for light patterns, this operation is very necessary in cases where heavy patterns putting a lot of colour on are printed. Its object is to prevent the tendering of the fibre during steaming, and to ensure a sharply defined discharge. The beneficial action of ammonia is probably due to the formation of stannous hydrate, which, being both insoluble and in an alkaline state, can neither "run" nor attack the fibre.

As a rule, the run through gaseous ammonia may be omitted when the goods are steamed in the rapid ager, but it is always better to include it in the process when an hour's steaming is essential.

Tin Discharge White F.

250	grms.	stannous chloride.
100	,,	sulphocyanide of ammonia.
75	,,	acetic acid 9° Tw.
10	,,	1 per cent. sol. of Methylene blue.
565	,,	starch paste.
1000		

Coloured Discharges.

20– 30	grms.	basic dyestuff.
150–140	,,	water.
80	,,	acetic acid 9° Tw. Dissolve and add to—
250	,,	antimony paste.
500	,,	discharge paste F.
1000		

Yellow =	Auramine conc.	(20 grms.)
Blue =	New methylene blue N.	(30 „)
Pink =	Rhodamine 6 G. extra.	(10 „)
Red =	Safranine A.N. extra	(15 „)
	Rhodamine 6 G. extra.	(10 „)
	Thioflavine T.	(5 „)
Green =	Auramine conc.	(15 „)
	Brilliant green	(10 „)
Violet =	4 Discharge pink.	
	1 „ blue.	
Orange =	Auramine conc.	(20 „)
	Acridine orange N.O.	(5 „)
	Rhodamine 6 G. extra	(2 „)

Antimony Paste.

120 grms.	starch.
200 „	acetic acid 9° Tw.
600 „	water.
80 „	sodium antimony fluoride.
1000	Boil and cool.

Discharge Paste F.

390 grms.	thick starch paste.
50 „	acetic acid.
400 „	stannous chloride.
160 „	sulphocyanide of ammonia.
1000	Stir till dissolved.

All the above colours are adapted for steaming in the rapid ager; if they are required to work in combination with "extract" and other "steam colours" the percentage of tin must be reduced. The amount of reduction will depend upon the strength of the engraving of the pattern to be printed, and also upon the intensity of the shade to be discharged. For ordinary work about 70 grammes per kilogramme of colour is ample, but heavier patterns require less and lighter patterns more. The reduction is most readily effected by replacing part of the Discharge paste F. with starch paste.

(*b*) Alkaline Tin Discharges on Direct Dyes.

These discharges find but little application except for producing coloured effects with pigments, and for certain "conversion" styles. These latter, worked out by Plusanski, are very pretty, but not very fast, and are rarely produced at the present time by this method.

For ordinary work, stannous hydrate mixed with British gum-starch paste, ammonium chloride, and a slightly alkaline tartrate of ammonia is the reducing agent employed both for white and coloured discharges.

White Discharge S.H.

350 grms.	stannous hydrate paste.
75 „	ammonium chloride.
90 „	British gum.
40 „	starch.
310 „	water. Boil, cool, and add
135 „	tartrate of ammonia 36° Tw.
1000	

Stannous Hydrate Paste.

700 grms. stannous chloride.
10 litres water. Dissolve, and add gradually—
500 grms. (about) soda ash.
10 litres water.

Wash the precipitate by decantation and filter to 2000 grammes.

Pigment Colour Discharges.

200 grms. Chrome yellow.
100 ,, 50 per cent. blood albumen.
690 ,, Discharge white S.H.
10 ,, turpentine.
1000

Print, steam, wash, and soap. The tartrate of ammonia dissociates in steaming, leaving the free acid to assist in bringing about a more complete discharge of the direct colour ground shade.

Plusanski's process for discharging direct colour grounds and resisting a black cover at the same time is merely an amplification of the above. The only difference between the two is that in the latter an excess of alkali, sufficient to prevent the development of the black, is employed. The process is principally used for light shades of direct colours; indeed, on dark shades it is impracticable, as the whole effect of a black cover would be lost if the ground were too deep. The best and most striking results are obtained on such shades as are dyed with about 1 per cent. of Erika pink, Diamine sky blue F.F., Chicago blue, Diamine green, Diamine yellow N., and Diamine brown B., etc. The following table shows the percentages of dyestuff used in dyeing some few of the many shades suitable for the style in question:—

	Pink.	Blue.	Green.	Fawn.	Violet.	Heliotrope.
Erika pink	1–2	...	...	...	½	½
Diamine sky blue F.F.	...	...	...	...	...	1
,, green G.	...	...	½	...	...	...
,, yellow N.	...	...	½	½	...	...
,, brown B.	...	...	...	1	...	...
Chicago blue	...	1–2	...	...	½	...
Glauber salt	10	10	10	10	10	10
Phosphate of soda	5	5	5	5	5	5

On the above dyed grounds, the colours given below yield satisfactory results.

White Discharge Resist P. I.

a
103 grms. water.
160 ,, tartaric acid.
Dissolve, and add—
80 grms. 6 per cent. tragacanth.
And then sprinkle in gradually—
80 grms. soda ash.
Stir until the reaction is finished, and then add—
200 grms. 6 per cent. tragacanth.
15 ,, glycerin.
200 ,, caustic soda 98° Tw.

b
102 ,, stannous chloride.
60 ,, 6 per cent. tragacanth thickening.

Add (*a*) to (*b*), carefully stirring vigorously all the time to prevent lumps from forming. It is well to grind the mixture before it is used for printing.

WHITE DISCHARGE RESIST P. II.

60 grms. tartaric acid.
320 „ water.
120 „ soda ash.
250 „ British gum (well torrefied).
125 „ water.
25 „ glycerin.

Boil, cool, and add—

100 grms. stannous chloride.

1000

This white is only suitable for producing a white pattern under an Aniline black "cover" on a dyed ground.

"Conversion effects," as they are termed, are obtained by printing a prussiate Aniline black containing a basic colour over White resist discharge P. I. Wherever the black falls on the discharge it will be destroyed, leaving the basic colour intact. For example, to obtain a four-colour effect of pink, black, green, and white, the following series of operations are gone through:—

(1) Print white discharge resist P. I. on *pink* dyed cloth in, say, a big spot pattern. Dry.

(2) Cover with a closely set oblique line pattern (a "slashed line") in Aniline black containing Brilliant green.

(3) Steam 3 minutes and then wash, etc.

The ultimate effect is that of a *Green and White striped spot* on a black and pink striped ground, the black line being "converted" into green wherever it crosses any spot. The basic colour is fixed by the tin ferrocyanide precipitated on the cloth, but it is only moderately fast to washing. The addition of a little tannic acid to the "colour black," or better still, the mordanting of the dyed cloth with antimony tannate, improves the fastness considerably, but is apt to impair the density of the black.

Colour blacks for conversion styles may be made up as under:—

	PINK.	GREEN.	BLUE.	VIOLET.
	grms.	grms.	grms.	grms.
Yellow prussiate of potash	60	60	60	60
Chlorate of soda	40	40	40	40
6 per cent. tragacanth	240	240	240	240
Water	250	250	250	250
Starch	50	50	50	50
Aniline salt	90	90	90	90
Aniline oil	10	10	10	10
Water	100	100	100	100
Rhodamine 6 G. extra	15	...	...	12
Auramine conc.	...	15	...	...
Thionine blue G.O.	...	5	20	4
Water	145	140	140	144
	1000	1000	1000	1000

Similar but much superior conversion effects are obtained by operating with mixtures of Hyraldite and zinc oxide, or Hyraldite, zinc sulphate, and acetate of soda, on dyed cloth previously padded in a 2 per cent. solution of zinc sulphate. Instead of the unfixed basic colour washing out of the black parts of the pattern and staining the light dyed ground, the whole of it is fixed as a zinc ferrocyanide lake. The white also is much purer, and many "direct colours" can be brought into use that are not readily discharged to a good white by any form of tin discharge pastes. A better method, perhaps, is to replace the preparation of the cloth in zinc sulphate by a run through a warm solution of the same after steaming. In this way all possibility of impoverishing the Aniline black is removed.

To secure the best results with tin discharges, the utmost care should be taken to observe the following precautions:—

(1) The discharge pastes ought not to be stronger than is necessary to "cut" the ground shade completely. If too strong, the colours "run," giving a clumsy impression; and the excess of tin salts not merely produces a white aureole round the colours, but attacks the fibre most energetically.

(2) The steaming ought to be as short as possible: and for this reason it is preferable to employ strong discharges and give a short run through the rapid ager, rather than to print weak discharges and steam for a longer period in the "continuous steamer." When this latter is unavoidable, the steam must not be too damp, otherwise the discharge colours, which are hygroscopic in character, will absorb a large amount of moisture, and "swell" in consequence.

(3) If the whites are yellowish, a little extra citric acid will improve them, or the goods may be soured in dilute hydrochloric acid after steaming. The longer the goods have been steamed, the yellower will the "whites" be; hence the advisabilty of a short steaming.

Properly carried out, the tin discharges are capable of giving a variety of fine effects; but they are limited to a much smaller range of ground shades than the hydrosulphite-formaldehyde discharges, and consequently they have been displaced to a great extent.

Discharging of Tannin Mordants.

This method of producing *white* patterns on deep, rich, basic colour grounds is much superior to that which depends upon the application of chlorate discharges to fully dyed cloth.

It is founded upon the observation that cloth mordanted with tannate of antimony can be stripped entirely of its tannin by boiling solutions of caustic alkalies. In practice, the mordanted cloth is first printed with strong caustic soda, then steamed in the rapid ager to effect the destruction of the tannin, and finally well washed, and dyed to shade with any suitable basic colour. The printed parts of the material having had their mordant dissolved out by the soda, show up as whites in the finished article, while the unprinted parts are dyed to a more or less deep shade, according to the strengths of the mordant and colouring matter employed.

PROCESS:—(1) Prepare the cloth in a 3 per cent. solution of tannic acid in a padding mangle; dry and—

(2) Fix in 1½–2 per cent. solution of tartar emetic, dry.

(3) Print the White Discharge given below:—

WHITE C.

500 grms.	caustic soda 77° Tw.
25 ,,	glycerin.
475 ,,	40 per cent. gum Senegal solution.
1000	

British gum may also be used for thickening.

(4) Dry after printing, and steam 2–4 minutes in the rapid ager.

(5) Wash well in water and dye as required. If the goods have become soiled in printing, they may be lightly soaped and washed again before dyeing.

The brightest colours and purest whites are obtained when the dye bath is slightly acidulated with sulphuric acid, or when it contains a little potash alum, tartar emetic, and glue size. These latter additions are specially efficacious in preserving the brilliancy of the white, enhancing the brightness, and increasing the fastness to both washing and rubbing of the colours. Furthermore, they promote the more complete exhaustion of the dye bath.

TYPE OF DYE BATH (100 kilos. cloth).

1–2	kilos.	dyestuff.
3	,,	tartar emetic.
2½	,,	potash alum.
1	,,	acetic acid 9° Tw.
4500–6000	litres	water.
7½	,,	10 per cent. solution of glue.

Dye 15 minutes in the cold; then raise within ¾ hour to the boil, and continue at this temperature for 15 minutes. Wash immediately and thoroughly; soap at 60° C. for a few minutes, and if the whites are not quite clean, give a rapid run through bleaching powder solution at ¼–½° Tw. Wash well again and dry.

Thickened solutions of strong caustic soda are exceedingly apt to "scum" in printing; and as their action on tannin mordants is very energetic, this drawback gave rise to a good deal of trouble when the "tannin discharge style" was first introduced. To overcome the detrimental effect of "scumming," and also of "doctor streaks," it is only necessary to pad the mordanted cloth in a 1–2 per cent. solution of ammonium chloride before printing. This counteracts the action of the caustic soda on tannin; and, at the strength given, it preserves the unprinted portions of the cloth from damage, while it is not sufficiently strong to affect appreciably the quality of the discharge on the printed parts. The protective action of ammonium chloride is of course due to the fact that it neutralises the caustic soda, which easily decomposes it, with the liberation of free ammonia and the formation of sodium chloride, neither of which substances have any injurious action on the mordant.

Including the several washings and dryings, and the preparation in ammonium chloride, the foregoing process involves at the least eleven distinct operations before the cloth is ready for dyeing. By mixing the ammonium chloride with the tannic acid padding solution, however, and by deferring the fixing in tartar emetic until after the printing and steaming have been done, *four* of these operations can be dispensed with, and a notable economy effected in time, labour, and steam. The results obtained in this way, by printing caustic soda on *free* tannic acid, are, if anything, better than those obtained on tannate of antimony; the discharge, even in fine patterns, is very complete, the "whites" appear to be less liable to staining in the dye bath, and are therefore more easily "cleared" in the final washing, and the whole process is cheaper and more expeditious.

The addition of aluminium salts to the tannin mordant acts favourably on the brightness of the ultimate colour. In presence of sufficient acetic acid, the precipitate of aluminium tannate is re-dissolved, but on drying the padded cloth, it is deposited again on the fibre in its insoluble state. As a rule, a solution of tannic acid containing 30 grms. per litre is strong enough for the general run of dark shades, but it can be increased as required; and if the cloth is padded in the wet state, 50 grms. per litre will not be too much to give results corresponding to 30 grms. on dry cloth. By wet cloth is understood cloth which comes straight from the bleach-house, where it has been well squeezed to free it from excess of water, but not dried in any way.

The following details are those employed in working on the large scale:—

(1) The cloth is padded in either of these solutions:—

TANNIN MORDANTS.

I.

3 kilos. tannic acid.
1 kilo. sal ammoniac (NH_4Cl)
100 litres water.

II.

600 grms. potash alum.
5000 ,, acetic acid 9° Tw.
20 litres water.

Dissolve, and add to—

3 kilos. tannic acid.
1 kilo. "sal ammoniac."
70 litres water.

Stir till any precipitate is redissolved, and make up to—

100 litres.

(2) Dry, and print "White C.X."

WHITE C.X.

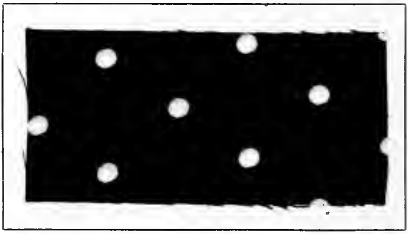
500	grms.	caustic soda 77° Tw.
100	,,	China clay paste 50 per cent.
400	,,	40 per cent. Senegal gum solution.
1000		

The China clay is added to prevent "swelling" during steaming.

(3) Steam 2–4 minutes in the rapid ager.
(4) Fix in a 1½–2 per cent. solution of tartar emetic and a little chalk. Wash well.
(5) Dye as usual, or with addition of acetic acid.

Dye bath :—½–2 per cent. dyestuff.
2½ ,, acetic acid.
2½ ,, potash alum.
2½ ,, tartar emetic (optional).

NAVY BLUE	=	2½	per cent.	New blue L., or 2 per cent. Fast cotton blue T.A.I.
DARK PURPLE	=	1	,,	Fast cotton blue T.A.I.
		1	,,	Methyl violet 6 R.
PEACOCK GREEN	=	2	,,	Methylene green extra yellow.
DARK OLIVE	=	2	,,	Methylene yellow H.
		1	,,	Fast cotton blue T.A.I.
CRIMSON	=	1½	,,	Methyl violet 6 R.
MYRTLE	=	¾	,,	Auramine conc. } on 4 per cent. tannin.
		1½	,,	Fast cotton blue T.A.I.



Tannin mordant discharged with caustic soda and dyed up with Fast cotton blue T.A.I.

Brighter and lighter shades are dyed with varying quantities of Rhodamine, Thionine blue G.O., Marine blue, Brilliant green, Auramine, etc. Fast cotton blue T.A.I. and Auramine must be dyed at a temperature not exceeding 80° C.; at higher temperatures they decompose.

HALF DISCHARGES ON TANNIN.—"Two-tone" and white effects are obtained on cloth prepared in tannic acid by printing, along with "White C." or "White C.X." (caustic soda), a thickened solution of either sodium carbonate, sodium silicate, sulphite of potash, or of a mixture of stannous chloride and potassium sulphocyanide. Of these, sulphite of potash is the best. It gives very regular work, and clean bright half discharges on 3–5 per cent. tannin mordants. After printing, the goods are steamed, fixed in tartar emetic, washed and dyed, as already described. The caustic soda destroys the tannin completely, while the sulphite, alkaline carbonate, etc., only discharge it partially, so that on dyeing a two-colour and white effect is obtained.

Print on cloth padded in a 4 per cent. solution of tannic acid a two-colour pattern in White C.X. and Half discharge K.S., steam 2–4 minutes, fix in tartar emetic (2 per cent. solution), wash well, and dye up in any desired basic colour.

HALF DISCHARGE K.S.

600	grms.	potassium sulphite 90° Tw.
200	„	British gum (dry).
100	„	water.
100	„	China clay paste 65 per cent.
1000		

A good half discharge is also given by soda ash (150 grms. per kilo. of colour), but it is apt to be irregular in working, and the same may be said of the other substances used for the same purpose. Potassium sulphite itself does not always give satisfactory results, but it is much more reliable than the rest of the half discharging agents, and is therefore generally preferred for this style of work.

When Aniline black is to be associated with white and half discharges, the cloth is best mordanted with tannate of antimony before printing; Aniline black does not develop well on free tannic acid, and is, moreover, not particularly successful on tannate of antimony, unless the cloth has been *soaped* and well washed before it is printed. Black and white designs on basic colour grounds are often, therefore, executed by the chlorate discharge process.

Apart from half discharge effects, coloured discharges are rarely produced on tannate of antimony mordants, except by means of the chlorate-albumen discharges on fully dyed cloth. Nevertheless, such discharges are possible; and Tigerstedt communicated a process for obtaining them to the Mulhouse Society some years ago. His process, however, was not a complete solution of the problem, and never came into use. Working on similar lines to Tigerstedt, but ignorant of his results, Caberti, Roggieri, and Barzaghi published in the *Revue générale des matières colorantes*, 1907, a process of their own, based upon the application of the Vat and Sulphide dyestuffs in strongly alkaline solution to the production of coloured discharges on tannate of antimony mordanted cloth. They found that, although these colouring matters were sufficiently well fixed in the ordinary way, they formed a tannin antimony lake; and that, in order to decompose this lake and get rid of the tannin, it was absolutely necessary to add extra quantities of reducing agents, a fact which escaped the observation of, or at least was not mentioned by, Tigerstedt.

The hydrosulphites give good discharge effects, and glucose also gives excellent results. Tin oxide, too, may be used, but in this case certain defects are developed by reason of the printing rollers becoming soiled.

The following are typical recipes of the colours recommended by Caberti, Roggieri, and Barzaghi:—

	BLUE.	YELLOW.
Indanthrene blue R.S. . .	200 grms.	...
Flavanthrene R.	...	100 grms.
Glucose 52° Tw.	150 ,,	120 ,,
Alkaline paste	650 ,,	680 ,,
British gum 50 per cent. paste .	... ..	100 ,,
	1000	1000

ALKALINE PASTE.

100 grms. British gum powder.
900 ,, caustic soda 77° Tw.

1000

With hydrosulphite the colours are mixed as follows:—

	VIOLET.	GREEN.	YELLOW.	BLUE.	RED.
Thio-Indigo red paste . .	80	...	...	...	100
Indanthrene blue R.S. . .	50	40	...	200	...
Flavanthrene R. . . .	...	60	100	...	...
Hydrosulphite N.F. conc. .	50	40	50	80	30
Water	120	110	50	100	80
British gum powder . . .	150	150	...	120	150
Caustic soda 77° Tw. . .	550	600	...	500	600
Alkaline thickening . . .	...	...	750	...	...
Glycerin	...	...	50	...	40
	1000	1000	1000	1000	1000

The colours, White C.X. and Half discharge K.S. are printed on cloth mordanted with tannate of antimony, dried, steamed for 2 minutes in the rapid ager, and then washed off in a bath containing 5 grms. tartar emetic and 5 grms. sal ammoniac per litre. The washing off is done at 60° C.; and when the cloth is free from alkali and the colours are in a forward state of re-oxidation, the goods are washed thoroughly in fresh water, and then well soaped and washed again. The leuco compounds of the discharge colours are now completely re-oxidised, and the cloth is ready for dyeing in the usual way with Basic colours, alum, and tartar emetic. Patterns containing Thio-Indigo red, either as such or in combination with Indanthrene blue, are improved by a run through a hot solution of ammonium sulphate (2 grms. per litre), followed by a wash, a slight sour, and a final wash before drying.

The same colours printed on cloth simply padded in tannic acid give equally satisfactory results. After printing, they are steamed 2 minutes, fixed in a 2 per cent. solution of tartar emetic containing 5 grms. ammonium chloride per litre, and then treated exactly as above.

RESISTS UNDER TANNIN DISCHARGES.—If the action of caustic soda is to be counteracted (or resisted), as for instance in the case of a discharge white "cover" thrown over a basic colour ground, a portion of which ground has to be "reserved" so as to form a pattern, the best resisting agent to use is nitrate of ammonia thickened with starch.

RESIST N.A.

I. 335 grms. nitrate of ammonia cryst.
665 ,, starch paste.
———
1000

or

II. 2050 grms. nitric acid 57° Tw.
1000 ,, ammonia 25 per cent. (Sp. g. 0·910).

Add the acid to the ammonia until the solution is neutral, and then pour the whole into

350 grms. starch.
100 ,, water.
———
3500

Boil and cool.

Print either of the above resists on tannate of antimony prepared cloth; dry, and cover in "White C.X." (caustic soda); dry, steam, wash, and dye up in basic colours. If printed on cloth prepared in tannic acid alone, the goods are passed through tartar emetic *after* steaming; they are then washed and dyed as usual.

Very pretty and useful effects, consisting of a two-colour pattern in solid white, and solid colour standing out clearly from a delicately figured ground, also in white and the same colour, are obtained by printing on tannin-mordanted cloth (1) a design in White C.X. and Resist N.A., and (2) a fine "cover" pattern in White C.X., the "cover," of course, being printed over the whole of the first design. Thus—

DARK BLUE AND WHITE SPOTS ON A DARK BLUE AND WHITE STRIPED GROUND.

On tannate of antimony mordant—

(1) Print a two-colour spot pattern in White C.X. and Resist N.A. Dry.
(2) ,, fine closely-set line stripe in White C.X. Dry.
(3) Steam for 2–4 minutes.
(4) Wash, soap lightly, wash and dye up in—

2 per cent. Marine blue B.I. (Höchst).
2½ ,, ,, alum.
2½ ,, ,, tartar emetic
and a little glue size.

Wash well, soap, etc. In this way, by varying the patterns, "covers," and dyestuffs, an immense variety of effects can be produced by very simple means.

Discharging of Aluminium, Iron, and Chromium Mordants.

The production of white discharges on aluminium and iron mordants has been dealt with in connection with the "Madder Style," and needs no further mention here. The discharging of chrome mordants is similar in most respects, and in many cases precisely the same ingredients may be used; indeed, the majority of the "acids" given for Madder mordants yield equally good results on Chrome mordants.

The cloth may be mordanted with either the alkaline chrome mordants of Koechlin or Knecht, the Gallois mordants (M., L. & B.), or with chromium bisulphite. With the Gallois mordants good whites are easily obtained by a short steaming, as the discharge is printed on before the chromium oxide is fixed on the fibre. With the other mordants, a more prolonged steaming is necessary to bring the hydroxide into solution.

Dark Gallois Mordant.

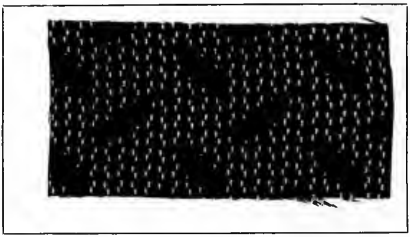
Chrome mordant Ga. II. 64° Tw.	200 grms.
Water	715 ,,
Glycerin	35 ,,
Gum tragacanth 6 per cent.	50 ,,
	1000

Pad the cloth in this solution; dry in the hot flue and print on the following Discharge white:—

Discharge White C.K.

85	grms.	citric acid.
75	,,	tartaric acid.
100	,,	China clay 50 per cent. paste.
740	,,	British gum paste.
1000		

Heat till dissolved and then cool.



Chrome mordant Ga. II., discharged and dyed with Cœruleïn olive.

After printing, steam the goods for 4–5 minutes, and then pass at once at full width through a 3 per cent. solution of soda ash at 50–60° C. Wash well and dye in any suitable mordant dyestuff. This method of working is well adapted to the production of white patterns on dark dyed grounds.

For "two-tone and white" effects a somewhat different procedure is adopted. The cloth is first padded twice (for levelling purposes) through the following weak mordant:—

Light Gallois Mordant (Mordant G.L.)

Chrome mordant Ga. II. 64° Tw.	100 grms.
6 per cent. tragacanth thickening	50 ,,
Water	850 ,,
	1000

The excess of liquor is expressed by the bowls of the padding mangle, and then, *without drying*, the cloth is passed at once through a second padding mangle, the box of which is charged with a 3–4 per cent. solution of soda ash at 75–90° C. Following this, the goods are well washed, and then dried for printing. On cloth fully mordanted in this manner a discharge white and a stronger mordant are printed, and after steaming (to effect the discharge and the fixation of the strong mordant), the goods are thoroughly washed and dyed up in Alizarin, Cœruleïn, Persian berries extract, or any other mordant dyestuff that forms a pleasing chromium lake.

WHITE DISCHARGE T.T.

15	grms.	citric acid.
12	,,	tartaric acid.
150	,,	China clay paste 50%.
823	,,	gum Senegal solution 50%.
1000		

DARK MORDANT FOR PRINTING.

100	grms.	Chrome acetate 32° Tw.
600	,,	thick starch tragacanth paste.
1000		

Print on cloth prepared as above in Mordant G.L.; steam for 1 hour in the continuous steamer; pass at full width through a 1 per cent. soda ash bath at 60° C. to ensure the complete fixation of the dark mordant; wash thoroughly in water, and then dye as under:—

FOR 50 KILOS. CLOTH.

CLARET:—

2500	litres	water.
1½	kilos.	Alizarin 20 per cent. (blue shade).
5	,,	10 per cent. glue solution.
1	,,	acetate of lime 32° Tw.
1	,,	acetic acid 9° Tw.

Dye ¼ hour in the cold, then raise the temperature gradually during ¾ hour to 90–100° C., and dye at this temperature until the shade is fully developed. Wash well, soap, and clear the whites in weak bleaching powder solution or in the "chloring machine."

TERRA-COTTA:—	As for Claret, but	1½ kilos. Alizarin orange 20 per cent., and no acetate of lime.
BROWN:—	As Terra-cotta, but	Anthracene brown.
BLUE:—	,, ,,	Alizarin blue S.
PURPLE:—	,, ,,	Gallein or Gallopurple.
OLIVE:—	,, ,,	Cœruleïn S.
OLD GOLD:—	,, ,,	Persian berry extract.
YELLOW:—	,, ,,	Alizarin yellow G.G.
BRIGHT VIOLET:—	,, ,,	Chromoglaucine V.M.
GREY:—	,, ,,	1 part Chromoglaucine V.M. 1½ ,, Alizarin yellow G.G.
BRIGHT BLUE:—	,, ,,	Gallophenine P.

The quantities of the above colours must be varied according to the shade required and to the amount of dark mordant on the cloth.

Phosphate of chromium is a much weaker mordant than the hydroxide, that is, it gives lighter colours than the latter with the same quantities of dyestuff. On this fact is founded a method of producing very fine half discharge effects on strong chrome mordants. A good mordant for the purpose is made up and applied as follows:—

CHROME MORDANT F.

I.	110	grms.	hydrosulphite N.F. conc.
	1000	,,	water.
II.	200	,,	bichromate of potash or soda.
	200	,,	acetate of soda.
	2000	,,	water.

Add I. to II. in the cold immediately before use, and make the whole to 4 litres with water. Pad the cloth in this solution, dry in the hot flue, steam 4 minutes and then pass through a boiling 2 per cent. solution of soda. Wash well, dry, and print Discharge white Z. and Half discharge P.S.

Discharge White Z.

300 grms. citric acid.
150 ,, China clay paste 50%.
550 ,, British gum paste.

1000

Half Discharge P.S.

150 grms. sodium phosphate (Na_2HPO_4)
850 ,, British gum paste.

1000

After printing, run twice through the rapid ager, wash well, and dye in any of the mordant dyestuffs already given. The phosphate of chromium dyes up a much lighter shade than the unprinted ground mordant, and thus yields half discharge effects which, when associated with Aniline or Diphenyl black and White discharge Z., give very pretty four-colour styles on a deep rich ground of subdued colour.

It is needless to add that the "chrome mordant discharge style" ranks with the fastest and highest class of printed goods.

Discharging of Slop-padded Chrome Shades.

In this method of obtaining discharges on coloured grounds, the dyestuff and its mordant (chrome) are applied together, and the formation and fixation of the colour lake is effected by steaming. The fixation of the lake may be prevented by printing on the padded cloth, before steaming, certain pastes which contain either organic acids or their alkaline salts, oxalate of antimony, sulphite of potash, or oxidising agents. These latter, which are practically restricted to the chlorate discharges, may, as a rule, be applied with equally good results, either before or after steaming.

The padding solutions contain, in addition to dyestuffs and mordant, certain solvents—*e.g.* soda, borax, glycerin, "oleine," etc.—which promote the even impregnation of the cloth and the production of level shades. In light shades most colours of the Alizarin group are sufficiently well discharged (in reality "resisted") by organic acids, antimony oxalate, tartrates, citrates, and sulphite of potash, with citrate of ammonia. On the other hand, dark shades (with the exception of Alizarin reds and pinks) can only be discharged to a satisfactory white by means of chlorate of soda; and colours containing the natural vegetable dyestuffs require the chlorate discharge whether they be dark or light.

In the following formulæ, all the colours are readily dischargeable with chlorate pastes in either white or colours, and most of them will also give fairly good results with citric acid, etc., if they are reduced to light shades by the addition of water.

	Terra-cotta.	Brown.	Blue.	Green.	Purple.
Alizarin orange 20 per cent.	100	...	...	...	...
Anthracene brown 40 per cent.	...	50	...	...	...
Alizarin blue S. (powder)	...	...	30	...	...
,, viridine F.F.	...	...	...	35	...
Chromoglaucine V.M.	...	...	...	...	60
Borax	20	20	...	...	...
Water	780	845	820	740	768
6 per cent. tragacanth thickening	50	50	75	50	50
Chromium acetate 32° Tw.	50	35	75	75	120
Acetic acid	...	...	...	100	..
Hydrosulphite N.F. conc.	...	...	...	...	2
	1000	1000	1000	1000	1000

A useful series of colours are obtained by mixing the four following standards in various proportions according to the principles described in the section on "The Mixing of Compound Shades" (p. 322):—

SERIES S.P.

	ELEMENTS.			
	1. RED.	2. YELLOW.	3. BLUE.	4. GREEN.
Chrome violet	50	...	...	...
Anthracene yellow powder	...	12	...	...
Alizarin blue S. powder	...	...	30	...
,, green paste	...	...	...	90
Water	750	858	845	810
Acetate of chrome 30° Tw.	150	80	75	50
6 per cent. tragacanth	50	50	50	50
	1000	1000	1000	1000

Grey,	1.3.9.9	Plum,	3.0.1.1	Dull t'cotta,	1.3.0.0
Iron grey,	1.8.1.3	Reddish purple,	8.0.1.0	Russet,	1 6.1.0
Holland,	0.20.1.0	Stone,	0.20.0.1	Lavender,	1.1.1.1 (dilute)
Drab,	0.8.1.0	Reseda,	0.8.0.1	Buff,	1.40.0.1 (dilute)

Bright olives of all descriptions are easily obtained from the above three elements, red, yellow, and blue, by the addition of a green made from Alizarin viridine, instead of Alizarin green, which is dull and blue in tone.

Pad the foregoing solutions on bleached cloth; dry and print on the discharge pastes; steam for from $\frac{3}{4}$ to $\frac{1}{2}$ hour; wash well and soap, etc., as for Alizarin colours in general.

Chlorate discharges, when printed in combination with steam colours, must not be so strong as to attack the fibre during the steaming process. A discharge containing 40–50 grammes of chlorate of soda per kilogramme of colour is about the usual strength for most classes of work, but it is increased or diminished according to circumstances.

If the padded cloth be steamed for an hour to fix the colour lake, and then, after washing and soaping (or without these operations), it be printed with chlorate discharges, these latter may be much stronger, because the cloth then only requires a short steaming (3–5 minutes in the rapid ager) to effect the discharge alone, the colour being already fixed by the previous steaming. If, however, "steam colours" form any part of the printed pattern, they will require a prolonged steaming for their proper fixation; and any chlorate discharges, therefore, that are worked in combination with them must be reduced in strength to 40–50 grms. per kilo., for the reason given above, and also because, in long steaming, smaller quantities of chlorate act quite as effectually as the larger quantities employed when the goods are merely passed through the ager.

Under any conditions of steaming, the employment of too strong a discharge is to be avoided on both technical and economical grounds; for, apart from waste of material, the excess of chlorate, etc., over that required to discharge the colour acts on the work injuriously in two ways, neither of which can be remedied. In the first place, it attacks and tenders the fibre; and secondly, it gives a rough, smudgy-looking, clumsy impression of the pattern, due either to the discharge "running" or to the too copious evolution of chlorine compounds, which naturally attack those portions of the ground colour immediately surrounding the printed pattern.

Any of the chlorate discharges already given for Indigo and the basic colours are equally suitable for application to the slop-padded chrome shades. If necessary, they may be strengthened by the addition of more chlorate and corresponding quantities of citric acid and yellow prussiate, or they may be reduced by the addition of more thickening paste.

Some of the other discharges used for light shades are given below :—

WHITE A.

200	grms.	citric acid.
100	,,	50% China clay paste.
700	,,	gum Senegal solution.
1000		

WHITE B.

150	grms.	oxalate of antimony.
170	,,	British gum powder.
680	,,	water.
1000		

WHITE C.

100	grms.	oxalate of antimony.
65	,,	tartaric acid.
100	,,	China clay paste 50%.
735	,,	British gum paste.
1000		

WHITE C.

150	grms.	British gum powder.
600	,,	sulphite of potash 91° Tw.
50	,,	China clay (dry).
200	,,	citrate of ammonia.
1000		

Print on padded, but unsteamed, chrome shades; dry, steam 1 hour, wash well, soap, and clear in the "chloring machine" with bleaching powder solution $\frac{1}{4}$°–$\frac{1}{3}$° Tw.

Brown shades obtained from alkaline solutions of Dinitroso resorcin are discharged by means of sulphite of potash.

The cloth may be padded as under :—

DARK BROWN.

I.	100	grms.	Dinitroso resorcin 40 per cent. paste.
	50	,,	borax.
	350	,,	water.
II.	60	,,	ammonia 25 per cent.
	5	,,	Turkey-red oil 40 per cent.
	200	,,	water.

Mix I. and II., stir well, and add—

25	grms.	alkaline copper solution.
100	,,	water.
50	,,	6 per cent. tragacanth.
60	,,	water.
1000		

ALKALINE COPPER SOLUTION.

400	grms.	copper chloride, cryst.
600	,,	water.
500	,,	tartaric acid.
1060	,,	caustic soda 86° Tw.
400	,,	glycerin.

Light Brown.

25 grms. Dinitroso resorcin 40 per cent. paste.
40 ,, borax.
250 ,, water.
5 ,, Turkey-red oil 40 per cent.
100 ,, water.
30 ,, chromium acetate 30° Tw.
25 ,, alkaline copper solution.
50 ,, 6 per cent tragacanth.
475 ,, water.
1000

Pad the cloth in the above solutions, dry, and print on the following discharges:—

White D.R.

200 grms. British gum.
450 ,, sulphite of potash 90° Tw.

Heat to 50° C., stir until dissolved; then cool, and add—

150 grms. China clay paste 50 per cent.
100 ,, bisulphite of soda 64° Tw.
100 ,, citrate of soda 50° Tw.
1000

Coloured Discharges.

	Blue D.R.	Yellow D.R.	Red D.R.	Green D.R.
Dianil blue H. 6 G.	30	...	...	7½
Aurophenine O.	...	30	...	22½
Dianil fast scarlet 4 B.S.	...	...	30	...
Water	410	410	410	410
British gum powder	220	220	220	220
Sulphite of potash 90° Tw.	290	290	290	290
Bisulphite of soda 64° Tw.	50	50	50	50
	1000	1000	1000	1000

After printing, steam the goods for an hour in the "continuous steamer," and then wash well and soap.

Dinitroso resorcin is put on the market under various fancy names—Fast myrtle, Solid green O., Resorcin green—but all the products they designate are practically the same, and can be applied after the method described above.

Discharges on Dinitroso resorcin brown grounds have little to recommend them beyond their scientific interest. The ground shade itself is dull compared with Para brown, and the discharge colours are neither particularly fast nor bright. On the other hand, the discharging of the Alizarin chrome shades is an important style, which, although to some extent displaced by the hydrosulphite discharges on insoluble Azo colours and the Sulphide colour resists, is still produced in large quantities for the Home Trade Markets on account of its fastness and the beauty and variety of its colours.

Discharging of Sulphide or Sulphur Colours.

The ever increasing importance of this group of colouring matters has naturally led to many attempts being made to produce white and coloured discharge effects upon grounds dyed with them. Of these attempts the most successful and convenient is that based upon the employment of powerful oxidising agents, and in this connection the chlorate discharges may be regarded as the best. Very few of the Sulphide colours yield good whites, even with "chlorate," and only then when the discharge is very strong. For imitations of such goods as men's suitings, a dull white is perhaps more useful than a pure white, but for most styles the impossibility of obtaining a perfectly pure white discharge on Sulphide colours is a fatal defect in the process. The colours are easily destroyed by the chlorate pastes, but unfortunately they form brownish or greyish oxidation products, which, in the majority of cases, cannot be removed entirely from the fibre. This drawback, as already noted, is of little moment for certain classes of work, but in the main it has resulted in the chlorate discharge process being discarded in favour of the newer, simpler, and more generally applicable Zinc Chloride Resist process, which allows of the production of a much greater variety of styles, and is, moreover, free from the serious risk common to all acid oxidation discharges, namely, that of tendering the fibre.

For white discharges on medium and light shades, and for coloured discharges in general, the chlorate pastes given for Indigo may be used satisfactorily for the Sulphide colours. For dark shades and blacks, the following aluminium chlorate discharge gives good results, especially in fine patterns. Large patterns are not suitable, as the impurity of the white shows up to greater disadvantage in proportion as the contrast between ground and pattern is diminished.

White Discharge C.A.L.

150	grms.	British gum.
600	,,	chlorate of alumina 42° Tw.
50	,,	China clay (optional, but useful sometimes).

Beat the clay to a cream with the chlorate, and then heat the whole to 75°–80° C. and add—

150	grms.	chlorate of soda.

Dissolve, cool, and add—

50	grms.	red prussiate of potash (powdered).
1000		

For pigment colour discharges the above white may be utilised thus:—

Discharge Yellow C.A.L.

300	grms.	Chrome yellow paste.
150	,,	albumen solution 40–50 per cent.
525	,,	White discharge C.A.L.
25	,,	citrate of ammonia 50° Tw.
1000		

Guignet green, vermilion, the ochres, lakes, etc., may be used in a similar way for other colours and compound shades.

Print the white and colour discharges on cloth dyed with Sulphide colours; dry and steam for 5 minutes in the "hydrosulphite ager" at 100° C.; wash well and soap at 80°–90° C. for 5 minutes; then wash again and dry. To obtain the best results, the cloth ought to be well soaped before printing. If the pattern consists of white alone, or in combination with Aniline black or a Logwood iron black, the goods are passed, after steaming, through a bath of dilute caustic soda (10 grms. NaOH 77° Tw. per litre) at 60° C., followed by soaping, etc. This treatment improves the white considerably, but if applied to pigment colour discharges it is apt to "strip" them off the fibre.

The dyeing of the cloth may be effected by any of the usual methods in use for Sulphide colours. Particulars of the processes will be found described in *A Manual of Dyeing*, by Knecht, Rawson and Loewenthal.

Discharging of Mineral Colours.

(*a*) Iron Buff.

This colour simply consists of ferric oxide, and, while very fast to light and boiling alkalies, it is extremely sensitive to the action of acids, which dissolve it out completely. To obtain white discharges, therefore, it is only necessary to print the dyed material with an acid, give a short steaming to increase its effect, and finally wash the goods in a copious supply of running water. Citric acid is most commonly used for the purpose, and usually a little oxalic acid is added to help in reducing the ferric oxide to the ferrous state. The addition of oxalic acid, however, while beneficial, is not absolutely necessary, as good whites are regularly obtained with citric acid alone. The iron is not precipitated from citrates by alkalies, and consequently a run through dilute ammonia or soda, *after steaming*, is permissible in order to neutralise the excess of acid on the fibre, and thus prevent it from acting upon those parts of the buff ground that are contiguous to the printed pattern.

The cloth is dyed by first padding it in a solution of ferrous acetate 9° Tw. (which see), then drying it, and passing it through a solution of caustic soda 4° Tw. at 75° C. to precipitate the ferrous hydrate. The goods are now allowed to lie exposed to the air for a short time (or they may be passed *at once* through a dilute solution of bleaching powder) to convert the ferrous into ferric hydrate, and then they are thoroughly washed and dried in readiness for printing.

White Discharges.

I.	II.	III.		
100	250	350	grms.	citric acid.
10	10	15	,,	oxalic acid.
890	740	635	,,	British gum paste (or Senegal gum).
1000	1000	1000		

Print on Iron buff dyed cloth, dry, steam 3–5 minutes in the rapid ager, pass through dilute ammonia, and then thoroughly wash and dry.

According to the depth of the buff is the strength of the discharge; deep shades require a stronger discharge than light ones.

(*b*) Prussian Blue.

The dyeing of Prussian blue was formerly an important branch of the calico printing industry, but since the introduction of basic Aniline blues it has fallen into almost total disuse in modern printworks.

Dyed in the usual way, Prussian blue consists of ferric ferrocyanide ($Fe_4\{Fe(CN)_6\}_3$); and although it is produced on a basis of Iron buff, its behaviour towards acids and alkalies is exactly the reverse of that colour. Prussian blue is fast to acids, whereas alkalies, and even boiling soap solutions, decompose it at once, leaving brown ferric hydroxide on the fibre.

Hence by printing thickened solutions of caustic soda, or alkaline carbonates, on cloth dyed with Prussian blue, a buff pattern on a blue ground is obtained. To convert this buff pattern into a white pattern, it is only necessary to "wince" the goods in dilute mineral acid, which dissolves out the ferric hydroxide without affecting the blue ground.

The most reliable method of obtaining level shades of Prussian blue on piece goods is first to dye the cloth a deep shade of Iron buff, and then precipitate the blue upon it by a run through an acidulated solution of yellow prussiate of potash (ferrocyanide). Wash well and dry.

$$\underbrace{2Fe_2(OH)_6}_{\text{Iron buff.}} + \underbrace{3K_4.Fe(CN)_6}_{\text{Yell. prussiate.}} + 6H_2SO_4 = \underbrace{Fe_4\{Fe(CN)_6\}_3}_{\text{Prussian blue.}} + 6K_2SO_4 + 12H_2O.$$

The following process, based on these lines, is used on the large scale:—

(1) Pad the cloth in acetate of iron 18° Tw. Dry.

(2) Steam 2 minutes.

(3) Pass through caustic soda 4° Tw. at 75° C. Allow to lie $\frac{1}{2}$ hour, and then wash in water until the last trace of ferrous hydrate (olive tint) has been oxidised to ferric hydrate (bright buff). Then—

(4) Pass through the developing bath:—

20	grms.	yellow prussiate of potash.
15	,,	sulphuric acid 168° Tw.
1000	,,	water.

(5) Wash thoroughly and dry.

Dyed in this way, the cloth is then printed with buff discharge, and, if desired, a prussiate Aniline black.

Buff Discharges.

	I.	II.	III.
Caustic soda 77° Tw.	300	...	300
Soda ash	...	150	...
China clay paste 50 per cent.	200	200	...
Gum Senegal 50 per cent.	500	650	600
Water	...	...	100
	1000	1000	1000

Print, dry, and wash off at once in plenty of running water, and at the full open width to avoid "marking off."

If Aniline black is also printed, the goods are passed through the rapid ager before washing, and the cloth is best prepared with a little tartaric acid in order to counteract the action of the caustic soda on the black. In fact, the padding of the cloth in a 2 per cent. solution of tartaric acid is advisable in any case, since alkaline printing colours are exceedingly liable to "scum" badly.

To convert the buff obtained as above into a white, the goods, after washing, are treated in sulphuric acid 2°–4° Tw. at 20°–30° C. This may be done in the rope state, and it is continued until the discharge is sufficiently white.

The chief precaution to observe in the discharging of Prussian blue is to avoid allowing the wash water to become too alkaline from the caustic soda it extracts from the printed goods. This is best prevented by conducting the earlier stages of the washing in open-bottomed becks fitted with an arrangement of "spirt pipes," between which the cloth is made to pass by means of suitably adjusted guide rollers. The jets of water from the "spirt pipes" play on the cloth with considerable force and wash it thoroughly, the waste water escaping through the bottom of the beck and carrying the caustic soda with it. In this way all risk of the alkali accumulating in the beck, to the injury of the blue ground shade, is eliminated.

(*c*) Chrome Green.

Chrome green is simply hydrated oxide of chromium fixed on the cloth by any of many methods of mordanting cotton with chromium salts. As a self colour it is of no importance at the present time, although formerly it was largely employed for light shades of a quiet and very fast shade of green. Being in reality a chrome mordant, it is discharged by methods identical with those employed for, and described under, "Chrome Mordants."

(*d*) Manganese Bronze.

Manganese bronze or bistre consists of hydrated peroxide of manganese produced on the fibre ; it is very fast to acids, alkalies, and soap, but is easily destroyed by acid reducing agents, which convert it into soluble manganous salts.

On this property of reducing agents is based the method of producing white and coloured effects on a ground of manganese bronze. The discharging agent employed is stannous chloride in conjunction with tartaric acid.

The cloth is dyed as follows :—

(1) Pad the goods through manganese chloride ($MnCl_2$) at 72° Tw. Dry.

(2) Pass through cold caustic soda 25° Tw. Squeeze out the excess and pass again through caustic soda 10°–12° Tw.

(3) Wash well, and treat in bleaching powder solution 2° Tw. until the manganous hydrate is completely oxidised into the dark brown manganic hydrate, then wash well and dry.

This process gives a dark, rich brown, which contrasts well with the patterns discharged upon it. If desired, the process can be shortened by adding the bleaching liquor to the caustic soda bath.

Coloured discharges can be prepared from either mineral colours, vegetable colours, or the basic Aniline colours. The recipes given below will illustrate the general principle of preparing typical discharge pastes.

DISCHARGE WHITE M.N.

400 grms.	water.
150 ,,	light British gum.
130 ,,	tartaric acid. Boil, cool, and add—
320 ,,	stannous chloride 120° Tw. (60 per cent. $SnCl_2.2H_2O$).
1000	

STANNOUS CHLORIDE 120° Tw.

960 grms.	tin crystals.
640 ,,	water.
1600 = 1 litre.	

DISCHARGE BLUE M.N. (PRUSSIAN BLUE).

Standard :—

605 grms.	water.
37·5 ,,	yellow prussiate of potash.
100 ,,	starch.
60 ,,	British gum. Boil, and add in order—
120 ,,	tartaric acid.
60 ,,	oxalic acid.
68·5 ,,	nitrate of iron 90° Tw. [40 per cent. $Fe_2(SO_4)_3$].
1050·0, or 1000 when finished and cold.	

For printing lake :—

8 litres	Discharge blue standard M.N.
2 ,,	stannous chloride solution 120° Tw.
10	

DISCHARGE YELLOW M.N.

Standard :— 550 grms. water.
200 ,, lead nitrate.
150 ,, light British gum.
150 ,, tartaric acid.
1050

Boil and cool.

For printing :—7½ litres Yellow standard M.N.
2½ ,, stannous chloride sol. 120° Tw.
10

DISCHARGE GREEN M.N.

5 litres Yellow standard M.N.
2½ ,, Blue standard M.N.
2½ ,, stannous chloride sol. 120° Tw.
10

Print the above colours on Manganese bronze dyed cloth; dry gently at as low a temperature as possible to avoid tendering the fibre, and then hang the goods in a cool chamber for a few hours. During the hanging the stannous chloride reduces the bronze (hydrated peroxide of manganese) to the manganous oxide, which dissolves in the acid present, forming the soluble tartrate, which, in turn, is subsequently dissolved and washed out of the cloth, leaving a white or coloured pattern as the case may be. After the goods have hung sufficiently long to allow of the ground colour being completely discharged, they are taken down and washed thoroughly in a large volume of running water flowing freely through the washing machine; they are next treated in chalk and water (15–20 grms. chalk per litre) and then "chromed" in a 1 per cent. solution of bichromate of potash at 40° C.–50° C. to develop the blue, yellow, and green. Finally, wash well and dry.

Before the advent of the Coal tar colours, the above yellow, blue, and green, together with a Brazil wood pink, were practically the only colours available for discharges on Manganese bronze. The basic Coal tar colours, however, allow of a much greater variety of effects being obtained, and much brighter shades.

BASIC COLOUR DISCHARGES ON MANGANESE BRONZE.

STANDARDS.	BLUE.	RED.	PINK.	YELLOW.	GREEN.
New methylene blue N.	25	...	...	...	...
Rhodamine 6 G. extra	...	25	10	..	...
Auramine O.	...	5	...	...	...
Thioflavine T.	...	...	...	20	...
Brilliant green	...	...	...	..	13
Auramine G.	...	...	...	...	20
Acetic acid 9° Tw.	175	170	175	175	175
Tartaric acid	100	100	100	100	100
Water	190	50	105	155	142
6 per cent. tragacanth	100	100	140	100	100
Starch	100	100	120	100	100
Tannic acid sol. 50 per cent.	160	300	200	200	200
	850	850	850	850	850

For printing:— { 850 grms. above standards.
{ 150 ,, stannous chloride (crystals).

1000

Dissolve in the cold.

Print on Manganese bronze dyed cloth; dry and hang for a few hours; wash in running water; give a chalk bath to neutralise the last traces of acid, and then wash again and dry. The various washings are best carried out at the full open width of the cloth, to avoid "marking off."

In common with other mineral colour discharge styles, the "Manganese Bronze Style" has declined in importance. At the present time it is produced in very small and constantly decreasing quantities, its place having been taken by the newer discharge and resist processes on Para and Paramine browns.

(5) RESIST OR RESERVE STYLES.

The "resist" or "reserve" styles, like the "discharge" styles, relate to the production of white and coloured patterns on variously coloured grounds. The difference between the two classes of work is not so much one of appearance as of process, for in many cases the appearance of a "resist print" is identical with that of a "discharge" print. In discharge printing, the discharging agent is applied to the cloth *after* it has been mordanted or dyed, whereas the distinguishing feature of "resist" printing is, that the reserving agent or "resist" is printed on the cloth *before* it undergoes any process of mordanting or dyeing. A discharging agent acts by destroying compounds that are already fixed (either wholly or in part) on the fibre, while a "resist" acts by preventing the fixation of the colour or mordant.

Resisting agents may be divided into two great classes—mechanical and chemical resists. The former consist, for the most part, of fats, resins, and plastic substances like China clay, zinc oxide, and the sulphates of lead and barium, and are used chiefly for the production of the older, coarser, and perhaps more decorative classes of dyed work, in which breadth of effect and variety of tone in the "white" are of greater importance than the sharp, crisp definition of the pattern, and the brilliant and even, but often somewhat harsh, purity of the "whites" that are so much admired in modern work. The chemical resists include many classes of chemical compounds—*e.g.* acids, alkalies, oxidising and reducing agents, and neutral salts—and are applicable to many colours which are difficult, and even impossible, to "discharge" successfully when once they are fully developed on the fibre.

Nearly every class of colouring matter is capable of being "resisted" in one way or another; and as each class possesses different properties, the nature and composition of the various resists required differ according to circumstances. At the same time it is possible to compound double and triple resists which are effective under two or three totally different groups of colours; and in the "two-blue, white, yellow, and green" Indigo resist style, "reserve" or "resist" pastes are used which, when printed upon light Indigo-dyed cloth, play the double rôle of "discharges" for the light blue, and of "resists" to the fixation of a darker blue which is applied to the cloth in a second run through the dye vat after printing.

Resists under Dyed and Printed Indigo.

White and coloured resist effects are produced under dyed Indigo by printing the resist pastes on white cloth, and subsequently passing the goods through or "dipping" them into the Indigo vat until the desired depth of blue is attained.

The most perfect and even resists are obtained on cloth which has been previously prepared in a thin solution of starch and afterwards cold calendered. The addition of a little copper nitrate or sulphate, nitrate of ammonia, or manganese sulphate increases the attraction of the cloth for Indigo, and has a favourable effect upon the production of dark blue shades. The beneficial influence of calendering is due to the flattening of the threads and fibres of the material—an advantage which allows of the resist paste forming a more perfect protective cover than if the threads were left projecting.

The resist pastes most commonly employed consist essentially of soluble salts which possess oxidising properties, and are fixed on the fabric by means of thickenings sufficiently tough and elastic not to chip off or crack during the subsequent dyeing operations. In order to prevent "running," and at the same time take advantage of mechanical obstructions to the penetration of the dye liquor into the fibres of the printed parts of the material, it is usual to add to the reserve pastes such solid plastic substances as lead sulphate and China clay.

The soluble metallic salts which suggest themselves as most suitable for resist work are those whose acid character is sufficiently pronounced to prevent them from dissolving out of the resist paste during the dyeing process in the alkaline Indigo, or other vat. Of these, the nitrates, sulphates, chlorides, chromates, and acetates of copper, zinc, lead, and manganese have all been proved by experience to yield good "resists" under the Vat dyestuffs. Copper, lead, and zinc salts form together the basis of most resist pastes, manganese salts being used but rarely, and then only for special styles of work.

The protective action of resist pastes is partly due to their oxidising properties, which have the effect of throwing the Indigo, etc., out of solution before it can reach the fibre, and partly to the fact that during the dyeing in the alkaline vat an insoluble crust or deposit is formed on their surfaces, which effectually prevents the penetration of the alkaline solution of indigo white. To this must be added the mechanical preventive action of the thickening, plastic bodies and fats (if any) in the paste, and also that of the film of colour which is precipitated on the surface of the resist paste by the oxidation of the leuco compound of whatever Vat dyestuff is employed.

In printing *fine* patterns by machine the use of China clay and lead sulphate is avoided as much as possible, since they are apt to "stick in" and fill up the engraving, and so give an imperfect result; but for heavy patterns, and for block work, the addition of solid plastic bodies is a great advantage; and if a brush furnisher is used in printing on the machine, all danger of "sticking in" is done away with.

Single white resists may or may not contain lead salts, but if they are intended to work in combination with yellow, orange, or green resists, they must, of course, be free from lead salts, otherwise, during the "chroming" operation for the development of the yellow, orange, or green, the white itself would be converted into a yellow by the formation of lead chromate.

By the addition of diazo solutions to lead-zinc resist pastes, it is possible, by printing on cloth prepared in β-naphthol, to obtain very bright, fast, red, pink, and orange resists.

To ensure good results in roller printing the engraving must be deep and uniform throughout the whole pattern, and a brush furnisher is indispensable if the resist contains China clay or lead sulphate.

The resists may be printed on simple white cloth, calendered cloth, or cloth which has been previously starched and calendered. The last mentioned is the best, especially for artificial Indigo and the modern Vat dyes like the Ciba colours, etc.

The following are a few of the starch "prepares" that have been found suitable in practice:—

	I.	II.	III.	IV.	V.
Wheat starch	20	15	20	15	25
Glue solution 10 per cent. .	150	150	150	200	150
Water	830	810	827·5	783	775
Ammonium nitrate . .	...	...	2·5	...	...
Copper sulphate . . .	...	...	...	2	...
Turkey-red oil 40 per cent. .	...	25	...	...	50
	1000	1000	1000	1000	1000

Pad the goods through any of the above starch prepares, and then, after drying, pass them between the bowls of a three-bowl cold calender.

On the starched and calendered cloth, print any of the resist pastes given below:—

White Resist I. (Dark Blue ground).

150 grms. copper sulphate.
60 ,, lead acetate.
400 ,, water.

Heat until the precipitation of the lead is complete, and then add—

190 grms. water.
90 ,, flour.
60 ,, British gum. Boil, cool, and add—
50 grms. copper nitrate 80° Tw.
1000

Resist White II. (Dark grounds).

200 grms. China clay paste 50 per cent.
100 ,, 40 per cent. gum Senegal solution.
80 ,, sulphate of copper (powdered).
90 ,, acetate of copper (powdered).
65 ,, flour.
30 ,, British gum.
335 ,, water. Boil, and add—
30 ,, tallow } previously melted together.
20 ,, resin }

Turn off steam and add—

50 grms. sulphate of alumina (powdered).
1000 Cool, and grind in a mill before use.

White or Yellow Resist III. (for Dark grounds).

75 grms. copper sulphate (powder).
75 ,, copper acetate (powder).
250 ,, water.
250 ,, lead sulphate 50 per cent. paste.

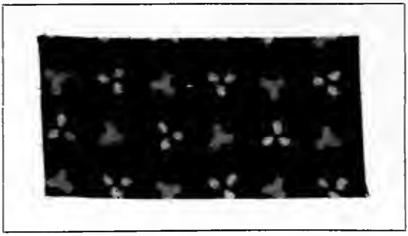
Heat together, and when the copper salts are in solution add—

35 grms. acetate of lead.
35 ,, nitrate of lead.

Stir the whole together at intervals during 12–24 hours, and when the lead salts are precipitated add—

30 grms. tallow.
250 ,, 30 per cent. gum Senegal solution.
1000

Boil for one hour, replace the water that has evaporated, and then cool and grind for a day or two in a mill.



White and Yellow Resists under dyed Indigo.

YELLOW RESIST IV.

200 grms. copper sulphate.
180 ,, lead nitrate.
520 ,, water.

Boil together, cool, and add

80 grms. flour.
20 ,, olive oil.

1000

Boil and cool; grind before using.

Each of the foregoing recipes contains solid matter (insoluble lead sulphate or China clay), and is suitable for either block work, if made a little thinner, or for heavy patterns printed by machine. For thin but deeply engraved line patterns and fine spots, the two following recipes are more suitable, since they contain no insoluble bodies, and therefore do not stick in the engraving on the copper printing roller:—

	WHITE V.	YELLOW OR WHITE VI.
Nitrate of copper 80° Tw.	100	90
Acetate of copper cryst.	90	50
Sulphate of copper cryst.	90	...
Lead nitrate cryst.	...	200
Water	560	550
Flour	80	80
British gum	50	30
Olive oil	30	...
	1000	1000

For medium and light Indigo blues the following resist is a good one:—

WHITE RESIST VII. (FOR LIGHT AND MEDIUM GROUNDS).

200 grms. British gum (dark).
450 ,, water.
50 ,, soft soap.

Boil, cool, and add—

150 grms. zinc sulphate cryst.
75 ,, nitrate of copper 80° Tw.
75 ,, thick flour paste.

1000

After printing, the goods are hung in a warm room to harden the resist paste. They are then dipped in the Indigo vat as many times as are required to produce the desired depth of blue. After this they are treated in different ways according to the colours in the pattern.

Simple white resists are well washed, and soured for 3 minutes at 50° C. in dilute sulphuric acid (25 grms. H_2SO_4 168° Tw. per litre), and then thoroughly well washed again and dried. If required, the lead sulphate may be entirely removed by a run through boiling dilute caustic soda, but this, as a rule, is not necessary.

For white and yellow (or orange) effects the goods are printed, for white, with Resists II. or V., and for yellow, with Resists I., III., IV., or VI. After dyeing, they are washed and soured as above; then washed again, and passed for 2–3 minutes through a cold solution of lime water (2½ grms. lime per litre); washed, and the yellow developed by a run through the following "chrome" bath:—

5	grms.	bichromate of soda.
5	,,	hydrochloric acid 4° Tw.
1000	,,	water.

The "chrome" is maintained at a temperature of 40° C., and the speed of the goods is so regulated that they receive an immersion of 5 minutes. This treatment gives *bright lemon-yellow and white effects* on cloth printed as above. If *white and orange* reserves are required, the cloth is further treated for 1 minute in the "orangeing" bath at the boil.

"ORANGEING" BATH:—

10	grms.	bichromate of soda.
100	,,	caustic soda 90° Tw.
900	,,	water.
1 litre		

Wash well and dry. All the washing, souring, and chroming operations are conducted at the open width and in a continuous manner.

From the fact that Chrome yellow forms the basis for the production of Chrome orange, it is obviously impossible to obtain reserve effects in which these two colours appear side by side. When, therefore, yellow and orange have to be printed in combination, some yellow other than lead chromate must be employed. The yellows that come into consideration in this connection are those of the direct dyeing group, which are capable of withstanding the process of vat-dyeing and the subsequent operations of washing, souring, etc. etc. Thioflavine S., fast Diamine yellows A., B., and F.F., Aurophenine O., Diphenyl chlorine yellow G., and Oxamine yellow 3 G. all fulfil these conditions, and have proved to be specially suitable for such work. Thioflavine S. and Oxamine yellow 3 G. give a brilliant sulphur or lemon yellow, the fast Diamine yellows B. and F.F. and Diphenyl chlorine yellow G. give yellow-gold shades, while fast Diamine yellow A. and Aurophenine O. give full golden yellows, sufficiently distinguishable from the pronounced reddish tone of Chrome orange. Fast Diamine yellow B. is very soluble, and possesses remarkable fastness to light and washing,—qualities which render it perhaps the most suitable of the group to employ. At the same time the others yield good results, and the redder shades especially are suitable for the production of olives by superposition on light Indigo.

RESIST YELLOW VIII.

50	grms.	fast Diamine yellow B.
180	,,	British gum paste.
770	,,	White Resist II.
1000		

Heat until the colouring matter is dissolved and then cool.

For a white, yellow, and orange effect print:—
For the white—Resist White II.
,, yellow—Resist Yellow VIII.
,, orange—Resist Yellows III., IV., or VI.

After printing, hang in a warm place; dye blue, wash, sour, wash, and then "chrome" and "orange" as already described.

There are several modifications of the simple "Indigo Resist Style." Of these the most important are the following:—

STYLE 1.—Dark Indigo, white, yellow, and orange patterns on a light Indigo ground.

Style 2.—Light Indigo, white, yellow, orange, green, and olive patterns on a dark Indigo ground.

Style 3.—White, green, and yellow patterns on dark Indigo.

Style 4.—Multicolour patterns on a figured ground of both dark and light Indigo.

Taken in the above order, these are produced according to the several directions given below.

Style 1.—On white cloth print Resist White II., Resist Yellow VIII., Resist Yellows III., IV., or VI., and a thickened solution of strong caustic soda, Paste N.A.

Paste N.A.

900	grms.	caustic soda 75° Tw.
100	,,	British gum powder.
1000		

Mix together in the cold, and then heat gently until the paste is smooth.

After printing, hang, dip blue to the required depth of shade, wash well, sour, "chrome" and "orange," etc., as usual. The caustic soda mercerises the cloth locally, and consequently, wherever it is printed, a darker blue appears on dyeing, since mercerised cloth possesses a much greater affinity for Indigo than plain cloth. The dyeing of the ground shade ought to be commenced in very weak vats in order to allow the Paste N.A. to soften, and eventually dissolve off the cloth. In this way the stronger dye liquors that follow the first "dipping" are enabled to penetrate into the fibre of the mercerised portions of the cloth and to dye it a full, even, deep blue, which contrasts well with the lighter shade they impart to the unprinted portions.

Style 2.—The production of a multicolour pattern which includes a light Indigo object on a dark Indigo ground calls for the employment of what are know as "discharge resists." The light blue object or pattern is obtained by first dyeing the cloth a light blue, then printing an ordinary white resist upon it, and finally dipping it into the vat again until the ground shade is sufficiently dark. On now washing off the resist a blue pattern, instead of a white one, appears on a darker blue ground. If white, yellow, and orange are also required in the reserved pattern, it is obvious that their respective reserve pastes must not only be capable of "resisting" the dark blue ground, but also of actually "discharging" the light blue ground upon which they are necessarily printed. To this end, therefore, the ordinary "resist pastes" are modified by the addition of an *insoluble chromate*. During the souring operation, after the final dyeing, free chromic acid is liberated from this chromate and discharges the light blue, in the same way as the well-known "Chromate Discharge" already dealt with. (See discharges on Indigo.) Green and olive resists are simply obtained by the superposition of yellow and orange on light blue.

The chromates of lead, barium, and zinc are all suitable ingredients of "discharge resists"—the first two for yellow and (or) orange, the third either for white, yellow, or orange. The lead and barium chromates are unsuitable for white effects, because they deposit on the cloth insoluble sulphates, which afterwards become converted into chromates again during the "chroming" operation after the final dyeing: zinc sulphate is soluble, and is removed from the fabric in process.

Discharge-Resists (for Indigo).

White D.R.:—	200	grms.	zinc chromate 65 per cent. paste.
	800	,,	thickening D.R.
	1000		

YELLOW D.R.:—
40 grms. Diamine fast yellow B.
100 ,, 20 per cent. British gum paste
100 ,, 50 per cent. China clay paste.
Boil and add—
610 ,, thickening D.R.
Heat until the dyestuff is dissolved, and then add—
150 grms. zinc chromate 65 per cent paste.
1000

ORANGE D.R. I.:—
300 grms. water.
100 ,, flour.
Boil, and add at 65° C.—
25 ,, copper sulphate (powder).
25 ,, copper acetate (powder).
100 ,, copper nitrate (100° Tw.)
250 ,, lead sulphate 50 per cent. paste.
Cool, and grind in—
150 ,, lead chromate 65 per cent. paste.
1000

ORANGE D.R. II.:—
150 ,, zinc chromate 65 per cent. paste.
850 ,, white (or yellow) Resist III.
1000

THICKENING D.R.
550 ,, water.
170 ,, flour.
30 ,, tallow.
Boil, cool a little, and add—
90 ,, copper sulphate.
100 ,, copper acetate.
60 ,, copper nitrate sol. 100° Tw.
1000 Cool.

For the production of a multicolour pattern consisting of white, yellow, orange, and blue flowers, with green and olive leaves, on a dark blue ground, the following colours are printed on *light* Indigo blue cloth:—

For White print:—	White D.R.
,, Yellow ,,	Yellow D.R.
,, Orange ,,	Orange D.R. I. or D.R. II.
,, Blue ,,	White resist II.
,, Green ,,	Resist yellow VIII.
,, Olive ,,	Yellow resist III., IV., or VI.

The blue, green, and olive colours simply resist the dyeing of the dark blue ground without affecting the lighter blue upon which they are printed; consequently, on washing off and "chroming," they leave light blue, green, and olive on a blue ground, the green and olive being obtained by the superposition of yellow and orange on light blue.

After printing, the goods are well dried, dipped dark blue in the Indigo vat, washed in water, and then passed through a discharging or "cutting" bath consisting of—

60 parts sulphuric acid 168° Tw.
25 ,, oxalic acid
1000 ,, water
at 50°–60° C.

After "cutting," in which the light blue is discharged by the chromic acid liberated from the zinc or lead chromates, the goods are well washed, passed through a cold solution of lime water, and then chromed and "oranged" as already described; finally, they are well washed again and dried.

Style 3.—White, green, and yellow effects on a dark blue ground are produced according to the methods of Style 2 above.

Style 4.—This style is based upon the same principle as Style 1, but instead of the dark blue registering with the resist colours, it is arranged to fall over them in a haphazard fashion; indeed, it is really a "cover" pattern. Effects of white, yellow, orange, etc., on a "two-blue" ground, are obtained by first printing the white cloth with ordinary resist colours, then, after drying, with the caustic soda paste already given under Style 1. On dyeing cloth so treated, the parts of the material to which caustic soda has been applied dye up darker than the rest of the ground, thus producing a "two-tone" effect. The reserved pattern runs through both shades of blue without any break in its continuity of line. The local contraction of the cloth due to mercerisation is got rid of in process,—the numerous washings, sourings, etc., tending to straighten out and flatten any "cockling" that may appear before dyeing.

Another method of attaining the same result is to print the caustic soda first on white cloth; then wash well and dry on a stentering machine, which effectually stretches the cloth out to its original width and frees it from all creases. The printing of the reserve pastes is then carried out in exactly the same manner as for ordinary cloth.

A process largely practised at one time, but now rarely used, depends upon the application of Manganese bronze. The cloth is first printed with a thickened solution of manganese sulphate or chloride. After drying, the bronze is developed in caustic soda and bleaching powder solution, well washed and dried. White and coloured resists are then "blocked in" on the unprinted parts of the cloth, and the "dipping," washing, souring, and "chroming" proceeded with as usual. The parts of the cloth upon which the "bronze" is printed dye up a darker blue like mercerised cloth, but, unlike the latter, only the lighter blue can be reserved, for wherever the "resists" fall over the "bronze," the result is a brown.

Azo Colour Resists under Indigo.

By adding the diazo compounds of para- and meta-nitraniline and ortho-nitroparaphenetidine to Indigo resist pastes, very fast and bright red orange and pink effects are obtained.

The cloth to be treated is prepared in β-naphthol, and starched at the same time.

β-NAPHTHOL PREPARE.

15	grms.	starch.
429	,,	water.

Boil, cool to 60° C., and add—

30	grms.	β-naphthol.
120	,,	caustic soda 50° Tw.
300	,,	water.
6	,,	tartaric acid.
5	,,	tartar emetic.
80	,,	water.
15	,,	Turkey-red oil 40 per cent.
1000		

Pad the cloth in the above, dry, and *cool*. Then print on any of the ordinary white resists together with the following:—

Red Az. R.:— 75 grms. Azophor red P.N.
45 „ water.
Grind to a paste and add
845 „ thickening X.
35 „ acetate of soda.

1000

Orange Az. R.:—as Red, but Azophor orange M.N.

Pink Az. R.:— 20 grms Azophor pink A.
40 „ water.
40 „ acetic acid 9° Tw.
Allow to stand 1½ hours, grind to a paste, and add—
880 grms. thickening X.
20 „ acetate of soda.

1000

Thickening X.

275 grms. 50 per cent. gum Senegal.
75 „ water.
200 „ lead nitrate.
Dissolve hot, and add—
300 grms. lead sulphate 66 per cent. paste.
150 „ zinc sulphate cryst.

1000

Cool, and grind a day or two in a mill.

After printing, dry the goods gently, and when quite dry proceed to dip in the vat, etc., in the usual manner. Owing to the facts that copper salts cannot be used in conjunction with the Azo colours, and that lead salts cannot be kept in solution at a strength sufficient to resist the darkest blues, the insoluble Azo colour resists are only applicable to the darker medium shades of Indigo.

In addition to those already described, there are other methods of obtaining resist effects under dyed Indigo blue. Strong solutions of tannic acid in combination with basic colours have been used, but the results leave much to be desired. Lead peroxide (PbO_2), a powerful oxidising agent, has also been employed with success for white or yellow and orange resists: it is not, however, in general use, and, except perhaps for special styles, it offers no advantage over the older copper-lead-zinc resist pastes.

Goods printed with resist pastes may be dyed in either the continuous dyeing machine or by alternate immersion in, and exposure to the air above, the "dipping vat" (which see). The latter method, though more tedious, is usually preferred for the Indigo resist styles. In continuous dyeing machines, where the cloth passes over and under a great number of guide rollers, the resist pastes are very liable to crack, and to break off or be rubbed off the fabric. In "dipping vats," on the contrary, the pastes remain quite undisturbed, the only danger being that they may slip if the dyeing is prolonged by the use of vats that are too weak. When this danger is apprehended, it may be avoided by dipping the goods at the outset in a vat containing an excess of lime, or by raking up the vat in which the goods are dipped first. The number of "dips" required to produce a given shade depends mainly on the strength of the vats. The best vat for the purpose is the zinc lime vat; and in works where the resist style is produced in large quantities, the vats are usually worked in series of from three to eight. Each vat is exhausted in turn, so that no delay occurs during the setting of a fresh vat. A full dark blue can be dyed in four "dips" with the vats "set" and worked as below.

	1st.	*2nd.*	*3rd.*
Water	20,000 litres	20,000 litres	20,000 litres
Zinc dust	7,200 grms.	10,800 grms.	20,250 grms.
Lime	16,000 ,,	24,000 ,,	45,000 ,,
Indigo pure B.A.S.F.	8,000 ,,	12,000 ,,	22,500 ,,

The cloth, stretched on the dipping frame, is immersed in the first vat for 15–20 minutes, then withdrawn and suspended over the vat for 10–15 minutes to drain and to allow the indigo white to oxidise. The frame is then reversed and plunged into the second vat, where it remains for 10 minutes. The operations of withdrawal, draining, and oxidation are repeated, the frame again reversed, and immersed in the third vat for 10 minutes. The cloth is then exposed to the air for about 10 minutes, again reversed, and the operations repeated. After the final immersion the goods are exposed to the air for 20 minutes, and then washed, soured, "chromed," and so on, according to requirements. The object of reversing the frame after each immersion is to ensure the level dyeing of the goods between selvedge and selvedge.

Most of the resist pastes used for Indigo vats may also be employed for the modern vat dyestuffs of the Ciba, Thio-indigo, Indanthrene, Helindone, and other groups, and therefore it is unnecessary to give special recipes for these products. Most of the new Vat dyestuffs are applied by methods essentially similar to those employed for Indigo, the main difference being that many of them are best dyed at a fairly high temperature (40°–60° C.). In other respects the process is practically the same, with, of course, slight variations according to the nature of the particular dyestuff employed.

The Ciba and the Helindone colours lend themselves admirably to the production of reserve effects, and they may be dyed, like Indigo, either *continuously* or *by dipping*. In dyeing by the former method, the goods pass successively through two dye vats, with an exposure to the air between the immersions.

The first dye vat has a capacity of 1500 litres and the second 500 litres. Both are fitted with an arrangement of guide rollers and a pair of squeezing bowls at their exit ends. The formation of creases is best avoided by using conical opening rollers at the entrance of each vat, and also immediately in front of the squeezing bowls; the alignment of the guide rollers must also be perfect, any slight deviation from parallelism giving rise to creases and double edges, with their inevitable result—streaky dyeing. The exposure to the air is effected by any of the systems in current use, but, taken altogether, the travelling band or "creeper" arrangement is the best, as the goods, after passing over a few rollers, are allowed to fall in regular pleats upon the moving band or apron. In this way the goods are "plaited down" gently in separate pleats instead of being piled up in a heterogeneous mass, to the almost certain damage of the resist paste.

For continuous dyeing with the new Vat dyestuffs, the best vat to use is the hydrosulphite vat. An example illustrates the principle of preparing the dye liquors :—

Dye Vat for Continuous Dyeing (Ciba Colours).

I. { 30 parts any Ciba dyestuff in powder.
22·5 ,, caustic soda 66° Tw. Mix into a paste and add—

II. { 500 parts cold water.
90 ,, Hydrosulphite of soda in powder 85 per cent.
25·5 ,, caustic soda 66° Tw.

Dissolve cold. Mix well together I. and II., and then pour over the whole—
1250 parts hot water.

Heat gently until the dyestuff is completely reduced to the leuco compound, and then make up to 10,000 parts by the addition of water to which a little hydrosulphite and caustic soda has been added to deprive it of its free oxygen.

Excess of either hydrosulphite or caustic soda is to be avoided, as both hinder the oxidation of the leuco compound on the fibre.

The two vats of the continuous dyeing machine are filled with liquor made up as above, the proportions being the same for both. The cloth, printed with suitable resists, is then passed through the first vat, aired for a few minutes, then passed through the second, aired again, and then rinsed in water. The goods are now soured in sulphuric acid (2 parts H_2SO_4 168° Tw. per litre) at 35°–40° C., well washed, and then, if only a white resist has been printed, they are soaped at the boil for a few minutes to obtain bright and fast shades, and finally well washed in water and dried. In the case of lead yellow or orange resists the soaping must be omitted, since lead sulphate is soluble to some extent in slightly alkaline soap liquors. In place of soaping, therefore, the full development of the dyed ground, together with that of the lead yellows, is brought about by treating the goods for a few minutes at 70° C. in a "chrome bath" containing 25–30 grms. of bichromate of soda and 15–20 grms. acetic acid 9° Tw. per litre of water. They are then well washed and dried.

With such modifications in the composition of the resists and dye liquors as are demanded by circumstances, the same general methods are applicable to other Vat dyestuffs as are employed for the Ciba colours.

Batticks.

A peculiar kind of "resist work," known as "Battick printing," has been practised since very early times in the East, and more especially in Java. The production of the native article depends upon the application to the cloth of purely mechanical "resists" composed of wax, resin, and fatty matters. These substances are applied in the melted state by pouring them from small vessels of calabash gourd or metal, through which openings of various sizes have been pierced; sometimes the openings are fitted with a small wooden spout, but usually the spout itself is the pointed part of the gourd, to which the stem is attached. The worker pours the melted wax over those portions of the cloth which are required to remain uncoloured; and when the resist has set and hardened, the goods are dyed in vegetable colours by "dipping in the vat." The resist is afterwards removed by treating the dyed material in boiling water, to which is sometimes added soda or potash (wood ashes) so as to form an easily removable emulsion. For a repeating pattern brass blocks are used in Java.

The characteristic feature of typical Batticks is the appearance of fine veins of colour running irregularly across the reserved parts of the pattern. Sometimes a fine network of two or three different colours extends over every white (or rather buff) object in the design, giving to the whole an extremely rich and beautiful quality. This artistic appearance is due to the cracking of the rather brittle waxy resists during the handling of the cloth in the dyeing process; and the more brittle and the thicker the protecting layer of wax, the more likely is it to crack. In dyeing, the dye liquor penetrates through the interstices in the resist and becomes fixed on the cloth so exposed, thus causing the curious marble-like veinings alluded to above.

Imitations, more or less successful, of the Battick style are obtained in Europe by printing melted wax from engraved rollers or plates, also by stencils; and many beautiful effects are produced by first dyeing in one colour, then breaking the resist and re-dyeing in another colour. If necessary, the resists can be applied afresh as often as desired, thus affording a means of obtaining a great variety of colour effects, both directly and by superposition.

The Battick style may, and is, also applied in Madder dyeing, as well as for the Vat colours. In such cases the cloth is mordanted after the resist has been printed, dried, and broken into cracks (by passing over small rollers). For example, a red, blue, chocolate, and buff effect is obtained in the following way:—(1) Print on melted beeswax, allow to set hard, and then pass the goods over a roller to break up the layer of wax. (2) Pad in cold acetate of alumina 8° Tw., squeeze out the excess of liquor, and hang the goods in a cool room until dry. Then raise the temperature to 30°–40° C. for the purpose of ageing the goods, taking care not to actually melt the resist, and then "dung" in the ordinary way; wash the goods in boiling water for 15 minutes; wash again in borax solution at the boil, and when the wax is quite dissolved off the cloth give a final wash in hot water, and proceed to dye with Alizarin exactly as for Madder reds. (3) Clear and brighten the red as usual, dry the cloth, and print any desired pattern upon it in melted wax. (4) Break the wax resist again and dip in the Indigo or any other blue vat; wash, sour lightly; wash in cold water; wash in borax or soda ash solution at 75°–80° C. to remove the last traces of wax, and then dry up. The ultimate effect will consist of red and white (where the second resist was printed), blue and chocolate, the last by the superposition of blue on red, and over the whole pattern various veins of red, blue, and chocolate will appear. The buff colour, in place of white, is obtained by finally tinting the cloth in the padding machine with a suitable direct dyestuff such as Chrysamine. Similar, but less permanent, effects can be obtained from basic dyestuffs on a tannin mordant, and, in short, the process is suitable for any colouring matter or mordant which can be applied at a temperature low enough to prevent the melting of the resist.

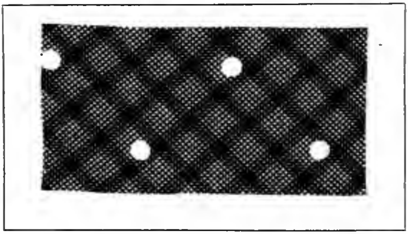
Resists under Printed Indigo.

White resists under printed Indigo are obtained by printing certain acid metallic salts, flowers of sulphur, lactic acid or ammonium nitrate under the ordinary printing pastes used for Indigo styles. For the glucose process sulphur is the best resist.

Resist S.

200	grms.	flowers of sulphur.
50	,,	lactic acid 50 per cent.
750	,,	30 per cent. gum Senegal solution.
1000		Grind several days until a perfectly smooth paste is obtained.

Print on glucose-prepared cloth, dry, and "cover" with a thickened mixture of Indigo and caustic soda, steam, wash, etc., exactly as described under the printing of Indigo. The same resist is also suitable under the hydrosulphite Indigo printing pastes; and for heavy resist patterns, the lead-copper resists may often be employed successfully.



Sulphur resist under printed Indigo.

Fast-coloured resists are obtained by mixing diazo solutions with sulphate of alumina and lactic acid pastes, and printing on cloth prepared with β-naphthol. After applying the resist paste, the Indigo is printed over it and steamed, etc., as usual.

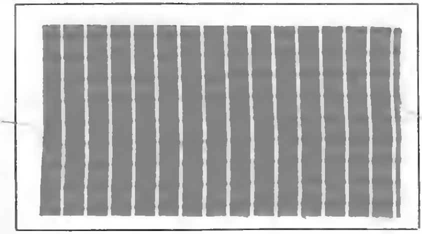
Resists under Steam Alizarin Reds and Pinks, etc.

The development and fixation on the cloth of steam Alizarin reds, pinks, and light purples is prevented in presence of citrates, tartrates, oxalate of antimony, and citric and tartaric acids. The resists are usually printed on cloth prepared with Turkey-red oil, and then "covered" or padded on the machine with the Alizarin colours.

The following are a few of the more typical "resists" in common use:—

Resist S.A. I. (for Pinks).	220	grms.	British gum.
	445	,,	water.
	200	,,	China clay paste 50 per cent.
	130	,,	citrate of soda 55° Tw.
	5	,,	citric acid.
	1000		Boil and cool.
Resist S.A. II. (Pinks).	850	grms.	50 per cent. gum Senegal.
	150	,,	oxalate of antimony.
	1000		Boil and cool.
Resist S.A. III. (Pinks).	200	grms.	China clay.
	100	,,	citrate of soda 55° Tw.
	100	,,	citrate of chrome 42° Tw.
	100	,,	water.
	500	,,	British gum paste.
	1000		
Resist B.N. (strong Reds).	330	grms.	citrate of chrome 48° Tw.
	5	,,	citric acid.
	75	,,	China clay.
	90	,,	British gum.
	500		Boil and cool.
Resist B.N.S. (Reds and Aliz. Bordeaux).	330	grms.	citrate of chrome 48° Tw.
	330	,,	citrate of soda 55° Tw.
	150	,,	China clay.
	180	,,	British gum powder.
	10	,,	tartaric acid.
	1000		Boil and cool.

The last two resists are excellent for white reserves under deep Alizarin reds, and colours obtained from Alizarin bordeaux, or grenat, and aluminium mordants. When reduced with six times their weight of gum or paste, they give good whites under light Alizarin pink pads and covers. For deep pinks less reducing paste must be taken.



Citrate of Chrome resist under Alizarin Pink.

Print the above resists on cloth prepared in Turkey-red oil (2½–5 per cent. fatty acid); dry, and over-print in steam Alizarin red, pink, or bordeaux as the case may be; steam for 1 hour in the "continuous steamer," and then wash well, soap, and dry. After steaming, the pattern printed in the resists has a decided yellow appearance, due to the presence of uncombined Alizarin, but on washing and soaping, the Alizarin and the soluble aluminium and tin compounds are removed entirely from the fibre, leaving it perfectly pure and white.

Coloured resist effects under steam Alizarin pink "pads" are obtained by adding citric acid to the ordinary steam basic colour pastes. This style was largely practised some years ago for the Eastern markets, and is still produced in notable quantities, although it has lost somewhat in popularity as a standard style.

Coloured Resists under Steam Alizarin Pink

	Yellow S.A.	Blue S.A.	Green S.A.
China clay	70	70	70
Water	60	60	60
British gum paste	620	620	619
Thioflavine T.	20	...	14
New methylene blue N.	...	20	7
Citric acid	10–15	10–15	10–15
Acetic acid 9° Tw.	100–95	100–95	100–95
Boil, cool, and add—			
Tannin 50 per cent. solution in acetic acid	120	120	120
	1000	1000	1000

Print on oiled cloth, dry, and "cover or pad" with a steam Alizarin pink containing 8 grms. Alizarin (20 per cent. paste) per kilogramme of printing colour; steam one hour without pressure, and then pass the goods through a solution of tartar emetic to fix the basic colours; wash well, soap at the open width, wash again and dry. The above recipes will serve for all basic colours. If a stronger pink ground is padded (on the printing machine), the proportion of citric acid must be increased accordingly.

White resists, and any steam colours deeper than the pink ground—*e.g.* Alizarin red, chocolate, Logwood black, etc.—are printed in combination with blue, yellow, and green resists when a greater variety of colour is required.

Another method of obtaining resist effects under steam Alizarin colours is based upon the employment of direct dyeing colouring matters with disodium phosphate as the resisting agent. This method does not yield very bright colours, nor is it of any great practical value, but it possesses a certain amount of interest, and may perhaps be of service in an emergency.

Phosphate Resists under Steam Alizarin Pinks.

Yellow:—	30 grms.	Chysophenine G.
	30 ,,	starch.
	500 ,,	6 per cent. tragacanth thickening.
	200 ,,	water.
Boil, cool, and add—		
	50 ,,	disodium phosphate crystals.
	190 ,,	water
	1000	

Blue:—	as Yellow but	30	grms.	Chicago blue 6 B.
Green:—	,,	20	,,	Thioflavine S.
		10	,,	Chicago blue.
Olive:—	,,	19	,,	Chrysophenine G.
		10	,,	Chicago blue O.G.
		1	,,	Benzo-fast scarlet 4 B.S.

Print on oiled cloth, dry, and print Alizarin pink with a "pad roller"; steam one hour, wash, and soap. Tungstate of soda has been suggested for the same purpose by A. Scheurer.

Coloured resists by any process are not successful under strong Alizarin reds, nor are they suitable under steam Alizarin violets (iron), on account of the formation of blue tannate of iron or of yellow ferric phosphate. Hence white resists alone are of any importance under Alizarin reds, bordeaux, or violets.

Resists under Albumen Colours.

Insoluble pigment colours, fixed in steaming by the coagulation of albumen, can be easily resisted by means of any substance capable of bringing about the coagulation before the albumen comes in contact with the actual fibres of the cloth. For this purpose zinc sulphate, citric or tartaric acids, and ammonium nitrate have been found by experience to give the best results. They are used either alone or in combination with one another and China clay. The organic acids by themselves are only suitable for pale ultramarine blues, and with these they produce very good white resists. The cloth is first printed with the resist pastes, then dried and over-printed with a "cover" or "pad" roller in the albumen colour; it is then steamed one hour, washed, and soaped.

Pigment Resist White I.

240 grms. nitrate of ammonia (cryst.).
110 ,, China clay.
470 ,, water.
180 ,, dark British gum.
————
1000

Boil and cool.

White Resist P. II.

300 grms. zinc sulphate (cryst.).
200 ,, China clay.
200 ,, citrate of ammonia 38° Tw.
150 ,, water.
150 ,, British gum.
————
1000

Boil and cool.

Any of the citric acid resists used under steam pinks may be utilised for resisting light shades of ultramarine blues.

Print the above resists on white cloth, dry, and cover in any of the pigment printing colours given under the "Steam Style"; steam one hour, wash, and soap.

Coloured resists are rarely produced under pigment colour "covers" and "pads." When required, they are best obtained by adding ammonium nitrate to the ordinary steam printing pastes, such as Alizarin red or pink. With mordant colours which form fast zinc lakes, like Alizarin blue, the requisite amount of zinc sulphate to resist the pigment colour acts also as a mordant for the blue, and no ammonium nitrate is required.

Resists under Basic Colours (Tannin).

Although antimony salts are the fixing agents *par excellence* for basic colours printed in combination with tannic acid, they are nevertheless, when used in excess, very efficient, and in fact the best resisting agents for those colours. The particular salts used are sodium tartar emetic and oxalate of antimony, together with zinc sulphate and citric acid, respectively. The white cloth is printed with the resisting paste; then dried, and over-printed with any of the basic colour tannin pastes given in the section on the "Steam Style"; steamed one hour, passed through a 1 per cent. solution of tartar emetic; washed, soaped, and dried.

If the antimony resist pastes contain, in addition to the usual ingredients, a little stannous chloride, they will serve as discharges for any suitable Direct dyestuff with which the cloth may have been previously dyed; and if the basic colour "cover" also contains a corresponding quantity of stannous chloride, it too will discharge the dyed ground, and an effect of a white pattern on a coloured discharged ground will be obtained.

White Resist B.T. I.

200	grms.	China clay.
250	,,	water.
150	,,	British gum.
200	,,	sodium tartar emetic (powder).
180	,,	zinc sulphate (cryst.).
20	,,	citric acid.
1000		Boil and cool.

Resist B.T. II.

550	grms.	water.
100	,,	China clay.
175	,,	British gum.
150	,,	oxalate of antimony.
25	,,	citric acid.
1000		Boil and cool.

Resist B.T. III.

200	grms.	China clay.
275	,,	water.
125	,,	British gum.
400	,,	sodium tartar emetic.
1000		Boil and cool.

Print any of the above on white cloth; dry, and print any Basic colours containing tannin; steam for one hour, fix, wash, and soap.

For obtaining a white discharge on a Direct colour ground with simultaneous resist of Basic colour cover, print the following instead of the above:—

Resist Discharge Z.

50	grms.	China clay.
300	,,	water.
200	,,	British gum.
350	,,	sodium tartar emetic.
50	,,	citric acid. Boil, cool, and add—
50	,,	stannous chloride.
1000		

Print on cloth dyed with 1–2 per cent. Erika pink; dry and print a basic green containing tannin and stannous chloride (5 per cent.); steam one hour, pass through a 1 per cent. solution of tartar emetic, wash, and soap. The ultimate result is a white pattern on a pink and green ground.

Multiple Resists under Steam Colours.

It is often required in practice to produce a white pattern on a multicolour ground (say a three-colour stripe or check), consisting of two or more quite distinct classes of steam colours.

The following white resist paste will act efficiently under Alizarin red and pink, basic colours and pigment colours, so that it affords a means of producing the effect alluded to above:—

TRIPLE RESIST—RESIST T.R.

200	grms.	sodium tartar emetic.
100	,,	China clay.
150	,,	zinc sulphate.
200	,,	citrate of chrome 46° Tw.
200	,,	water.
100	,,	British gum.
1000		Boil and cool.

Print on oiled cloth; dry; cover with a three-colour pattern in Alizarin pink, Methylene blue, and Pigment grey (lampblack and albumen), or any other similar basic and pigment colours; steam one hour, wash, fix, and soap. The oxalate of antimony resist (Resist B.T. II.) will also give a good white under either (or both) Alizarin and basic colours, but not under strong pigment colours.

Resists under Iron and Aluminium Mordants.

These have already been dealt with under the "Madder Style" (Dyed Styles, *q.v.*).

Resist Effects under Insoluble Azo Colours produced on the Fibre.

White and coloured reserve or resist effects are produced under this important class of colouring matters by printing, on naphthol-prepared cloth, either (*a*) reducing agents like stannous salts and alkaline sulphites, which reduce the diazo compounds, or (*b*) substances like the persulphates and citric and tartaric acids, which greatly retard, or counteract entirely, the coupling of the naphthol with the diazo compounds. Tannic acid is also an efficient resisting agent; and although it is unsuitable for white resists, it affords a valuable means for the production of dark, rich basic colour resist effects, very fast to washing and soaping.

In addition to the above-mentioned substances, various insoluble bodies, such as China clay, waxes, and fats, are often incorporated with the resist pastes, especially those used for white resists. They act mechanically, and exercise a beneficial influence upon the perfectness of the resist and the purity of the white.

There are four methods in general use for the resisting of dyed insoluble Azo colours:—

(1) Tin Resists.
(2) Sulphite Resists.
(3) Tannin Resists.
(4) Persulphate Resists.

Strong caustic soda has also been tried as a resist for insoluble Azo dyes. Its action depends upon the conversion of the diazo compound into a nitrosamine.

The preparation of the cloth in naphtholate of soda, and the subsequent dyeing, are carried out with the naphthol prepares and the diazo solutions already given in the section on Dyeing, under the heading of "Insoluble Azo Colours."

Tin Resists.

The white and coloured resists obtained, under dyed Azo colours, by means of tin salts, are produced in larger quantities than any similar style executed by other methods.

Stannous salts, and particularly stannous chloride (tin crystals), exercise a powerful action upon diazo compounds, which they reduce to hydrazines which are incapable of combining with β-naphthol.

Used alone, stannous chloride, while giving a perfect resist, imparts an undesirable yellow tinge to the white cloth, which cannot be easily "cleared." The addition of organic acids—citric and tartaric—obviates this defect; and as such acids are themselves moderately good resisting agents, they generally form one of the ingredients of "Tin Resists" of all kinds. To obtain the best results, the "tin crystals" employed should be fresh and free from all oxidation products; the salt must be readily soluble, and have no appearance of white efflorescence. Needless to say, it ought also to be as white as possible; any yellowish appearance is certain to give dirty whites, and flat, dull shades of colour.

For coloured resists, stannous chloride can be added to almost any of the basic colour tannin printing pastes, and in certain cases to Chrome yellow or orange and Chrome green (Guignet's green). With the last three, somewhat *looser* colours are obtained, since the addition of albumen is out of the question; but taking this into account, the colours are remarkably fast to washing—much more so than if printed on plain white cloth under similar conditions. Naphthol prepares containing antimony salts are always employed for basic colour resists, and are, moreover, the best in all circumstances, as they are less liable to develop brown stains in drying.

White Resist T.A.

500 grms. 50 per cent. gum Senegal solution.
400 ,, stannous chloride.
100 ,, tartaric acid.
1000

White Resist T.B.

600 grms. glue-starch thickening.
100 ,, China clay.
50 ,, tartaric acid.

Beat the clay into the paste; add the acid, and heat till it is dissolved; cool, and add—

250 grms. stannous chloride.
1000

Glue-Starch Thickening.

100 grms. glue.
200 ,, water. Soak till soft, then add—
250 ,, acetic acid 9° Tw.
90 ,, paraffin wax.
285 ,, water.
75 ,, starch.
1000

Boil the whole until the glue is dissolved, and then cool.

Resist D. (to resist both the ground and the basic colour reserves).

{ 100 grms. British gum.
{ 250 ,, water.
300 ,, sodium tartar emetic.
100 ,, zinc sulphate.
50 ,, tartaric acid.
Boil, cool, and add
200 ,, stannous chloride.
————
1000

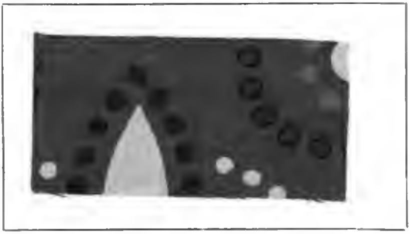
Resist D. is used chiefly for small white objects in the "blue and red style."

COLOUR RESISTS WITH BASIC DYESTUFFS.

STANDARD PASTES.	RED.	PINK.	ORANGE.	YELLOW.	BLUE.	GREEN.
Rhodamine 6 G.extra	25	10	5	...	...	...
Thioflavine T.	5	...	15	20	..	...
Pure blue II. (B.A.S.F.)	...	...	...	...	12·5	...
Brilliant green	...	...	...	...	...	13
Auramine G.	...	...	...	...	...	20
New methylene blue N.	...	...	...	...	12·5	...
Citric acid	25	25	25	25	25	25
Acetic acid 9° Tw.	200	200	200	200	250	200
Starch	100	120	100	100	100	100
Water	45	105	155	155	100	142
6 per cent. tragacanth	100	140	100	100	100	100
Boil, cool, and add—						
50 per cent. tannic solution (in acetic acid)	300	200	200	200	200	200
	800	800	800	800	800	800

For Printing take :— { 800 grms. above colour pastes.
{ 200 ,, stannous chloride
————
1000

Other basic colours, such as Victoria blue, Auramine O., Auramine conc., Marine blue, Phosphine, etc., may be also applied according to the formulæ given above.


Tin resist under α-naphthylamine claret.

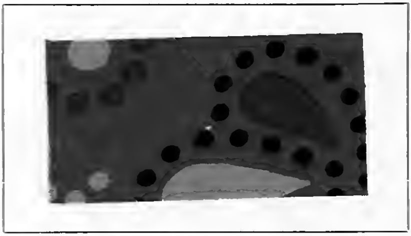
The white and coloured resists are printed on cloth prepared in a 3 per cent. solution of β-naphthol containing 1 per cent. of tartar emetic; dried carefully in hot air or over rather cool cylinders, to prevent the tendering of the fibre, and then passed through various diazo solutions, according to the shade of ground required. After dyeing, the goods are well washed, soaped, washed, and dried. The run through the diazo compound constitutes the dyeing, and is usually carried out in a specially designed machine, to be described later.

A type of the Pigment Resists is the following:—

RESIST YELLOW C.

300	grms.	Chrome yellow paste.
75	,,	glycerin.
425	,,	6 per cent. tragacanth thickening.
200	..	stannous chloride.
1000		

Print exactly as for the preceding. Dry, dye, wash, etc.



Resists under α-naphthylamine claret.

Sulphite Resists.

WHITE K.S.:—

680	grms.	bisulphite of soda 66½° Tw.
170	,,	water.
85	,,	potassium carbonate (65 per cent. K_2CO_3)

Boil to expel carbonic acid, cool, and add—

100	grms.	starch.
50	..	British gum.
1000		

Boil and cool.

WHITE K.S.Z.:—

100	grms.	water.
200	,,	zinc oxide.
50	..	starch.
115	,,	50 per cent. gum Senegal solution.
5	,,	paraffin wax.
30	,,	Turkey-red oil 40 per cent.

Boil, cool, and add—

500	..	potassium sulphite 105° Tw.
1000		

WHITE K.S.M.:—

800	grms.	potassium sulphite 105° Tw.
200	..	British gum.
1000		

Boil and cool.

Coloured sulphite resists with pigments are based on the following type:—

Blue K.S.U.:—

250	grms.	Ultramarine blue.
40	,,	glycerin.
160	,,	water.

Beat up to a paste, and add—

150	,,	6 per cent. tragacanth thickening.
150	,,	50 per cent. albumen solution.
250	,,	potassium sulphite 105° Tw.
1000		

Sulphite resists are printed on naphtholated cloth, dried, and then dyed, etc., as usual. Coloured resists are given a quick run through the rapid ager to fix the pigment, and afterwards treated as above.

Under Para-nitraniline red sulphites give a better white than tin crystals, but under α-naphthylamine clarets the reverse is the case.

Tannin Resists (Rollfs & Co., Germ. Pat. 113,238).

Owing to the fact that tannic acid does not give a pure white resist under the Azo colours, the tannin resists are only suitable for the production of *dark rich colourings* in blue, green, pink, and yellow, in combination with, and on grounds of, various Azo colours. For this style of work, however, they are much superior to the coloured tin resists, which, at their best, are only capable of yielding light and moderately fast shades, for the unavoidable precipitation of the colour lake—a double tannate of tin and colour base—in "Tin Resists" precludes the possibility of obtaining dark colours of sufficient fastness to washing by this method. On the contrary, with "Tannin Resists" no such precipitation takes place until the printed goods are steamed, so that the colour lake, being produced on the fibre itself, possesses the maximum degree of fastness to soaping. In order to secure the most permanent results, the Tannin Resists are, for the most part, printed on naphthol prepares containing alumina and tartar emetic, both of which form insoluble tannates. The fastness of the colours may also be increased by a run through tartar emetic, after dyeing in the diazo solutions; but, as a rule, this is not necessary.

A suitable naphthol prepare is the following:—

Naphthol Prepare T.R.

I.	25	grms.	β-naphthol R.
	40	,,	caustic soda 36° Tw.
	120	,,	hot water.
II.	25	,,	aluminium hydrate 50 per cent. paste.
	20	,,	caustic soda 36° Tw.
	250	,,	hot water.
	30	,,	ricinoleate of soda 50 per cent.
	75	,,	6 per cent. tragacanth thickening.
III.	10	,,	tartar emetic.
	12	,,	tartaric acid.
	50	,,	glycerin.
	80	,,	caustic soda 36° Tw.
	250	,,	water. Make the whole to—
	1 litre		

Mix I., II., and III., and heat gently until the solution is clear; then add water to make up to volume.

On cloth prepared in the above solution, the following resist colours may be printed:—

TANNIN RESIST COLOURS.

	ROSE T.R.	YELLOW T.R.	GREEN T.R.	BLUE T.R.
Rhodamine 6 G. extra	15	...	...	...
Auramine (concentrated)	...	25	15	...
New methylene blue N.	...	...	5	...
Marine blue S. (Geigy)	...	..	...	12·5
Brilliant green cryst. extra	...	...	5	...
Pure blue II. (B.A.S.F.)	...	...	...	12·5
Crystal violet O.	...	...	...	5
Acetic acid 9° Tw.	250	250	250	240
Acetin	50	50	50	50
Water	240	230	230	200
Starch	120	120	120	100
6 per cent. tragacanth	100	100	100	100
Tartaric acid	25	25	25	10
Oxalic acid	...	...	...	50
Boil, cool, and add—				
Tannin 50 per cent. sol. (in acetic acid)	200	200	200	200
	1000	1000	1000	1000

Print on naphthol-prepared cloth (Naphthol Prepare T.R. for preference); dry and steam 2 minutes in the rapid ager; develop the ground shade by a run through the required diazo solution, and then pass, if required, through a 2 per cent. solution of tartar emetic at 40°–50° C.; wash well, soap, and dry.

Other naphthol prepares may be used, but the above is one of the best for resisting the detrimental action of hot steam. In order further to reduce the unfavourable influence of steaming on the depth of the Azo colour grounds, the goods must be prevented from coming in contact with the copper guide rollers in the rapid ager. Hot metal, especially in conjunction with steam, acts injuriously on the naphthol prepare, and gives rise to irregularities in the dyeing operation. For this reason, therefore, the cloth is best insulated from the guide rollers by fixing lengthwise on the latter a series of wooden bars, thus converting them into a sort of wince.

If it be required to work a resist white in combination with tannin resists, the White Resist K.S.Z. (Sulphite) is suitable. On Para red grounds, claret and black are obtained by printing α-Naphthylamine claret and Azophor black respectively; a brown, by printing a thickened solution of Brown salt R. or G. On claret grounds, only a fairly good red is obtainable, and that by employing a tannin resist colour containing Rhodamine and Auramine, or other suitable yellow and red basic dyestuffs. All these colours may be printed on naphthol grounds along with any class of resists, be they tin, sulphite, or tannin; but the tannin reserves cannot be employed along with tin resists since the latter *cannot* be steamed without tendering the fabric.

For a white resist under both the Azo colour ground and its printed resist, *Resist D.* (sodium tartar emetic and tin crystals—see tin resists) is first applied to the naphtholated cloth, which is then dried and treated in the way described above. Care must be taken to reduce the quantity of tin crystals to its lowest effective point, otherwise, in steaming, the cloth is liable to be tendered. For this reason only small objects, spots and the like, are printed in Resist D.

Another way of working the tannin resist method is to print the colours on white cloth unprepared in any way; steam for an hour, and then, without washing, to prepare the goods in naphthol, dry and dye up at once in the diazo solutions. The preparation in naphthol, if not done on the printing machine, is carried out on a padding mangle, the bottom squeezing bowl of which works partly immersed in the naphthol solution; the goods pass straight through the "nip," face downwards, and are impregnated by the liquor carried up by the bottom bowl, which, as a rule, is wrapped with several thicknesses of calico, in order to transfer a sufficient quantity of liquor to the cloth. By this method of working, it is not possible to print insoluble Azo colours in combination with the resists.

Persulphate Resists.

The employment of persulphates as reserving agents is, in practice, restricted to one style, namely, the production of blue and red effects, obtained by printing a Dianisidine copper blue containing a persulphate on naphtholated cloth, followed by a run through para-nitro-diazo-benzene for the development of Para red (Schäppi).

The presence of persulphates in the blue printing paste has no injurious effect upon the coupling of the tetrazo compounds of Dianisidine with the naphthol in the prepare; but, under the influence of the heat in the drying apparatus attached to the printing machine, the persulphate oxidises any excess of naphthol that may remain on the printed parts, so that no Para red forms on these in the subsequent developing bath. The blue naphthol Azo dyestuff of Dianisidine, already existing on the fibre, remains unaffected in drying, and consequently the ultimate result is a blue pattern on a red ground, or *vice versâ*, according to the pattern printed in blue.

In order to prevent the "dulling" of the red by the copper salt which dissolves out of the blue, the usual developing bath of diazo-p-nitraniline is modified by the addition of ammonium oxalate, and the same addition is made to the final soaping liquors. The goods, too, are developed by passing straight through the "nip" of the mangle bowls, instead of through the liquor in the box beneath.

The following recipes have given good results in practice:—

NAPHTHOL PREPARE B.R.

25 grms. β-naphthol.
40 ,, caustic soda 36° Tw.
850 ,, hot water.
50 ,, Turkey-red oil 40 per cent.
35 ,, acetate of soda. Make to—

1 litre.

BLUE B.R.

16·5 grms. Dianisidine salt (powder).
100 ,, hot water.
12 ,, hydrochloric acid 30° Tw.

Dissolve, cool, and add—

200 grms. ice.
31 ,, nitrite of soda solution 25 per cent. $NaNO_2$.

Allow to stand some time, then add—

540·5 grms. thick flour paste.
50 ,, persulphate of potash crystals
50 ,, cupric chloride 75° Tw.

1000

Make up to 1 litre with a little water or thickening.

RED DEVELOPING BATH.

14 grms. Paranitraniline.
75 ,, hot water.
26·4 ,, hydrochloric acid 30° Tw.

Heat till dissolved, then cool, and add—

150 grms. ice.

And then, at not above 2° C.,—

29 grms. 25 per cent. solution of nitrite of soda.

Allow to act 15 minutes, stirring at frequent intervals; then strain and add—

500 grms. cold water.
30 ,, acetate of soda.
20 ,, oxalate of ammonia crystals, and sufficient water to bring the whole up to 1 litre.

I litre.

On cloth padded in Naphthol Prepare B.R., print Blue B.R., dry quickly over cylinders or in hot air, cool the goods, and pass them at once through the above developing bath, wash them well in the open width with plenty of running water, and then soap at 60° C., also in the open width, through a solution of soap containing 0·5 per cent. soap and 0·2 per cent. oxalate of ammonia; wash, and again soap at 60° C. for 15 minutes in the rope state, and with a soap liquor of the same composition; finally, wash well and dry.

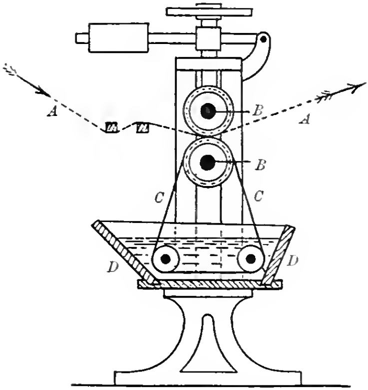


FIG. 75.—Padding machine for Azo resist styles.

With the single exception of "persulphate resists," all other Insoluble Azo colour resist styles are dyed with the several diazo solutions for which formulæ have been given under "The Dyeing of Plain Shades with Azo Colours."

For red grounds:—	Paranitraniline.
,, claret ,,	a-Naphthylamine.
,, scarlet ,,	Chloranisidine.
,, orange ,,	o-Nitrotoluidine.
,, chocolate ,,	Benzidine.
,, brown ,,	mixtures of Benzidine and o-Nitrotoluidine.

In all insoluble Azo colour resist styles the dyeing of the ground, unlike that of plain shades in which the goods pass through the dye liquor, is best carried out by running the printed pieces directly between the bowls of the padding mangle, the dye liquor being supplied to them either by means of a perforated pipe, or from an endless woollen blanket circulating between the mangle bowls and the liquor in the box below. In both cases the washing, etc., arrangements are the same. The two accompanying diagrammatic sketches will make the working details of these machines sufficiently clear.

In fig. 75 A A represents the printed cloth passing through the machine, printed side to the lower bowl; B B the mangle bowls, both of sycamore, wrapped with several thicknesses of calico; C C the woollen colour-feeding blanket; and D D the colour box beneath.

In fig. 76, which shows in section the full arrangement of a dyeing machine for reserve styles, A A A represents the cloth running in the direction of the arrow; B B, the mangle bowls, the *upper one* of sycamore wrapped with calico, the lower one of copper working half immersed in the dye liquor which runs off the cloth; C, the perforated pipe which supplies the dye liquor to the cloth; D, a trough to catch the excess of liquor; O, the overflow pipe of D communicating with the tub F, in which the dye liquor is collected, and from which it is ladled again into the vessel connected with the perforated supply pipe C; E, a brass doctor to clear the copper bowl B of any colour that may be transferred to it from the printed cloth; G G, hot water washing becks; H H, series of hot-water "spirt pipes"; S, soaping beck; M M M M, squeezing bowls, the top one of rubber, the bottom one of copper; W, a cold water washing beck fitted with squeezing bowls P P.

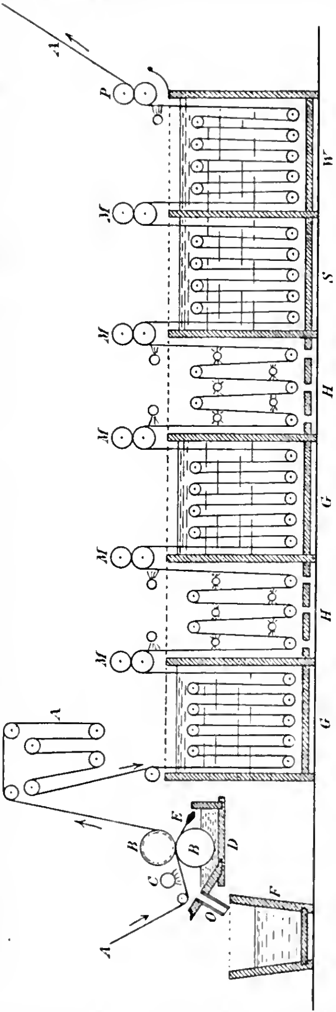


FIG. 76.—Dyeing and washing machines for Azo resist styles.

The cloth, after passing through the first pair of bowls, is allowed to travel some distance in the air, in order to allow time for the naphthol Azo colour to develop completely. The rest of the diagram is self-explanatory. It may be noted that each pair of squeezing bowls is fitted with screw and lever pressure, so that they may be regulated as required for thicker and thinner cloth.

The use of padding mangles constructed on lines similar to the above overcomes two of the most serious difficulties that are likely to be encountered in the dyeing of Azo resist styles. In the first place, regularity and evenness of colour, both as regards depth and shade, is ensured by reason of the fact that the dye liquor being used in small quantities, must be freshened up at very short intervals, and consequently the accumulation of tin salts in the bath is prevented, and with it the destruction of the diazo solution; secondly, the "marking off" of the printed pattern on the ground colour is also avoided by the manner in which the cloth runs through the machine. Being passed through the bowls face downwards, any "marking off" takes place on the feeding blanket or the lower copper bowl: from the first, the stannous chloride is washed off or neutralised in the dye liquor, which suffers a little, but is renewed too rapidly to show any appreciable loss of tinctorial strength; and from the second (copper bowl), the stannous chloride, colour lakes, and thickening are either removed in the same way or scraped off altogether by the brass doctor (E, fig. 76).

Modifications of the Azo Colour Resist Style.

There are two useful methods of producing resist effects under figured or patterned grounds of insoluble Azo colours. In the first, used mainly for white resists, plain bleached cloth is first printed with a tin or a sulphite resist white, then dried gently and *covered* with a fine all-over pattern in a thickened solution of β-naphthol. Hereafter the process is identical with that for dyed grounds described above. The naphthol printed pieces are dyed in the padding machine with any suitable diazo solution, well washed, soured if necessary to clear the white, well washed again, soaped, washed, and dried. In the second and more largely employed method, the goods are prepared in the ordinary way with naphthol. After drying, white and any sort or number of coloured resists are printed, and then the whole is over-printed or "covered" with a fine pattern (check, zephyr, fine line or delicate scroll) in either Red P.N. or Claret A.N., according as Para red or Naphthylamine claret is required in the ground. Goods printed with tin resist colours are now passed at once through tartar emetic (1½ grms. per litre), well washed, soaped, washed, and dried. Tannin resists and coloured sulphite pigment albumen resists require steaming for 2–3 minutes in the rapid ager before they are washed and soaped. Tannin resists are fixed like tin resists in tartar emetic before washing. By operating in this way a great variety of very pretty fancy effects are easily obtainable.

By combining the Azo resist style with the chlorate discharge on Indigo it is possible to obtain many curious mixed effects in red, chocolate, blue, white, and yellow, effects which are suitable for the Eastern and West Coast of Africa markets. These styles depend upon the opposite behaviour of Indigo and Para red towards oxidising and acid-reducing agents. Indigo is destroyed by the former and practically unaffected by the latter, whereas Para red is prevented from developing by the latter, and, when once formed, is almost entirely unacted upon by the former at the strength used to discharge Indigo.

The following is a *résumé* of the operations necessary to the production of combined resist and discharge effects on Indigo and Para red.

(1) Dye the cloth a light shade of Indigo. Dry.

(2) Prepare in β-naphthol. Dry.

(3) Print on a stannous chloride resist white. (White Resist T.B., p. 498.) Dry.

(4) Dye in para-nitro-diazo-benzene (14 grms. Paranitraniline per litre). Wash, sour, wash, soap, wash, and dry. At this stage the goods present the

appearance of a dark chocolate pattern on a light blue ground. The chocolate results from the superposition of red on blue.

(5) Print Chlorate white and Chlorate yellow (see below) with a two-colour pattern of such a design as will ensure the falling of the two colours over both the blue and chocolate.

CHLORATE DISCHARGES.	WHITE.	YELLOW.
Water	475 grms.	125 grms.
British gum	250 ,,	180 ,,
Chlorate of soda	100 ,,	100 ,,
Lead nitrate	... ,,	175 ,,
Boil and add		
Citric acid	50 ,,	50 ,,
Cool and add		
Red prussiate of potash	25 ,,	20 ,,
Water	100 ,,	50 ,,
	1000	1000

(6) Steam 4–5 minutes, or less, in the rapid ager. This discharges the Indigo, leaving, at this stage, a red where the colours fall on the chocolate, and a white where they fall on the blue.

(7) Pass through a solution of sulphate of soda (150 grms. Glauber salt, and 25 grms. sulphuric acid 168° Tw. per litre) at 40° C.; wash well.

(8) Chrome in a ½ per cent. solution of bichromate of soda neutralised with ammonia; treat for 5–8 minutes at 40° C., wash well, and dry if for yellow. If orange is required, treat further for 1 minute in a bath containing 10 grms. bichromate and 40 grms. quicklime per litre of water at the boil; wash again and dry.

If the first and second patterns consist of longitudinal and transverse stripes respectively, the ultimate effect of the above series of operations will be that of a six-colour check, namely, the original blue of the ground, white and yellow (or orange) where the blue has been discharged, red where the chlorate white has crossed the chocolate formed by red falling over blue, and a reddish-orange or a scarlet where the chlorate yellow (or orange) is superposed on red.

The same result is attained by printing Para red on the naphtholated Indigo-dyed cloth instead of the Resist White T.B. With the exception of dyeing, which in this case is unnecessary, the rest of the process is precisely as above.

Resists under Nitroso-blue.

The formation of Nitroso-blue, which is produced on the fibre by the condensation of the nitroso bases of tertiary amines with phenols, can be prevented by means of reducing agents like stannous salts and alkaline sulphites. On this property is based the process of resisting Nitroso-blue.

The cloth padded in the Nitroso-blue bath is carefully dried in the hot flue and then printed with the resist pastes; steamed for 3 minutes in the rapid ager to develop the blue ground; passed through a solution of tartar emetic to fix the colours, and then washed and soaped.

"Tin resists" are only suitable for coloured effects, since they give an impure white, due in part to the presence of tannin in the blue padding liquor, and in part to the yellow tinge always given by tin salts to white calico. "Sulphite resists," on the other hand, yield a perfect white; but as they do not destroy the tannin, the white is apt to become tinted with blue, from the loose colour removed from the cloth during the washing operations. Nitroso-blue, being in point of fact a basic colour, is precipitated by tannin, so that if any tannate of antimony is left on the white reserved portions of the cloth, it acts as a mordant for the colour washed out of the ground shade. In many cases the ground shade loses no colour at all in washing, and in such cases a simple "sulphite white" may be used with success. On the other hand, it is always safer to guard against any possible chance of the "white" being soiled by adding sufficient caustic soda to the sulphite to effectually destroy the tannin. In this way only can perfect white resists be obtained with certainty.

A fruitful cause of imperfect white resists under Nitroso-blue is to be found in the over-drying of the padded cloth. The drying of these blues is always best carried out in hot-air chambers at as low a temperature as possible; and if properly performed, the cloth ought to be quite a bright yellow colour without a trace of grey. If hot-air machines are not available, cylinder machines may be used; but the first few cylinders must be wrapped with calico, and the rest kept as cold as is consistent with perfect drying. With cylinder drying, a white resist may be printed on the cloth before padding in the blue liquor: this method ensures a better white, since the blue cannot develop on the printed parts however hard the cloth may be dried.

The following recipes, taken from practice, have given good results, and will illustrate the principles of the Nitroso-blue Resist style:—

Nitroso or Resorcin Blue Padding Liquor I. (for Hot-air Drying).

24	grms.	Nitroso-base M. 50 per cent. paste (Höchst).
60	,,	warm water.
10	,,	hydrochloric acid 36° Tw.

Dissolve and add—

20	grms.	Resorcin.
50	,,	water.
35	,,	tannic acid.
35	,,	water.
70	,,	10 per cent. solution oxalic acid.
50	,,	6 per cent. tragacanth thickening.
396	,,	water.

Mix well, and before use stir in for some time—

10	grms.	phosphate of soda.
240	,,	water. Make up to—
1 litre.		

Nitroso-Blue Padding Liquor II. (for Cylinder Drying).

25	grms.	Nitroso-base M. 50 per cent. paste.
30	,,	ortho-phosphoric acid 50 per cent.
75	,,	warm water.
20	,,	Resorcin.
50	,,	water.
50	,,	tannic acid.
200	,,	water.
5	,,	oxalic acid.
200	,,	water.
50	,,	6 per cent. tragacanth thickening. Make up with water to—
1 litre.		

Pad the white cloth in either of the above solutions, dry gently, and print on any of the following resists:—

White Resist I.

250 grms. British gum (powder).
750 ,, potassium sulphite 90° Tw.
1000

Heat to 70° C. and cool.

White Resist II.

225 grms. British gum (powder).
600 ,, potassium sulphite 90° Tw.
175 ,, caustic soda 90° Tw.
1000

Heat to 70° C. and cool.

White Resist II. is the most generally useful. Coloured resists are made from basic colours; they contain no tannin, as there is sufficient for their fixation in the blue padding liquor. The resisting agent may be either stannous chloride or potassium sulphite.


Sulphite resist under Nitroso-blue.

Tin Resists.

	Red N.	Pink N.	Yellow N.	Green N.	Blue N.
Auramine O.	5	...	30	20	...
Rhodamine 6 G. extra	25	10	...	...	...
New methylene blue N.	...	...	...	...	10
Brilliant green cryst. extra	...	...	...	10	...
Acetic acid	200	200	200	200	200
Citric acid	25	25	25	25	25
Water	355	355	355	355	375
Starch	90	90	90	90	90
6 per cent. tragacanth	150	170	150	150	150
Acetin	50	50	50	50	45
Boil, cool, and add—					
Stannous chloride	50	60	50	50	55
Acetate of soda	50	40	50	50	50
	1000	1000	1000	1000	1000

Sulphite Resists.

The following coloured resists are based upon the process published by Messrs Meister, Lucius & Brüning, the patentees of Nitroso-blue. They give bright, fast colours, and a sharp, clear-cut impression of the engraving. In composition they consist essentially of basic colouring matter, thickening, and sulphite of potassium. The addition of antimony salts is not absolutely necessary, but it adds to the fastness and brightness of the colours, and is therefore an advantage.

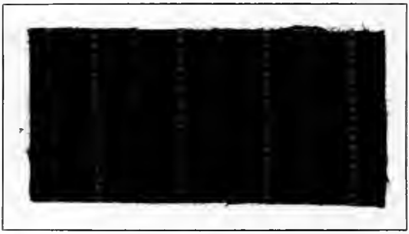
Coloured Sulphite Resists B.S.

	Red.	Pink.	Yellow.	Blue.	Green.	Olive.
Auramine O.	5	...	30	...	20	23
Rhodamine 6 G. extra	25	15	...	...	...	1
Malachite green cryst.	...	...	...	...	10	...
New methylene blue N.	...	...	...	10	...	6
Water	200	215	200	220	200	200
Glycerin	30	30	30	30	30	30
Thickening A.T.	590	590	590	590	590	590
Potassium sulphite 90° Tw.	150	150	150	150	150	150
	1000	1000	1000	1000	1000	1000

Violet = mixtures of pink and blue.
Brown = ,, red, yellow, and a little blue.
Orange = ,, red and yellow.

Thickening A.T. (for above).

40 grms. antimonin.
300 ,, water.
50 ,, starch.
200 ,, 6 per cent. tragacanth thickening.
590 Boil and cool.



Red and Green resists under Nitroso-blue.

After printing either tin or sulphite resists on the cloth padded in Blue liquor I. or II., the goods are dried, and steamed for 3 minutes in the rapid ager at 100° C.; then passed through a tartar emetic bath, and finally washed and soaped.

For obtaining white effects by printing on plain cloth before padding in Nitroso-blue, either of the two following resists are suitable. Both yield a good white, and both withstand the run through the blue padding liquor, and drying over steam-heated cylinders.

Resist White III.

55 grms. glue.
180 ,, water.

Allow to soak until the glue is quite soft and then add—

200 grms. British gum.
305 ,, water.
30 ,, acetic acid 50 per cent.
70 ,, sodium tartar emetic. Boil, cool, and add—
120 ,, stannous chloride.
40 ,, acetate of soda.
1000

Resist White IV.

150 grms. China clay paste 50 per cent.
170 ,, water.
90 ,, starch.
220 ,, gum Senegal 50 per cent. solution.

Boil, turn off steam, and whilst hot add—

20 grms. white wax } previously dissolved.
75 ,, turpentine }

Mix well in, cool, and add—

275 grms. potassium sulphite 90° Tw.

1000

Print on plain white cloth; dry well, and then pad in Nitroso-blue H. in a mangle similar to that used for Azo colour resists; dry at once, but not too hard, over a cylinder drying machine, the first four cylinders of which are wrapped with calico. Then steam for 3 minutes in the rapid ager at 100° C.; pass through a solution of tartar emetic; wash well, soap, wash, and dry.

The Nitroso-blue style finds its chief application in the production of flannelette goods, and especially of those in which the printed pattern is "raised" through to the back of the material.

Aniline Black Resist Styles.

The introduction by Lightfoot, in 1863, of a practical method of printing Aniline black, almost immediately suggested to calico printers the desirability of producing white and coloured effects under printed "covers" and "pads" of so important and fast a colour. The first experiments in this direction were based upon the fact that Aniline black is an oxidation product; hence the earliest resists consisted of reducing agents. Later on it was ascertained that the presence of a mineral acid, either free or produced in steaming or ageing, by the dissociation of an unstable salt, was quite as essential as the presence of an oxidising agent to the development of the black. Alkaline salts and other neutralising substances, therefore, were employed, either as such or in combination with reducing agents, to prevent the formation of Aniline black in certain parts of the cloth. By printing patterns in colours containing sulphocyanides, xanthates, thiosulphate of soda, tannin, sodium carbonate, chalk, etc., many excellent results were obtained; but it was not until Prud'homme brought out his well-known process that the "Aniline Black Resist Style" became popular in the calico-printing industry. Up to that time it had only been possible to dye the cloth on one side, and that by means of printing with a "pad roller." The goods were first printed with a resist, then dried, and padded with thin Aniline black paste on the printing machine. In Prud'homme's process, however, the second printing is dispensed with, the cloth being "blacked" by passing through a solution of Aniline, containing all the ingredients necessary to the formation of Aniline black when the cloth is subsequently steamed. In this way the material is dyed uniformly on both sides, and has a much richer appearance than when the black ground is printed by machine.

Although all patterns on Aniline black grounds, except those produced by direct "blotch" printing, are obtained by means of resist pastes of one sort or another, they are classed in two different categories according to their mode of execution. If the resist pastes are printed on the cloth before the black padding liquor is applied to it, the effects so obtained are known as "resists"; if, on the contrary, the cloth is padded with the black liquor before the resists are printed, they are known in the trade as "discharges." Properly speaking, they are not discharges at all, for the black is only developed by steaming *after* the "resists" have been printed, and is not developed on the printed parts; but the term "discharge" is useful to distinguish between the two methods.

The resist and the "discharge" processes both have their advantages and disadvantages. In the first, pure whites and bright colours are almost always obtained without the slightest difficulty, but the impression of the pattern is often lacking in sharpness. On the other hand, a crisp definition of the design, with clear-cut edges, is characteristic of the "discharge" process; but unless the utmost care is exercised at every step in its application, the whites and colours are very liable to become dull and dirty in appearance. In spite of its greater difficulty, however, the "discharge" process is usually preferred for high-class work, because, when employed under favourable conditions, it yields colour effects of greater depth, richness, fastness, and variety than can be obtained from the resist process.

Prud'homme Aniline Black Resist Styles.

Prud'homme's original process is still in use at the present time, but many improvements and some modifications of it have been introduced by various chemists and practical calico printers, most of the improvements having been effected in the direction of applying new colouring matters and different resisting agents.

Briefly described, the process is as follows:—The white bleached cloth is first padded in "Prussiate black" (Aniline hydrochloride, chlorate of soda, and potassium ferrocyanide); it is then gently dried, care being taken not to oxidise the Aniline, and then printed with the resist pastes, dried, and steamed 3–4 minutes in the rapid ager to develop the black ground and to fix the reserve colours; finally, it is "chromed," washed, soaped, and dried. This method of working constitutes the "discharge method" so called.

The resist method is almost identical with the above, except that the resists are printed on plain white cloth, well dried, and sometimes steamed, then padded in the black liquor, dried again, steamed 3–4 minutes, "chromed," washed, and soaped.

Resist colours for the discharge process may either contain, or be entirely free from, insoluble plastic bodies, but those for the resist process only give good results when they contain insoluble resisting agents such as zinc oxide, chalk, etc.

The most commonly used resisting agents are zinc oxide, zinc acetate, sodium acetate, magnesium acetate (all of which neutralise the acidity of the black), and sulphite of potash and sulphocyanide of potash, which act as reducing agents.

For coloured resists, a good many colouring matters are available; but, with the exception of Basic colours, Pigment colours, and Direct colours, very few find any extensive application in practice. The alkalinity of the vat dyestuff printing pastes has been utilised with success in special styles, and the Sulphide colours are also occasionally employed for faster classes of work. On the whole, however, the Basic colours give the finest and largest range of colours; and being miscible in any proportions, they are consequently the most useful, since they yield both brilliant and subdued tints, and dark, full shades. The pigment colours are used mainly for yellows and oranges in goods for the foreign markets; and the direct colours are employed solely for "crimps,"—a style requiring the colours to withstand the action of strong caustic soda solutions.

Within recent years Plusanski has succeeded in perfecting a process for producing Azo colour resists under Aniline black; so far, however, the process, though yielding excellent results under both "covers" and dyed blacks, has not become general.

Numerous formulæ have been suggested and employed for resisting Aniline black; for they are all founded on the same principles, and no good purpose would be served by enumerating them. In the following descriptions of the more important methods of resisting Aniline black, the recipes are taken, for the most part, from actual practice, or from the results of bulk trials; and where this is not the case, they are quoted from the published articles of those who have had experience of their practical working. The same remarks apply equally to the handling of the goods, so that, on the whole, the processes given below may be taken as representing not merely concrete, but also typical examples of the means and methods in current use.

"Discharge" Styles on Aniline Black.

In this process, as already mentioned, the cloth is padded in Aniline black liquor before the colours are printed upon it. The condition of the cloth after padding and drying is perhaps the most important factor in determining the purity of the white and the brilliancy of the colours in the finished print.

In order to secure the best results, the following precautions must be observed:—

(1) The "discharge" pastes must be printed on cloth on which the black is unoxidised. This is absolutely essential, and can only be ensured by using a freshly prepared "black" solution, and by drying the cloth at as low a temperature as the speed of the drying apparatus will allow. Aniline black liquors which have stood for some time become partly oxidised and impart a greenish colour to the cloth. The same effect is also produced by drying at too high a temperature. In either case dirty whites and flat colours are the result. On emerging from the drying machine the goods ought to be of a light yellow tint without a trace of green. If they are at all green they are unsuitable for light-coloured effects, and must be utilised if possible for the printing of opaque pigment yellows, oranges, or greens.

(2) After drying, the padded goods are cooled at once to prevent the oxidation of the aniline, and are then printed as soon as possible. In the warm atmosphere of a printworks, the black develops very rapidly, especially if the pieces are warm.

(3) Over-drying after printing must be carefully avoided, since the richness and beauty of the black is impoverished thereby.

(4) The printed goods must be steamed immediately after printing, and before the cloth has become a dark green shade. The steam must be at 90°–95° C. and ought not to be too moist, otherwise the colours are apt to "run," and the "whites" invariably become yellowish.

(5) The whole process, from start to finish, must be carried out without any considerable interval being allowed to elapse between the various operations. This applies in an equal degree to the washing and chroming, etc., which should be proceeded with as soon as convenient after the goods are steamed.

PROCESS:—Pad the cloth in Black P. or Black P.S.

BLACK P.

I.	75	grms.	Aniline salt.
	200	,,	water.
II.	35	,,	chlorate of soda.
	400	,,	water.
III.	40	,,	yellow prussiate of potash.
	250	,,	water.
	1000		

Mix I., II., and III. immediately before use. Black P. is useful for heavy goods and ordinary mercerised goods; for the latter it may even be diluted somewhat (3 parts black, 1 part of water), and still give a full shade.

Black P.S.

I.	85	grms.	Aniline salt.
	150	,,	water.
	50	,,	6 per cent tragacanth thickening
II.	39	,,	chlorate of soda.
	300	,,	water.
III.	45·5	,,	yellow prussiate of potash.
	330·5	,,	water.
	1000		

Mix I., II., and III. in the cold, and make to 1 litre before use. Black P.S. is employed when a denser black is wanted; for most purposes, however, the weaker and cheaper Black P. is sufficiently dark.

After padding, which is done in any of the ordinary types of padding machine, the goods are carefully dried, and then printed with any of the resists or "discharges" given below.

Pigment "Discharges."—Pigment and lake colours are fixed by albumen. The resisting agents employed are either soda ash or acetate of soda.

	Yellow P.	Orange P.	Red P.	Blue P.	Green P.
Chrome yellow paste	400	...	...	...	...
,, orange ,,	...	350	...	...	...
,, lemon ,,	...	...	...	...	150
Ultramarine blue	...	...	...	330	...
Guignet's green	...	...	...	...	200
Vermilion	...	...	200	...	...
Glycerin	...	...	...	30	30
Water	...	...	250	105	...
Soda ash	75	75	75	75	...
Acetate of soda	...	...	...	...	200
Gum tragacanth 6 per cent.	325	375	200	110	200
Albumen solution 50 per cent.	200	200	250	350	200
Turpentine	...	...	25	...	20
	1000	1000	1000	1000	1000

Grind the ingredients together in a mill before use. Print on black padded cloth; steam 3–4 minutes in the rapid ager; pass through a $\frac{1}{2}$ per cent. solution of bichromate of soda at 50°–60° C., wash well, soap, and dry.

Zinc Oxide "Discharges."—In these discharges, the colouring matters employed are the basic colours. Their fixation is effected by the zinc ferrocyanide formed by double decomposition during the steaming. The zinc oxide process was worked out and patented by W. E. Kay at the Thornlie Bank Printworks, and yields very bright and fairly fast colours, especially when magnesium acetate is used along with the zinc oxide. The addition of albumen increases the fastness of the colours, and their brilliancy is further increased by padding the cloth in Turkey-red oil previous to passing it through the black bath. Excess of oil must be avoided, otherwise the development of the black is retarded. In practice, a solution of ammonia-oleine (sulphoricinoleate of ammonia), corresponding to $1\frac{1}{4}$ per cent. of fatty acid, is used with success in conjunction with either Black P. or Black P.S. Pad the cloth in the oil, dry over cylinders, cool, and pass through the "black" bath, dry in hot air, and print on the "discharges." Then steam, etc., as above.

The best whites are produced by a mixture of potassium sulphite, sodium bisulphite, and acetate of soda. Light colours are improved also by the addition of the same mixture to the paste used for reducing them to shade. For dark colours, zinc oxide and magnesium acetate give satisfactory results, without any further addition of other resisting agents.

In all zinc oxide resist colours it is advantageous to add a little albumen for the purpose of rendering them more resistant to the action of soap. Soaping increases the beauty of the black, the brightness of the colours and white, and in many cases is necessary, if only to get the cloth into fit condition for finishing. Hence, if the balance of the colour scheme is to be preserved, each colour must be fairly fast to soaping.

In this respect the following colours can be recommended: they give very bright and transparent shades, of excellent fastness to washing and soaping, especially when printed on "oiled" cloth, and they possess the further merit of having withstood the test of several years' practical application on the large scale.

BASIC COLOUR RESISTS OR "DISCHARGES" (ZINC OXIDE AND MAGNESIUM ACETATE).

	RED.	PINK.	GOLD.	YELLOW.	GREEN.	BLUE.	NAVY.	PURPLE.
Rhodamine 6 G. extra	23	10	0·5	...	...	...	...	...
Rhodamine B. extra	...	2	...	...	...	..	...	.
Auramine O.	2	...	20	...	...	...	...	...
Acridine yellow G.	...	..	...	20	22	...	...	...
New solid green 2 B.	...	...	...	...	10	...	...	..
Thionine blue G.O.	...	...	...	...	...	20	...	...
Marine blue S.	...	...	...	...	...	...	20	...
Methyl violet B. extra	...	...	...	...	...	..	...	20
Glycerin	30	20	30	30	30	30	30	30
Water	150	133	114·5	115	110	115	115	115
Dissolve, and add—								
Cold water	...	35	35	35	30	35	35	35
6 per cent. tragacanth thickening	95	100	100	100	98	100	100	100
Discharge paste A.	600	600	600	600	600	600	600	600
Mix well in, and add—								
Albumen solution 50 per cent.	100	100	100	100	100	100	100	100
	1000	1000	1000	1000	1000	1000	1000	1000

Orange = { 1 part red.
3 parts gold.

Olive 1.6.2 = { 1 part pink.
6 parts yellow.
2 ,, blue.

Brown 8.24.1 = { 8 ,, pink.
24 ,, yellow.
1 part blue.

Peacock blue = { 1 ,, green.
3 parts blue.

Grey shades are difficult to mix from basic colours, for reasons already dwelt upon in the section on "Compound Shades"; they are usually made, therefore, from pigments. Thus—

Grey :— { 140 grms. Ultramarine blue (powder).
70 ,, lampblack (powder).
490 ,, 6 per cent. tragacanth. Grind together, and add—
200 ,, 50 per cent. albumen solution.
200 ,, acetate of soda.

1 litre. Grind the whole before use.

Discharge Paste A. (for Basic Discharge).

100	grms.	zinc oxide.
150	,,	magnesium acetate.
250	,,	6 per cent. tragacanth thickening.
100	,,	starch paste.
600		

Reducing Paste (for Light Shades).

700	grms.	Discharge paste A.
250	,,	White discharge B.
50	,,	40 per cent. egg albumen solution.
1000		

White Discharge B.

100	grms.	starch.
60	,,	British gum.
300	,,	potassium sulphite 90° Tw.
290	,,	water. Boil, and add—
150	,,	sodium acetate. Cool, and add—
100	,,	bisulphite of soda 66° Tw.
2	,,	Ultramarine blue (for sightening).
1000		

The above paste gives an exceedingly pure white on freshly padded cloth. If the cloth has become slightly green, a good white can still be obtained by printing Resist B.N.F., which contains a little "hydrosulphite."

Resist White B.N.F.

385	grms.	starch paste.
385	,,	6 per cent. tragacanth thickening.
30	,,	Hydrosulphite N.F. conc.

Heat to 60°–70° C. to dissolve the hydrosulphite, cool, and add—

200	grms.	acetate of soda.
1000		

The above colours and white discharges are printed on cloth prepared as follows:—

1*st.* Pad in:— 100 grms. ammonia Turkey-red oil 25 per cent.
1900 ,, water.
2000 = 1¼ per cent. fatty acid.

Basic colour "discharges" on Aniline black.

2nd. Dry and pad in either Black P. or Black P.S.; dry gently, so that the cloth leaves the drying machine with a light yellow tint only.

After printing, the goods are dried carefully and steamed at 90° C. for 2–3 minutes in the rapid ager. They are then passed in the open width through a lukewarm "chrome bath" (5 grms. bichromate of soda per 1000 grms. water), washed well, soaped lightly at 60°C., washed and dried.

Coloured "discharges" may also be obtained with zinc acetate instead of the foregoing, but they are neither so bright nor so fast.

COLOURED "DISCHARGE" WITH ZINC ACETATE.

20	grms.	basic dyestuff.
200	,,	water.
50	,,	acetic acid.
Dissolve, and add		
280	,,	6 per cent. tragacanth thickening.
300	,,	starch paste.
150	,,	zinc acetate in crystals.
1000		

The zinc acetate prevents the development of the black during steaming and, by double decomposition with the yellow prussiate, forms zinc ferrocyanide, which fixes the basic colour. Albumen has been recommended as an addition to zinc acetate resists, but its use is somewhat irrational, since soluble zinc salts have a tendency to coagulate the albumen in the printing paste.

Zinc oxide alone gives very bright resist effects, but the colours have the appearance of pigments, owing to the large amount of solid matter they contain In some styles this is an advantage, whereas for sateens and flannelettes the more transparent the colour the better.

Generally speaking, the zinc oxide content of colours for these latter classes of work ought not to exceed 10 per cent.

BROWNING'S PROCESS.—As tannate of antimony is the best mordant for basic colours, many attempts were made to apply it in the Aniline black resist styles. The earlier experiments, which consisted in adding various reserving agents to mixtures of basic colour and tannin, gave very inferior results, and the problem was left unsolved until Browning, of the Broadoak Printworks, Accrington, introduced his patented process. This consisted in padding cloth mordanted in the usual way (as for dyeing) with tannic acid and tartar emetic in a prussiate black, drying as usual, and then printing on a thickened mixture of basic colour solution and acetate of soda, followed by steaming, "chroming," and washing. Acetate of magnesium and acetate of zinc may also be used as resists, and are indeed to be preferred, as their hydrates exercise little or no injurious influence on the basic colours. Acetate of soda, on the contrary, if used in excess, is apt to yield bad results with some of the basic colours, especially if they be delicate in shade.

Acetate of soda "discharges" contain from 15–20 per cent. by weight of acetate of soda, according to the depth of the engraving.

During steaming, the basic colour combines with the tannate of antimony to form an insoluble lake, while the metallic acetates prevent the development of the black on the printed parts of the cloth. White effects are best obtained by means of a strongly alkaline "sulphite" or "acetate" paste, which destroys the tannate of antimony on the cloth, but in many cases, such, for instance, as superposition effects of colour on white, this is inapplicable, and must be replaced by the ordinary acetate of soda, zinc, or magnesium, or the sulphite of potash pastes. Although, under proper conditions, these give sufficiently good whites, they cannot compare with the white obtained by Prud'homme's method for purity.

The following is a *résumé* of the Browning process:—

(1) Pad the cloth in—
12·5 grms. tannic acid.
1000 „ water. Dry.

(2) Fix the tannin by a run through—
10 grms. tartar emetic
5 „ chalk
1000 „ water
at 30°–40° C.

Well wash in water.

(3) Open soap at 75°–80° C. in a neutral soap bath containing $2\frac{1}{2}$ grms. soap per litre. Wash well and dry. Soaping, curious though it may appear, is one of the most important operations in the process. Experience has shown beyond doubt that good whites, good colours, and a full, rich black cannot be obtained unless the tannin mordanted goods are soaped, and thoroughly well washed afterwards.

(4) Slop-pad in any type of mangle padding machine with Black P. or P.S. Dry as usual for Aniline black resist styles and then—

(5) Print on the discharge colours given below.

(6) Dry and steam for 2–4 minutes in the rapid ager at 85°–90° C.

(7) "Chrome" in a $\frac{1}{2}$ per cent. solution of bichromate of soda at 30° C. Wash well, soap lightly, wash and dry.

The whites and colours are prepared according to the following directions:—

WHITE "DISCHARGES."

	1	2	3	4	5
Zinc oxide 50 per cent. paste	200	...	...	...	...
Starch paste 12 per cent.	400	...	...	300	400
Tragacanth 6 per cent.	250	...	...	425	225
British gum	...	80	200	...	...
Water	...	290	180	...	...
Caustic soda 90° Tw.	...	...	120	...	...
Sulphite of potash 90° Tw.	...	300	500	...	...
Bisulphite of soda 66° Tw.	...	100	...	...	125
Hydrosulphite N.F. conc.	...	...	...	25	...
Ultramarine blue	2	2	2	2	2
Acetate of soda	150	150	...	250	250
Starch	...	80	...	...	...
	1000	1000	1000	1000	1000

Nos. 1, 2, 4, and 5 are suitable for most classes of work; No. 3 for styles in which large white objects appear, or which have no superposition effects over or under the white. All five are strong enough for the finest patterns.

The coloured discharges may be made up from either sodium, zinc, or magnesium acetates. The two last give the brightest colours taken altogether, and zinc acetate gives the fastest, by reason of the fact that an additional mordant is introduced by the formation of ferrocyanide of zinc. In preparing the printing pastes, the basic colour is first dissolved in suitable solvents, and then added to a mixture of water and British gum; the whole is then heated to dissolve the gum, and when the paste is perfectly smooth it is cooled down to about 30° C., at which temperature the zinc and sodium acetates are added. They dissolve readily in the lukewarm paste without any other assistance than an occasional stirring up. With magnesium acetate, which is most conveniently prepared in solution, the procedure is somewhat different. The dyestuff solution, together with a little thickening, is added lukewarm to a thickened solution of the acetate previously prepared, and kept as a stock paste.

BASIC COLOUR DISCHARGES FOR BROWNING'S PROCESS (ACETATE OF SODA).

	RED.	PINK.	ORANGE.	YELLOW.	GREEN.	BLUE.	VIOLET.
Rhodamine 6 G. 100 per cent.	23	15	7·5	...	...	...	...
Auramine O.	2	...	22·5	20	...	...	...
Acridine yellow G.	...	...	...	...	8	...	...
New solid green 2 B.	...	...	...	...	16	...	...
Methyl violet B. extra	...	...	...	...	...	...	20
Thionine blue G.O.	...	...	...	...	...	20	...
Water	305	310	300	310	326	310	310
Acetic acid 9° Tw	150	155	150	150	150	150	150
Glycerin	50	50	50	50	50	50	50
Methylated spirits	20	20	20	20	...	20	20
British gum	200	200	200	200	200	200	200
Heat, and cool to 30° C., and add							
Acetate of soda	250	250	250	250	250	250	250
	1000	1000	1000	1000	1000	1000	1000

For a Dark royal blue replace Thionine blue by Marine blue.
,, ,, Bluish green use Solid green 2 B. without any yellow.
,, ,, Brown take = { 14 grms. Auramine O. / 4 ,, Methyl violet B. extra / 5 ,, Rhodamine 6 G. extra } per kilo. of colour as above.
,, ,, Reddish Purple = { 16 ,, Methyl violet 6 R. / 4 ,, ,, ,, B. extra } per kilo. of colour.

Olives and various other compound shades may be made in a similar manner from suitable mixtures of blue, yellow, and pink.

BASIC COLOUR "DISCHARGES" FOR BROWNING'S PROCESS (ACETATE OF ZINC).

Instead of 250 grms. of acetate of soda use 150 grms. of zinc acetate (crystals). Thus—

20–25	grms.	basic colour.
310–305	,,	water.
150	,,	acetic acid 9° Tw.
50	,,	glycerin.
20	,,	methylated spirits.
200	,,	British gum. Heat and cool, then add
150	,,	zinc acetate.
100	,,	water or gum solution.
1000		

BASIC COLOUR "DISCHARGES" (MAGNESIUM ACETATE).

Type:—

20–30	grms.	basic dyestuff.
205–195	,,	water.
100	,,	acetic acid 9° Tw.
25	,,	methylated spirit.
50	,,	glycerin.
100	,,	British gum. Dissolve, cool, and add—
500	,,	magnesium thickening.
1000		

MAGNESIUM ACETATE THICKENING.

400	grms.	magnesium acetate 40° Tw.
100	,,	British gum.
500		

The magnesium acetate is prepared by saturating acetic acid with magnesium carbonate:—

1000	grms.	magnesium carbonate.
3000	,,	acetic acid 12° Tw.
4000		

Add a slight excess of the carbonate, and when no more carbonic acid is evolved heat the solution gently until the filtered liquor contains no more iron, which is always present in commercial carbonate of magnesium; then allow to settle, decant the supernatant liquor, and neutralise with acetic acid. Set at 40° Tw.

The printing, steaming, etc., of the three foregoing classes of "discharge" colours, are identical in every respect.

Another method of working the Browning process consists in utilising sulphite of potash as reserving agent in colour resists. The preparation of the printing pastes is practically the same as for Nitroso-blues, except that no tartar emetic is necessary, and that the percentage of sulphite is increased. Sulphite of potash may also replace a portion of acetates of soda, zinc, and magnesium in the colours given above, but care must be taken to employ only such basic dyestuffs as will withstand its powerful reducing action.

The colours produced by Browning's method have the advantage of containing no insoluble matter, neither do they impart any stiffness to the cloth, nor fill up the fibre like the zinc oxide resists. They possess a beautiful quality of transparency, and are unsurpassed for softness of effect. In brightness, however, they fall far behind the zinc oxide colours; and as the latter also yield subdued effects, with a considerable amount of transparency, they have practically displaced the acetate basic colour discharges on antimony tannate.

Apart from all questions of artistic value, the Browning process is too expensive and slow to compete with the zinc oxide process, which, when properly handled, leaves little to be desired in the way of either brightness, softness, transparency, or fastness of the colours, and which, as regards the purity of the whites, is superior.

For flannelettes and certain sateen goods, in which a maximum softness of the cloth is essential to the attainment of the best results, and for rich effects of dark colours on cotton velvet, the Browning process is still used to a limited extent; for all other styles it has been discarded by most printers.

With a view to shortening the process, the direct addition of tannin to the black padding liquor has been suggested. Such an addition certainly does away with the six operations of tanning, drying, fixing, drying, soaping, and drying, that the cloth is put through before padding black, but it is open to several objections, and is at most only a poor substitute for the previous mordanting of the cloth. In the first place, not more than 2½ grms. of tannic acid per litre of black solution can be used without affecting the beauty and fulness of the ultimate black; secondly, this quantity of tannin is insufficient properly to fix even medium shades of basic colours; and thirdly, the colours themselves are neither so bright, nor so fast, nor so intense as those obtained by means of the original and more rational process.

CABERTI, ROGGIERI, AND BARZAGHI'S PROCESS.—Owing to the difficulty of obtaining satisfactory resists with large patterns on flannelette goods by the ordinary methods, the above three chemists devised the following process, which they claim has given excellent results.

With the intention of fixing the basic colours, they employ the condensation product of resorcin with formaldehyde, and along with this they use hydrosulphite in place of the usual resisting agents. In this way they state that greater regularity of work and brighter shades are assured, especially when Hyraldite W. is employed.

COLOUR "DISCHARGES."

	RED.	YELLOW.	GREEN.	BLUE.
Rhodamine 6 G.	30	...	...	...
Thioflavine T.	10	35	10	...
Acridine orange	...	5	...	...
Thionine blue G.O.	...	...	10	...
Marine blue	...	...	...	30
Gum Senegal 50 per cent.	250	250	250	250
Water	100	100	100	100
Glycerin	50	50	50	50
Hyraldite W.	500	500	500	500
{ Resorcin	50	50	50	50
{ Alcohol	50	50	50	50
Paste H. sufficient to make	1 litre.	1 litre.	1 litre.	1 litre.

PASTE H. 500 grms. Hyraldite W.
250 „ gum Senegal 50 per cent.
———
750

Print on cloth padded in Black P. or P.S.; steam 2–4 minutes, chrome, wash, soap, wash, and dry.

Colours prepared as above yield fairly bright and fast shades.

The same authors also recommended the use of Hyraldite W. in conjunction with mordant colours for the production of "discharge" effects on Aniline black. For this purpose they give the following recipes (*Revue générale des matières colorantes*, 1906, p. 164):—

	VIOLET.	YELLOW.	GREY.
Modern violet 40 per cent.	40 grms.	...	20 grms.
Modern yellow paste	...	100 grms.	...
Persian berries ext 52½° Tw.	...	...	30 „
Water	160 c.cs.	160 c.cs.	150 c.cs.
Glycerin	50 „	50 „	50 „
Hyraldite W.	500 „	500 „	500 „
6 per cent. tragacanth	250 „	250 „	250 „
Acetate of chrome 32° Tw.	100 „	100 „	100 „

Phenocyanine may also be used alone for blues and in combination with Persian berries extract for greens.

Print on padded cloth, steam, chrome, wash, soap, dry.

OTHER METHODS OF "DISCHARGING" ANILINE BLACK.—(1) In place of albumen for fixing pigment "discharges," Baumann and others, at Zündel's Works in Moscow, worked out a process based on the coagulating action of formaldehyde on glue. For this purpose they employ a compound of formaldehyde which splits up in steaming, and has no effect on glue in the cold.

GLUE THICKENING.

240 grms. glue.
150 ,, water. } Soak till soft.
430 ,, 5 per cent. tragacanth thickening.
30 Turkey-red oil 40 per cent.

Boil, cool, and add

150 grms. acetate of soda.

1000

FORMALDEHYDE SOLUTION.

1000 grms. formaldehyde 40 per cent.
1250 ,, ammonia 25 per cent.

EXAMPLE OF COLOUR.

400 grms. Ultramarine blue.
1000 ,, glue thickening.
35 ,, formaldehyde solution.

Print on padded cloth, steam, chrome, wash, etc.

(2) The firm of Wegelin, Tetaz & Co., Mulhouse, send out a range of fairly bright zinc oxide colours which merely require mixing with thickening, and are said to be fast without the addition of albumen: they are put on the market under the name of "Express Colours."

(3) The use of sulphocyanides, xanthates, etc., has been practically discontinued, and the processes founded thereon are of too little interest to merit description.

Resists under Aniline Black.

The resist method proper differs from the so-called "discharge" method of producing white and coloured effects on Aniline black, in that the resist colours are printed on *white* cloth *before* it is passed through the black bath. After printing, the goods are dried, padded in Aniline black, steamed, chromed, washed, soaped, and dried. The advantage of carrying out the operations in this order is, that the printed cloth may be kept in stock any reasonable length of time before padding in black,—an advantage which, besides simplifying the process, allows of a large number of pieces being dyed black at the same time. In working the "discharge" process, the production of the black padding machines must be arranged to balance, and must be kept down to the consumption of the printing machines, for if more cloth is padded than can be printed on the same day it is liable to become useless, especially in warm weather, owing to the partial development of the black. Hence the "discharge process," though generally preferred for the best work, entails a good deal of organisation, demands the making of special arrangements, and requires constant supervision at every stage. On the other hand, the course of the "reserve" process runs more or less on the lines of the ordinary works routine; the reserve colours—containing nothing that is likely to deteriorate by several days' exposure to dry air—can be printed at any time, and the printed goods can then be kept until it is convenient to pad them in the black liquor.

For white resists, chalk or zinc oxide, together with soda ash, sulphite of potash, acetates of soda, zinc, or magnesium, sulphocyanide of ammonia, and caustic soda, are the reagents most commonly employed.

The quantity of soluble matter is kept as low as possible to avoid all chance of the resists "running" during the subsequent padding; but chalk or zinc oxide do not give good results without the addition of other resisting substances, hence their inclusion.

Chalk is perhaps the best for white resists, but zinc oxide also gives satisfactory "whites," and is always used for coloured resists on account of its conversion into the ferrocyanide, which acts as a mordant for basic colours. A little albumen may be added to increase the fastness of the colours, but as a rule it is unnecessary, except, of course, in pigment resists.

The following recipes, taken from practice, will be ample to illustrate the principle of the resist process for Aniline blacks dyed on the padding mangle.

RESIST WHITE R.S.

200	grms.	precipitated chalk.
50	,,	potassium sulphite 90° Tw.
50	,,	acetate of soda.
95	,,	water.
5	,,	Ultramarine blue. Beat into a smooth cream, and add—
600	,,	starch paste.
1000		Grind the mixture before use.

BASIC COLOUR RESISTS R.S.

	RED.	PINK.	BLUE.	YELLOW.	GREEN.	VIOLET.
Rhodamine 6 G. extra	16	8	...	...	...	...
Auramine O.	4	..	...	30	...	...
Rhodamine B.	...	8	...	...	...	28
Brilliant green	...	...	...	...	25	...
Thionine blue O.	...	...	20	...	...	...
New methylene blue N.	...	...	...	...	...	3·5
Glycerin	...	...	..	...	...	...
Water	100	100	100	100	150	100
Starch paste	230	234	230	220	175	218·5
Warm together, cool, and add—						
Paste R.S.	650	650	650	650	650	650
	1000	1000	1000	1000	1000	1000

A brighter green, which is more regular in working, is made up of New solid green 2 B. (Geigy) and Acridine yellow G. (Leonhardt).

GREEN R.S.2.

20	grms.	Acridine yellow G.
9	,,	New solid green 2 B.
30	,,	glycerin.
170	,,	water. Dissolve, and strain into—
81	,,	warm water.
40	,,	starch. Boil, cool to 60°–70° C., and add—
650	,,	Paste R.S.
1000		

PASTE R.S.

170	grms.	zinc oxide.
100	,,	water.
20	,,	glycerin.
300	,,	starch paste 15 per cent.
30	,,	turpentine.
30	,,	bisulphite of soda 52° Tw.
650		

TYPE OF PIGMENT RESIST.

GREY R.S. { 100 grms. Ultramarine blue.
60 „ lampblack.
150 „ albumen solution 40 per cent. Grind and add—
40 „ 6 per cent. tragacanth.
650 „ Paste R.S.
1000

Print any of the above colours on white cloth, allow to lie a day or two in a warmish dry place, then pad (straight through the "nip") in Black P. or P.S., dry, steam 3–4 minutes in the rapid ager, chrome, wash, and soap in the open width.

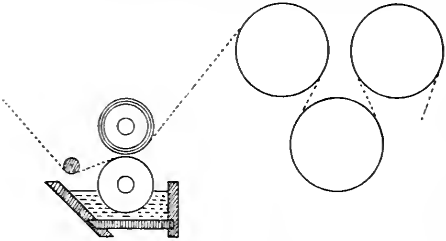


FIG. 77.—Padding machine for Aniline black resist styles.

The padding mangle has two bowls, the lower one of brass and the upper of india-rubber; the cloth runs with the printed side to the brass bowl, which revolves partly immersed in the padding liquor (Black P. or P.S.), as shown in fig. 77.

Resist effects under printed "covers" of Aniline black can be obtained by analogous means. In the case of pigment and basic colours with zinc oxide, albumen is the fixing agent employed; while for basic colours with acetate of soda, fairly good and bright resists are produced with tannin, together with a little "hydrosulphite" and phenol.

(*a*) PIGMENT RESISTS UNDER PRINTED BLACK COVERS.

	YELLOW I.	YELLOW II.	BLUE I.	BLUE II.
Zinc oxide	80	...	80	...
Magnesium acetate 40 per cent.	150	...	150	...
Acetate of soda	...	150	...	150
Starch paste	120	100	...	...
6 per cent. tragacanth . .	200	200	220	300
Albumen 50 per cent. . .	150	150	150	150
Chrome yellow	300	400	...	...
Ultramarine blue	...	...	300	300
Water	...	...	100	100
	1000	1000	1000	1000

(*b*) BASIC COLOUR RESISTS WITH ZINC OXIDE AND ALBUMEN (UNDER PRINTED COVERS).

{ 20 grms. basic dyestuff.
100 „ water.
30 „ glycerin.
50 „ 6 per cent. tragacanth. Cool and add—
650 „ Paste R.S.
150 „ 50 per cent. albumen.
1000

(*c*) BASIC COLOUR RESISTS UNDER PRINTED COVERS (ACETATE OF SODA TANNIN, ETC.).

20 grms. basic dyestuff.
30 ,, glycerin.
10 ,, acetin.
130 ,, water.

Dissolve and add to

100 grms. 6 per cent. tragacanth.
240 ,, water.
60 ,, starch.

Boil and add

50 ,, phenol.

Cool and add

50 ,, tannic acid.
75 ,, Hydrosulphite N.F. conc.
80 ,, water.
5 ,, formaldehyde 40 per cent.
150 ,, acetate of soda.
1000

This recipe, based on that of the Höchst Farbwerke, gives fast resists of sufficient brightness under either copper, vanadium, or prussiate black covers.

Print any of the above cover resists on white cloth ; dry, and over-print with Aniline black ; steam 2–4 minutes, chrome, wash, soap, and dry. The basic colour resists fixed with tannin are passed through tartar emetic before "chroming."

AZO COLOUR RESISTS UNDER ANILINE BLACK.—The property possessed by metallic carbonates of preventing the development of Aniline black has been ingeniously utilised by Pluzanski for the production of directly developed insoluble Azo colour resists under padded or printed Aniline blacks.

A diazo solution containing an acetate of lime, zinc, or lead is printed on naphthol-prepared cloth The cloth is then passed through a solution of soda ash or gaseous ammonia (which precipitates the carbonate or oxide respectively of the metal), and finally well washed to remove all traces of β-naphthol and alkali. After drying, the goods are printed or slop-padded with Aniline black, steamed, washed, etc., and dried.

White, red, and claret resists are obtained by the use of acetate of lime (or zinc, if they are unassociated with lead yellows), and yellow by means of lead acetate. Basic colours may also be employed for pink, green, and blue if printed with zinc oxide and albumen.

Prussian blue and a green obtained from a mixture of Prussian blue and Chrome yellow are also producible by printing ferrous acetate and a mixture of ferrous and lead acetates, followed by suitable treatments to develop the colours.

For white and Azo colour resists alone the process consists of the following sequence of operations:—

(1) Pad the cloth in a 3 per cent. β-naphthol prepare. Dry.
(2) Print on white, red, claret, or orange resists. Dry.
(3) Pass the goods through a tepid solution of soda ash.
(4) Wash in warm water to remove the naphthol and alkali.
(5) Dry, and "cover" or slop-pad in Aniline black P. or P.S.
(6) Dry, and steam 2–3 minutes in the rapid ager.
(7) Wash, soap, and dry.

The treatment in soda ash converts the acetates of zinc, lime, or lead contained in the resists into insoluble carbonates which withstand the subsequent washing operations, and thus act as reserves under the black. If necessary, they may be removed completely after steaming by a short treatment in dilute acid.

For Chrome yellow and Prussian blue resists in combination with the above, the cloth, after steaming, is chromed in—

1000 parts water.
150 ,, sulphate of soda.
10 ,, bichromate of soda.

Neutralise with ammonia and use at 50° C.

Then wash, pass through a slightly acidulated solution of potassium ferrocyanide to develop the Prussian blue, wash again, and re-chrome (if necessary) in a slightly acid ½ per cent. solution of bichromate, wash and dry.

For the production of a white, red, claret, blue, yellow, and green effect on a black ground the following colours may be employed.

Resist Yellow:—250 grms. lead acetate.
600 ,, water.
150 ,, British gum.
1000 Boil and cool.

Resist Blue:— 450 grms. ferrous acetate 30° Tw.
400 ,, acetate of lime 30° Tw.
100 ,, British gum.
50 ,, starch.
1000 Boil and cool.

Resist Green:— 200 grms. acetate of lead.
150 ,, ferrous acetate 30° Tw.
75 ,, acetate of zinc.
400 ,, water.
175 ,, British gum.

Azo Colour Resists.

	Orange.	Red.	Claret.
Metanitraniline	28 grms.	...	...
Paranitraniline	...	22 grms.	...
α-Naphthylamine hydrochloride 36 per cent.	...	...	70 grms.
Hydrochloric acid 36° Tw.	44 c.cs.	35·2 c.cs.	29 c.cs.
Hot water	150 ,,	100 ,,	...
Dissolve, cool, and add—			
Ice water	90 ,,	124·8 ,,	143·5 ,,
Ice	36 grms.	75 grms.	120 grms.
Nitrite solution (28 per cent. $NaNO_2$) .	52 c.cs.	43 c.cs.	37·5 c.cs.
Filter into—			
Resist paste L.P.	600 grms.	600 grms.	600 grms.
Make up to .	1 litre.	1 litre.	1 litre.

Resist Paste L.P.

4000 grms. acetate of lime 30° Tw.
1000 ,, 10 per cent. gum tragacanth thickening.
900 ,, starch. Boil, cool, and make up to 6 litres with acetate of lime 30° Tw.

6 litres.

Print the above six colours on naphthol-prepared cloth; pass through a warm bath of soda ash; well wash in warm water; dry; print a "cover" pattern in Aniline black; steam 2–3 minutes in the rapid ager; pass through gaseous ammonia to neutralise the acidity of the cloth, and to re-precipitate any oxide of iron that may have been converted into chloride; chrome in a neutral bath of bichromate and sodium sulphate to fix the lead salts; soap lightly, wash well, and develop the blue by a run through an acidulated 2 per cent. solution of yellow prussiate of potash; wash well again, and chrome a second time in—

5	grms.	bichromate of soda
7½	,,	sulphuric acid 168° Tw.
1000	,,	water

at 50° C.

Finally, wash well in warm water, then in cold running water, and dry.

Basic colour resists for working along with the foregoing colours require no special description, since they consist merely of zinc oxide, dyestuff, albumen, and thickening. After printing, they are steamed 2–3 minutes to coagulate the albumen, and the goods are then treated exactly as above. Basic colours are used only in conjunction with Azo colours, and sometimes with Chrome yellows, not with Prussian blue.

VAT COLOUR AND SULPHIDE COLOUR RESISTS.

For the production of fast-coloured resists under Aniline black, the Vat and Sulphide colour printing pastes are particularly suitable on account of their being applied in a strongly alkaline solution. In order to preserve the resists from injury by the black, a little acetate of soda and a little extra "hydrosulphite" may be added to the printing pastes. As a rule, however, these additions are not necessary, since the colours usually contain more alkali and reducing agent than is required for their fixation. In such cases the excess resists the Aniline black and neutralises its oxidising action.

The printing colours previously described—see Indigo, Ciba colours, Indanthrenes, and Sulphide colours, etc.—are used, either with or without the addition of sodium acetate.

For the most part the Vat and Sulphide colours are employed as resists under printed "covers" of Aniline black: they may also be used to "discharge" previously padded cloth, but practical difficulties have prevented their extensive use in this connection. In combination with Azo colour resists, the Vat dyestuffs and Sulphide colours yield a variety of effects, of great fastness and brightness, under black "covers." Although the process is not in general use, it is nevertheless a very valuable one for the production of fast colours on shirtings and dress goods: the colours are very permanent, and withstand the operations of the laundry exceedingly well.

The following example of a Sulphide-colour Resist will serve as type:—

VIOLET B.D.

25	grms.	Thiogene violet B.D. extra.
150	,,	water.
50	,,	caustic soda 77° Tw.
25	,,	hydrosulphite conc. powder.
100	,,	China clay paste 50 per cent.
200	,,	British gum paste 20 per cent.

Dissolve at 50° C. and add to—

350	grms.	caustic soda 77° Tw.
100	,,	light British gum.
1000		Heat the whole to 50° C., and cool before use.

Print on white cloth: dry; cover print in Aniline or Diphenyl black; dry; steam twice for 2–3 minutes in the rapid ager: wash, soap, and dry.

In applying the Vat dyestuffs, any of the alkali hydrosulphite pastes may be used for printing, and acetate of soda may be added as required. Recipes for these colours have already been given, and need not be repeated here. The colours are printed on white cloth, covered with a pattern in Aniline black, steamed, allowed to air until re-oxidised, and then washed and soaped. Ciba colours are best soaped at the boil or "chromed" at 85°–100° C.: these operations bring about the full development of the colour and increase its brilliancy.

Resists under Paramine Brown.

During the course of a series of experiments on the oxidation of various amines and diamines, Grandmougin discovered that Para-phenylene-diamine yielded an excellent brown of great fastness. The use of p-phenylene-diamine as a brown colouring matter was patented by the Badische Anilin und Soda Fabrik in 1905, and by them a preparation of the base is put on the market under the name of "Paramine brown."

Paramine brown is produced from Para-phenylene-diamine in a manner analogous to that by which Aniline black is obtained, and like that colour it must be produced upon the fibre by a process of oxidation. With chlorate it yields a fine pure shade of brown, fast to air, light, and soap, and fairly fast to chlorine.

Being an oxidation product, Paramine brown can be resisted by means of reducing agents. Alkalies, acetate of soda, and zinc oxide also prevent, to a certain extent, the development of the colour, but they give imperfect whites, and can therefore only be used in combination with reducing agents. Of these latter, the most efficient are the stable hydrosulphite-formaldehyde compounds and sulphite of potash. A mixture of "hydrosulphite" and "sulphite" gives a purer white than "hydrosulphite" alone.

Coloured resists are obtained with basic colours in conjunction with tannin, aniline oil or phenol, and rongalite (hydrosulphite-formaldehyde). Colours like Modern violet, Blue 1900, Phenocyanine, etc., which form leuco compounds on reduction, and also Persian berries extract, may also be employed for the production of fast-coloured resists. As a rule, however, the brighter basic colours are preferred.

The resists are printed on cloth padded in a solution of Paramine brown, containing the necessary oxidising agents. After drying, the printed goods are steamed in the rapid ager, passed through a tartar-emetic bath for the fixation of basic colours, well washed, soaped, and dried. The whole series of operations is carried out in the open width and in a continuous manner (after steaming).

As in the case of Aniline black styles, the resists under Paramine brown must be printed on freshly padded cloth, otherwise imperfect resists will be obtained. The other precautions mentioned in connection with Aniline black styles also apply equally to Paramine browns.

Resist effects in white and colours under printed "covers" of Paramine brown are obtained by printing the reserve pastes on white cloth, drying well, and then printing an "all-over" cover pattern in a thickened brown mixture of similar composition to the padding liquor. The goods are afterwards steamed and treated as above.

Resist effects on a plain ground of Paramine brown are produced by the following series of operations:—

1. Pad the bleached cloth in Brown P.

Brown P.

20	grms.	Paramine brown.
300	,,	hot water. Dissolve and add—
400	,,	cold water.
1·5	,,	Rongalite C. Cool and add—
20	,,	chlorate of soda.
50	,,	water.
20	,,	ammonium chloride.
2·5	,,	tartar emetic.
100	,,	water.
37·5	,,	glycerin.
15·5	,,	vanadium solution 1/1000 (see Mordants).

To 1 litre with water.

Allow to stand one hour or until colourless; then filter through calico and pad the cloth; dry at 45°–50° C. in hot air. The addition of Rongalite reduces the oxidation products always present, to a slight extent, in commercial Paramine brown; and the tartar emetic has the useful property of retarding the oxidation of the padded cloth for 18 to 24 hours. Made as above, the padding liquor itself will keep in good condition for 48 hours.

2. On the padded and dried cloth print any of the resist pastes given below. Dry.

Resist Whites.	I.	II.
British gum paste . .	750 grms.	...
Rongalite C.	250 ,,	150 grms.
Acetate of soda. . . .	...	100 ,,
Sulphite of potash 90° Tw.	...	250 ,,
British gum	...	200 ,,
Water	...	300 ,,
	1000 ,,	1000 ,,

No. II. gives the better white.

Coloured Resists with Basic Dyestuffs.

	Pink.	Yellow.	Blue.	Green.
Rhodamine 6 G. extra	10	...	...	...
Thioflavine T.	...	20	...	15
Thionine blue G.O.	...	...	25	5
Glycerin	40	40	35	40
Acetin	20	40	40	40
Water	100	100	100	100
Starch-tragacanth paste	230	200	200	200
Dissolve, cool, and add—				
50 per cent. solution of tannin in alcohol	100	100	100	100
Resist Paste R.G.	500	500	500	500
	1000	1000	1000	1000

Resist Paste R.G.

20	grms.	starch.
90	,,	water.
340	,,	6 per cent. tragacanth thickening.
150	,,	aniline oil. Boil, cool to 60° C., and add—
400	,,	Rongalite C.
1000		Stir until the paste is perfectly smooth, and then cool.

Rhodamine pinks require a long exposure to the air before they develop to their full shade. Where this is inconvenient, the Discharge Pink II. (Erythrosin) used for Azo colour discharging may be employed.

3. After printing the resist pastes, the cloth is steamed 4 to 5 minutes in the rapid ager.
4. Pass through a 1 per cent. to 2 per cent. solution of tartar emetic.
5. Wash in running water.
6. Soap at 60°–70° C.
7. Wash.
8. Dry over cylinders.

Operations 4, 5, 6, 7, and 8 are conducted in the open soaping range, and in a continuous manner.

For resists on figured grounds (printed "covers") of Paramine brown, the same reserve pastes are applicable. Print white and colours on bleached cloth; dry well: "cover" in a printing paste of Paramine brown; dry, steam, fix in tartar emetic, and wash, soap, and dry as above.

BROWN P. (FOR PRINTING).

100	grms.	starch.
30	,,	British gum.
503	,,	water.

Boil, turn off steam, and add—

25	grms.	Paramine brown
2	,,	Rongalite C.
175	,,	boiling water.

Cool and add—

25	,,	chlorate of soda.
40	,,	water.
30	,,	nitrate of ammonia.
50	,,	water.
20	,,	vanadium sol. 1/1000.
1000		

Brown P. printing paste will withstand a prolonged steaming, and may therefore be used as a "blotch" in the ordinary steam styles.

Resists under Sulphide Colours.

Owing to the several drawbacks attendant upon the use of oxidation discharges for the production of white and coloured effects on dyeings of the Sulphide colours, many attempts have been made from time to time to devise a practical method of obtaining similar and more satisfactory results by the reverse process, namely, by reserving or resisting the dyestuffs during the operation of dyeing.

Certain metallic salts possess the property of preventing the fixation of Sulphide colours on the fibre, and on this fact is based the resist process patented by the firm of Leopold Cassella & Co. (Eng. Pat. 12540, 1901).

This process depends upon the employment of zinc salts, which not only give exceedingly good resists, but also have no injurious action on the strength of the cloth. Other salts, such as those of manganese, cadmium, iron, tin, and aluminium, are similarly effective for certain styles of work, but none of them are quite so effective as the zinc salts, nor are any of them applicable to so many varieties of coloured reserves.

The two zinc salts which naturally suggest themselves as most suitable for the purpose are just those which yield the best results—namely, the sulphate and the chloride. The use of sulphate of zinc formed the subject-matter of Cassella's first patent, but later on it was found that the chloride gave much superior results, and consequently it has replaced the sulphate almost entirely.

The resisting action of zinc and other metallic salts is due to their property of precipitating the Sulphide colours from their solutions in alkali and sodium sulphide. What really takes place has not been definitely ascertained, but it is probable that they combine with the dyestuff to form insoluble metallic leuco compounds of the colour.

This supposition, however, does not afford a complete explanation of their action, since it has been proved that different salts of the same metal, when used in quantities corresponding to equal weights of the same oxide, yield widely different results in practice.

Salts possessing strongly marked acid properties invariably give the best resists; hence the acid character of a salt doubtless determines, to a great extent, its suitability as a resisting agent. At the same time the base is also an important factor, for similar salts of different bases by no means behave alike towards the Sulphide colours.

The salt in which the combined resisting action of base and acid is most pronounced is zinc chloride,—a product which, owing to its great sólubility, is particularly well adapted to the production of resist effects with comparatively fine patterns, under dark shades of Sulphide colours. It is noteworthy that zinc chloride, although it possesses strongly acid properties, has no detrimental action on the fibre, unless, of course, it contain free mineral acid. The absence of free acid ought to be ensured before the resist pastes are prepared.

In view of the ever-increasing employment of the "Sulphide Colour Reserve or Resist Process," it is somewhat curious to note that, until within quite recent years, the introduction of any such process would have excited but little interest in calico-printing circles generally. This attitude was not due to any lack of interest in the Sulphide colours themselves, but almost solely to the practical difficulties encountered in their application,—difficulties which arose entirely out of the great impurity and irregularity in working of most of the Sulphide dyestuffs then available. Another cause of the scant attention paid to the earlier Sulphide dyestuffs was that they afforded an extremely limited range of shades, none of which were, at one and the same time, sufficiently fast and bright to be of any commercial value as "self shades."

Fortunately these various objections have been overcome by improvements in the manufacture of the dyestuffs and in the modes of their application. The introduction of pure and readily soluble Sulphide colours has resulted not merely in removing the practical difficulties of dyeing, but in rendering easily possible the production of a great variety of fast, level, and to a limited extent bright shades. In conjunction with zinc chloride resists, these facilities afford a ready means of obtaining many novel effects in white and fast colours on dark shades of Sulphide colour grounds.

The dyeing of resist styles is best carried out in a continuous manner by giving the printed goods a single run through a padding machine, provided with a comparatively small colour box. In this way, dark shades of blue, brown, green, and even black may be obtained of excellent fastness; and the short immersion of the fabric in the dye liquor has the advantage, over other methods, of allowing no time for the reserving agents to dissolve in the dye bath, and thus throw the colouring matter out of solution.

In order to obtain the best results with regard both to the sharpness of impression and purity of the resist effects, and to the thorough and uniform absorption of the dye liquor by the material, it is recommended by Baumann and Thesmar (*Zeitschrift für Farben-Industrie*, April 15, 1908) to dissolve the

Sulphide dyestuff in glucose and caustic soda, rather than in sodium sulphide or hydrosulphite and caustic soda.

Padding liquors containing sodium sulphide are at once the least satisfactory and the most difficult to use: on the one hand, any excess of sodium sulphide, however slight, has the effect of "dulling" the white and coloured resists, whereas, on the other hand, a deficiency of sodium sulphide causes uneven dyeing by reason of the fact that the zinc chloride resists dissolve in the dye liquor, and by combining with the solvent to form zinc sulphide, precipitate the colouring matter in the dye bath. Even under the most favourable conditions, sodium sulphide dye baths yield inferior results to those obtained from either the "hydrosulphite" or "glucose" solutions. Hence the use of sodium sulphide is not to be recommended, except in cases where the alternative methods are inadequate.

On the contrary, the "hydrosulphite alkali" and the "glucose-alkali" processes of dyeing Sulphide colours are easy of application, and require no more than ordinary care. With both, excellent resist whites (by the zinc chloride method) under full and level shades are readily obtained; and with neither is any precipitation of colouring matter in the dye bath to be feared, since a considerable excess of either alkali or reducing agent has, practically speaking, no detrimental effect on the resist pastes. So far as the production of good whites and uniform ground colours are concerned, there is little to choose between the two processes; but the "glucose-caustic-soda dye bath" has the advantage of being more stable than the "hydrosulphite-caustic soda bath," and is therefore preferable on economical grounds. If anything, too, the glucose process gives slightly better results than the other.

An important operation in the dyeing of Sulphide colours is the steaming of the goods in the *wet* state after padding. The actual dyeing of the material is not effected during the padding, but by the subsequent oxidation on the fibre of the reduced dyestuff it has absorbed. Formerly the padded goods were given a more or less prolonged exposure to the air to bring about the necessary re-oxidation, but this has now been replaced by a short steaming in a mixture of low-pressure steam and warm air. Under the influence of steam, the dye liquor penetrates the fibre more evenly and thoroughly, the colour is more completely developed, and darker, richer, and faster ground shades are obtained without in any way affecting either the purity of the resists or the strength of the fabric. With equal quantities of dyestuff, the shade produced by steaming is often twice the depth of that produced by air oxidation, so that, apart from its other technical advantages, it is by far the most economical process to employ, since it allows of the dyestuff being utilised to the utmost advantage.

The method of applying the zinc chloride resist process is as follows:—The goods, printed in the usual manner with resist colours, consisting essentially of zinc chloride, with or without the addition of China clay, are padded on a two-bowl padding machine through a solution of the desired Sulphide colour. The box of the padding machine is constructed to contain between 75 and 100 litres, so that the printed resists are not liable to be injured by too long an immersion in the dye liquor. After squeezing out excess of liquor, the padded cloth is passed directly, without intermediate drying, through a steam box situated immediately behind the padding machine. Any sort of a closed chamber fitted with top and bottom guide rollers is suitable for steaming purposes so long as it is large enough to allow of the pieces being steamed for 4–6 minutes. The presence of air in the steaming apparatus is an undoubted advantage, and must be provided for if the best use of the dyestuff is to be made. Usually an ordinary ager fulfils all the conditions required for steaming Sulphide colours, but in many works equally satisfactory results are obtained in simple wooden steaming boxes, furnished with guide rollers and a good supply of low-pressure steam: the necessary amount of air enters the chamber by way of the slit through which the cloth itself enters. The printed and padded cloth, after steaming, is rinsed in water, soured in dilute hydrochloric acid, washed, soaped, washed again, and dried. The whole process is extremely simple and, when carried out with reasonable care, very reliable. The two main points to observe are, that the cloth must pass through the dye liquor in the full open width, and that a sufficient steaming must be given to fully develop the colour before the goods are "soured"; creases in the cloth and too short a run through the steamer are the most fruitful causes of uneven dyeing.

The zinc chloride resist process is well adapted to the production of a great variety of styles on either plain or figured (printed) grounds; and as the resist colours are for the most part as fast as the ground colours, it is scarcely too much to say that the process is likely to meet with considerable success.

It has already displaced many of the older methods of obtaining similar effects, and will probably, in course of time, replace entirely the "chrome mordant discharge" for the production of mode shades fast to light, air, and soap.

The following recipes for resist colours and dye baths will illustrate the far-reaching importance of the process described above. The fact that so many groups of dyestuffs are applicable is in itself sufficient to prove that the zinc chloride process offers many advantages over those hitherto employed for similar but less comprehensive classes of resist work.

Resist White Z.N.

200 grms. British gum.
250 ,, water.
400 ,, zinc chloride.
150 ,, water.
———
1000

Heat till the gum and salt are dissolved.

If the resist white is found to run when printed with heavily engraved rollers, it may be improved by the addition of 75 to 100 grms. China clay per kilogramme of colour: as a rule, however, this addition is not necessary with ordinary patterns.

For fast red, pink, claret, and orange resists, the Azo colours developed on the fibre lend themselves admirably.

Resist Red Z.P.

450 grms. 6 per cent. tragacanth thickening.
200 ,, zinc chloride.
165 ,, China clay paste 50 per cent.
15 ,, oxalic acid.

Dissolve, cool to 0° C., and add—

150 grms. diazo solution P.
20 ,, acetate of soda.
———
1000

Diazo Solution P.

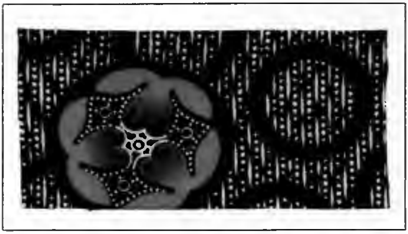
100 grms. Paranitraniline C.
55 ,, nitrite of soda.
350 ,, ice and water. Stir well together, and add—
240 ,, hydrochloric acid 30° Tw.
170 ,, ice.
———

Make up to 1 litre with ice water.

For claret, pink, and orange, take the Diazo solutions of α-naphthylamine, Azo rose B.B., and Metanitraniline, respectively, in place of p-nitraniline.

It is almost needless to say that all Azo colours should be printed on cloth prepared in β-naphthol.

Fast blue, violet, and green or olive resists are best obtained from such mordant colours as will withstand the action of the alkali in the dye bath. Of these Modern blue, Modern violet, Blue 1900, the Chrome blues and violets for printing (Cassella), Modern yellow, Anthracene yellow, and Persian berries extract.



Benzidine chocolate, Para red and white resists under Immedial black N.N.O. (Cassella).

Mordant Colour Resists (under Sulphide Colours).

	Blue.	Violet.	Yellow.	Green.	Grey.
Chrome blue F.	50	...	...	20	...
Chrome violet M.	...	50	...	...	...
Anthracene yellow B.N.	...	...	40	40	...
Modern violet 40 per cent.	...	...	...	...	20
Persian berries extract 52½° Tw.	...	...	...	...	30
Water	300	300	310	300	320
China clay paste 50 per cent.	150	150	150	150	150
Formic acid	20	20	...	10	...
British gum powder	200	200	200	200	200
Dissolve, cool, and add—					
Acetate of chrome 32° Tw.	100	100	100	100	100
Zinc chloride solution 75 per cent.	180	180	200	180	180
	1000	1000	1000	1000	1000

Other colours of the same groups may be applied according to the above directions.

The basic Aniline colours are likewise suitable for the production of resist effects, but they demand more careful handling, and, though brighter, are neither so fast nor so reliable in working as the Azo and mordant colours.

Type of Basic Colour Resist.

30 grms. dyestuff.
70 „ acetic acid 9° Tw.
50 „ acetin.
100 „ water.
200 „ British gum.
100 „ water.
150 „ China clay 50 per cent. paste. Boil, cool, and add—
150 „ tannin sol. 50 per cent. (in acetic acid).
150 „ zinc chloride solution 75 per cent.
1000

Victoria blue is one of the best basic colours for the purpose; its tannin lake resists the action of alkali very well; and though converted into a brown, it is re-developed again on washing and "souring."

When the mordant and basic colours are used, either alone or in combination with the Azo colours, the printed goods are steamed in the rapid ager before dyeing, in order to fix their colour lakes on the fibre. In other respects they are treated exactly like the Azo colours.

As already noted, the dyeing of the printed pieces may be carried out by either of the two methods in general use, namely,—

(*a*) With sodium sulphide and the ordinary Sulphide dyestuffs, or—

(*b*) With the pure soluble Sulphide colours, and caustic soda and glucose.

(*a*) Sodium Sulphide Process.

The dyeing of the material is effected by padding *once* through a solution of the dyestuff in sulphide of soda and soda ash, with or without the addition of Turkey-red oil. The concentration of the dye bath varies with the depth of shade required. As a rule, the following proportions may be taken as representing a typical dye bath:—

	Light. Dark.	
Grms.	10 to 60	Immedial or other suitable Sulphide colour.
,,	15 to 90	sodium sulphide crystals.
,,	20 to 25	soda ash.
,,	4 to 5	Turkey-red oil 25 per cent.
,,	1000 to 1000	water.

Light shades are usually padded in the cold, whereas in the case of dark shades better levelling and a fuller colour are obtained by keeping the dye bath at a temperature of between 50° and 60° C. After dyeing, the goods are steamed, rinsed, soured in dilute acid, washed, and soaped.

(*b*) Glucose Alkali Process.

The number of Sulphide dyestuffs that are soluble in caustic soda without the addition of sodium sulphide is limited, but the range is being constantly extended by the introduction of new colours, and in course of time the glucose alkali method of dyeing will in all probability displace the more sensitive sulphide method altogether.

The "soluble" Immedial colours (Cassella) are especially suitable for working with caustic soda and glucose; and although many of the pure sulphide dyestuffs made by other firms give equally good results, the Immedial colours "soluble" are perhaps the best known in this connection. They are dyed in exactly the same manner as the ordinary Sulphide dyestuffs, the only difference between the methods being in the preparation of the dye bath, which is made up as follows:—

Light. Dark.		
10 to 60	grms.	soluble Immedial colour or other suitable Sulphide colour.
10 to 60	,,	caustic soda 77° Tw.
20 to 40	,,	soda ash.
10 to 60	,,	glucose.
4 to 5	,,	Turkey-red oil.
1000 to 1000	,,	water.

Pad, squeeze, steam 4–6 minutes, rinse in cold water, sour in dilute hydrochloric acid ($\frac{1}{4}$°–$\frac{1}{2}$° Tw.), wash, soap well, wash thoroughly, and dry.

The sketch below (fig. 78) illustrates the general disposition of the plant employed in the dyeing of printed goods with Sulphide colours.

The various zinc chloride resist colours given above serve equally as resists for cover patterns printed in Sulphide colours. In this style the cloth is first printed as usual with the resists, and then, after well drying, instead of padding it in the dye bath, it is over-printed or "covered" with a second pattern in a Sulphide colour, and finally steamed for 4–5 minutes, washed, soured, soaped, and dried. In this way it is possible to obtain many novel and fast effects in coloured patterns on patterned grounds—effects that are otherwise unobtainable.

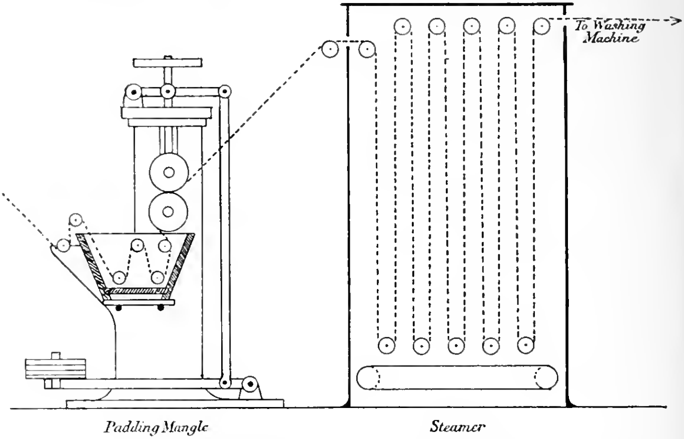
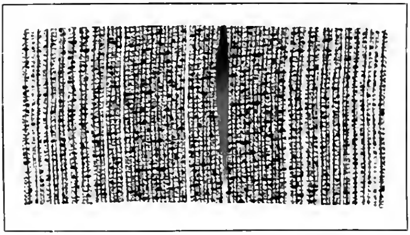


FIG. 78.—Mangle for Sulphide and Vat resist styles.



Benzidine chocolate, Para red and white under printed cover of Immedial Indone B.

A further and very interesting and valuable property of zinc chloride is its power of effectually preventing the fixation on the fibre of many of the Vat dyestuffs.

For the production of resist styles with these colours the cloth may be treated in exactly the same way as for Sulphide colour resist styles, but the Vat dyestuffs in general are only suitable for light ground colours when dyed on the padding machine; hence they are used chiefly for classes of work analogous to the well-known "cover and pad" style, in which a pattern in white and a dark colour appears on a lighter coloured ground. The white resist consists of zinc chloride, while the dark colour may be obtained from either a Sulphide colour, a Vat dyestuff, a zinc chloride resist colour, or Aniline-diphenyl or an Azo black. The lighter ground, similarly, may be either a Sulphide or a Vat dyestuff, or a mixture of the two. If, for example, a two-blue and white effect with Ciba colours is desired, the cloth is first printed with a dark Ciba blue and a zinc chloride resist white, well dried, and then, if for padding, steamed in the rapid ager, and "aired" to fix the dark blue. Hereupon the goods are passed through a weaker Ciba blue dye bath in the padding machine, and finally steamed in the wet state, exactly as for Sulphide colours. On the other hand, if the goods are intended for "covering" with another pattern, the steaming after the first printing may be omitted, since there is no likelihood of the darker blue "running" during the second printing into the weaker colour. After the second or cover printing the goods are dried, and then steamed in the ager for 3–4 minutes, washed, soured, soaped, and dried. Aniline or Diphenyl black must always be steamed after the *first* printing, otherwise its development would be prevented by the alkalinity of the covering colour.

Ciba blue may be replaced in the above style by Ciba violet, the various Indanthrene colours, Thio-indigo red, Vat red B., Indigo, and the Helindone series; and as one of these may be used in the first printing and another in the second printing, or the dyeing, it is obvious that the process is capable of yielding a vast variety of styles.

Another method of producing resist effects under Sulphide colours and various Vat dyestuffs was patented by the Badische Co. in 1909. It depends upon the oxidising action of manganic salts or manganese dioxide, and is applicable to the Indanthrenes, Thio-indigo, Indigo, Ciba colours, and Sulphide colours. It consists in printing the cloth with a mixture of a soluble manganous salt and an oxidising agent such as bichromate of soda, and then, after drying the material, dyeing it in one of the above-mentioned colours, according to any convenient method. Coloured resists can be obtained by adding Diazo compounds to the white resist, and printing on naphthol-prepared cloth. During the drying after printing, Manganese bronze is formed, and by both its mechanical and oxidising action it effectively prevents the fixation of the colour subsequently applied in the dye vat. Manganese bronze is very fast, a feature which allows of the material being dyed at any desired temperature and in any desired manner, whether it be in the padding machine, the continuous dyeing machine, or in the "dipping vat."

WHITE RESIST M.N.

500	grms.	manganous chloride.
350	,,	50 per cent. gum Senegal solution. Dissolve, and add—
75	,,	China clay.
50	,,	water.
25	,,	bichromate of soda (ground).
1000		

RED RESIST M.N.

850	grms.	White resist M.N.
150	,,	diazo solution M. (Paranitraniline).
30	,,	acetate of soda.
1030		

DIAZO SOLUTION M.

69	grms.	Paranitraniline.
175	,,	hot water.
175	,,	hydrochloric acid 32 per cent. Cool and add—
200	,,	ice, and then—
38	,,	sodium nitrite.
200	,,	ice.
143	,,	water.
1000		

A 10 per cent. diazo solution is better than the above.

Similarly, α-naphthylamine may be employed for a fast claret.

Print the Azo colour resists on naphtholated cloth, and the white resist on the same or unprepared cloth, according to circumstances. After printing, the cloth is well dried, dyed in Indigo, etc. etc., well washed, and finally treated in an acid bath containing 10–20 c.cs. sulphuric acid 168° Tw. per litre to remove the manganese salts still remaining on the fibre. Most of the manganese bronze is reduced during the dyeing, but if any remain it may be readily removed by the addition of 2–5 grms. of potassium sulphocyanide per litre of the acid bath; or a solution of bisulphite of soda may be used. Wash the goods again, soap them, wash, and dry up.

Various "discharge resists" and other modifications of the zinc salt resist style under Sulphide and Vat dyestuffs have been suggested from time to time, and may possibly be in use to a limited extent. For the most part they consist of mixtures of zinc salts with the hydrosulphites of commerce, and their object is to discharge Azo colour dyed grounds, and simultaneously prevent the fixation on certain parts thereof of other hydrosulphite discharge colours such as Indigo, Thio-indigo, Ciba blue, Indanthrene blues and yellows, and the Sulphide colours, all of which are "resisted" by the presence of zinc compounds in any paste over which they may be printed. By means of these "resist discharges," a white or coloured pattern on a multicolour ground of Paranitraniline red, discharged with several other colours, is obtained. The addition of finely ground sulphur improves the "resist discharge effect."

For the production of a white, blue, green, and yellow pattern on a mixed ground of Para red, Indigo, Flavanthrene, etc., the following process was patented by Ribbert in 1906 (*Revue générale des matières colorantes*, p. 201, 1907):—The red-dyed cloth is printed with the discharge resists, dried, printed again with suitable discharge pastes, dried, steamed for 3 minutes at 102°–106° C., dried, aired, and then chromed (for yellow and green), washed, and soaped.

WHITE RESIST DISCHARGE P.R.

200	grms.	Rongalite C.	Heat to dissolve the zinc salts. Cool whilst stirring and add—
200	,,	zinc acetate.	
50	,,	zinc sulphate.	
450	,,	British gum solution.	
100	,,	ammonium chloride.	
1000		Heat the whole again and cool.	

WHITE RESIST DISCHARGE P.X. (FOR INDIGO AND THIO-INDIGO).

250	grms.	zinc sulphoxylate.
150	,,	ammonium chloride.
350	,,	British gum paste. Heat together, cool, and add—
150	,,	finely divided sulphur.
100	,,	lactic acid 50 per cent.
1000		Grind well before use.

YELLOW RESIST DISCHARGE P.R.

200	grms.	lead sulphate 50 per cent. paste.
180	,,	lead acetate.
60	,,	China clay.
40	,,	water.
100	,,	British gum.
100	,,	water. Heat together, cool, and add—
225	,,	hydrosulphite N.F. conc.
95	,,	water.
1000		Stir till the hydrosulphite is perfectly dissolved.

Blue discharge resists are obtained with Modern violet, Blue 1900, Chromoglaucine, Phenocyanine, and similar dyestuffs, in combination with chromium acetate, hydrosulphite N.F. conc., and zinc salts.

Greens are merely mixtures of blue and yellow.

Print the above colours and whites on cloth dyed Para red; dry and cover-print with any of the usual Indigo, Indanthrene-, Ciba-, or Sulphide-colour discharge pastes (hydrosulphite); steam for three minutes at 103° C.; sour at 50° C. in dilute sulphuric acid (¼°–½° Tw.) after the steamed goods have been exposed to the air; wash well, and "chrome" at 50°–60° C. to develop the yellow and green; wash again and soap; wash and dry. In this way the "discharge resists" first printed stand out clearly from a patterned background of Paranitraniline red and Indigo, or whatever other vat or sulphide colour was printed with the final covering pattern.

These complex styles are little used, and the above example will suffice to illustrate the general principles upon which they are founded.

(6) "RAISED" STYLES.

The term "raised" is an old expression used to signify the method whereby an insoluble metallic salt or oxide or an insoluble colour lake is produced and fixed on the fibre at one and the same time by a process of precipitation. The most typical example of a "raised colour" is Chrome yellow, which is obtained by printing or padding the cloth with a soluble (or insoluble) lead salt, and then, after drying, precipitating the lead as lead chromate by a run through bichromate of soda. Other mineral raised colours are Iron buff, Manganese bronze, and Chrome green. Included also in the raised colour category are the lakes produced by passing goods printed with Catechu solutions and the extracts of Quercitron bark, Persian berry, Logwood, and other vegetable dyestuffs, through hot solutions of bichromate of soda, or of this and ferrous sulphate. Prussian blue is also regarded as a raised colour, since, when printed, it requires oxidising in "bichrome," and when dyed it is produced by the double decomposition of Iron buff and ferrocyanide of potash.

Any colours which are raised by the same "raising liquor" may be printed in combination. Thus Manganese bronze, Iron buff, and sometimes Chrome green may be printed side by side; and similarly, Chrome yellow, steam Prussian blue, and Catechu, Logwood black, Persian berry, and some of the red wood extracts, may all be printed together in multicolour patterns.

(*a*) **Chrome Yellow and Orange.**

These colours are merely the normal chromate (yellow) and basic chromate (orange) of lead. They are both precipitated on the fibre, from a lead salt previously applied, by bichromate of soda or potash, and the orange is obtained by treating the yellow in a bath of boiling lime water which converts it into the basic chromate. The deepest oranges are produced from basic lead acetate.

The thickened solutions may be printed on either plain white cloth or on cloth padded in a 2½–3 per cent. solution of sulphate of soda. Aniline black and any other colour fixed by a short steaming, and unaffected (or developed) by bichromate, may be used in combination with lead yellows.

Yellow P.B.

120	grms.	lead acetate.	Dissolve together, and without cooling add—
100	,,	lead nitrate.	
450	,,	water.	
80	,,	flour	previously mixed into a paste.
250	,,	water	
1000		Boil and cool.	

YELLOW P.B.C.

650	grms.	lead carbonate 50 per cent. paste.
250	,,	British gum paste 25 per cent.
100	,,	starch paste 12½ per cent.
1000		

This yellow is suitable for working with Aniline black

LEAD CARBONATE (FOR ABOVE).

{ 34 kilos. lead acetate.
{ 100 ,, water.

Add gradually, whilst constantly stirring,

{ 12 kilos. soda ash.
{ 100 ,, water.

Neutralise with the soda; allow to settle, and wash 3 times by decantation; then filter until the paste contains 50 per cent. of lead carbonate. The above quantities = 47·9 kilos. of 50 per cent. paste.

ORANGE P.B.

200	grms.	lead acetate.
100	,,	lead nitrate.
550	,,	water.
90	,,	British gum paste.
50	,,	flour or starch.
1000		

Boil and cool.

ORANGE P.B.B.

{ 50 litres basic lead acetate solution.
{ 5 kilos. flour.

Boil and cool.

BASIC LEAD ACETATE SOLUTION.

900	grms.	water.
600	,,	lead acetate.
225	,,	litharge.

Boil one hour, allow to settle, and use the clear supernatant liquor for Orange P.B.B.

All the above colours are printed, dried, and developed at once in various Chrome baths according to the shade desired.

CHROME BATHS.

For—	YELLOW P.B.	YELLOW P.B.C.	ORANGE P.B. or P.B.B.
	grms.	grms.	grms.
Bichromate of soda	25	25	100
Sulphate of soda	100	...	...
Common salt	...	100	200
Water	1000	1000	1000

The printed goods are "chromed" at the full open width and in a continuous manner at 80°–85° C.; the rate at which they pass through the "chroming beck" depends upon its size, but should be adjusted so that the cloth is given about two minutes' immersion in the liquor. After chroming, the goods are well washed and, if required, open-soaped before drying.

For oranges, the pieces after "chroming" are washed and passed through a clear boiling lime water bath containing 40 grms. of quicklime and 10 grms. bichromate of soda per litre of water. Wash well and dry.

Patterns containing Aniline black and the extracts of Logwood, Bark, etc., or steam Prussian blue, must be steamed in the rapid ager before "chroming."

(*b*) Iron Buff.

Iron buff (oxide of iron) is produced by printing ferrous acetate or ferrous sulphate, followed by a run through caustic soda and subsequent exposure to the air.

IRON BUFF PRINTING COLOUR.
500 grms. ferrous acetate. (See Mordants.)
500 ,, British gum paste.
1000

Print, dry, and pass the goods through caustic soda 4° Tw. at 75° C.; allow to lie in pile until the ferrous hydrate is fully oxidised, and then wash off in water.

The process is expedited by a short steaming through the rapid ager before "raising" in caustic soda, or the pieces may be treated in a dilute solution of bleaching powder after the caustic bath, or, again, the bleaching powder may be added to the caustic soda.

Iron buff in combination with Aniline black is largely used as a blotch in the production of black and buff handkerchiefs for the East. It is very fast to soap and alkalies, but sensitive to the action of acids.

(*c*) Manganese Bronze.

The dyeing of Manganese bronze for discharging has already been described in detail. The production of printed patterns is practically identical, the only difference being that Manganese chloride is printed instead of being padded on the cloth. In other respects the process is the same.

MANGANESE BRONZE PRINTING COLOUR.
850 grms. manganese chloride 70° Tw.
150 ,, British gum.
1000

Print, dry, pass through caustic soda, wash, pass through bleaching powder solution, wash, and dry. For full details of these operations, see Bronze Discharge Styles.

(*d*) Chrome Green.

This colour is seldom used as a self shade. It may be produced by any of the many methods of mordanting cotton with chromium oxide. The cloth may, for example, be printed or padded in a strong solution of a basic chromium sulphate (say chrome alum made basic with soda ash), dried, steamed 2–3 minutes in the rapid ager, and then passed at once through a hot solution of soda ash, which precipitates the chromium hydroxide, or chrome green.

The well-known Khaki shade is a mixture of Iron buff and Chrome green, and is obtained by precisely the same means, from a solution containing chromium and ferrous acetates or other salts of these two elements.

(*e*) Prussian Blue.

The production of Prussian blue has been described at length elsewhere in this volume. (See Discharge and Steam Styles.) Steam Prussian blue always requires a run through a "bichrome bath" to bring about the full development of its shade, and for this reason it is mentioned here, although, properly speaking, it is not a "raised colour" in the general sense of the term. On the other hand, Prussian blue dyed by treating Iron buff dyed cloth in an acid solution of "yellow prussiate" is a true raised colour, since both the buff and the blue are precipitated directly upon the fibre.

(*f*) "Raised" Vegetable Colours.

A modification of the well-known wool-dyeing method of "stuffing" and "saddening" may be applied, in certain cases and for particular styles, to the fixation of some vegetable dyestuffs on cotton cloth. Of these, Catechu is the most important; but others, such as Persian berries, Quercitron bark, and Logwood, are also useful, inasmuch as they permit of compound shades being obtained and multicolour effects produced without any variation of process. The multicolour effects obtained are limited to combinations of brown, yellow, olive, drab, fawn, grey, and such mode colours as can be mixed from Catechu, Logwood, and the yellow dyestuffs.

Much variety, however, can be introduced by the printing of steam Prussian blue, Aniline black, and (or) the Logwood iron black J. (already described in the sections on the Steam and Azo Colour Styles, see p. 397), along with the colouring matters mentioned above.

The process consists in printing thickened solutions of Catechu and other natural dyestuffs on white cloth, and then, after drying, passing the printed goods through a hot bath of bichromate of soda, which reacts with the dyestuff to form an insoluble colour lake. A slight addition of alkali to the printing colour improves both the shade and the intensity of the ultimate result, and a run through the rapid ager before "chroming" has a beneficial influence upon the fastness and evenness of the colours. If Prussian blue, either as a "steam colour" or in the form of a solution in oxalic acid, is used in conjunction with Bark, Persian berries, or Logwood extracts, for olives, greens, and slates, the alkali must be omitted from the printing pastes, otherwise the blue will not form.

Bright greens, yellows, and blues are obtained from lead salts, Prussian blue, and mixtures of the two, and blacks from Aniline black, Diphenyl black, and Black J. (p. 397). Logwood alone "raised" in chrome does not give a good black; it is only suitable for greys and compound shades. Alizarin blue S. with zinc or chromium mordants yields a fine bluish shade of slate, and may be added to the vegetable dyestuffs.

All patterns containing steam colours, in addition to the raised or developed colours, must be steamed in the rapid ager for 3–4 minutes previous to chroming; and only such steam colours as are fixed by a short steaming should be employed, as prolonged steaming causes the raised colours to run.

The following recipes are taken from practice:—

GREY R.L.

160	grms.	Logwood ext. 32° Tw.
20	,,	glycerin.
800	,,	tragacanth thickening 4 per cent.
20	,,	caustic soda 70° Tw.
1000		

Brown R.C.

240	grms.	Catechu (in cubes).
320	,,	water. Dissolve and strain into—
40	,,	water.
480	,,	tragacanth thickening 6 per cent. Boil, cool, and add—
40	,,	caustic soda 70° Tw.

And, before printing,

5	grms.	copper sulphate 10 per cent. solution.
5	,,	magnesium acetate 32° Tw.
1000		

Yellow R.B.

760	grms.	tragacanth thickening 4 per cent.
100	,,	Persian berries extract 52° Tw.
100	,,	Bark extract 52° Tw.
20	,,	glycerin. Boil, cool, and add—
20	,,	caustic soda 70° Tw.
1000		

Olive:— 4 to 8 Yellow R.B.
1 to 1 Grey R.L.

Fawn:— 6 Brown R.C.
6 Yellow R.B.
1 Grey R.L.

Green:— 2 to 6 Yellow R.B. (without caustic soda).
1 to 1 Prussian blue sol. 30 per cent. (in oxalic acid).

Bright Green:— 4 to 8 Yellow P.B. (see raised yellows).
1 to 1 Prussian blue sol. 30 per cent.

Yellow:—Yellow P.B. or P.B.C. (raised yellow).
Black:— Aniline, Diphenyl, or Logwood iron blacks.
Blue:— Steam Prussian blue.
Slate:— Alizarin blue S., with zinc sulphate.

Print all the foregoing colours on white unprepared cloth; dry and steam 3–5 minutes in the rapid ager; pass continuously through a 1–2 per cent. solution of sodium bichromate, wash well and dry. Somewhat better results are secured by hanging the steamed goods in a warm chamber before "chroming." In the case of Catechu, a darker shade is obtained after a 2–3 days' exposure to warm air.

The above described style is almost obsolete, though it is still used occasionally on the Continent for certain classes of heavy dull-coloured furniture cretonnes.

(7) PRINTING OF LININGS (PASTE COLOURS).

Most of the linings used by clothiers and dressmakers are printed with striped patterns, and where the whole surface of the material displays the same texture they are produced by means of the ordinary "steam colours."

Some classes of linings, however, have the appearance of brocade stripes, that is, one stripe is lustrous while the next has a dull matt surface. This latter effect is obtained by printing zinc oxide either alone or tinted with pigment, direct, or basic colours. The zinc oxide is fixed with albumen, and it retains its dull, pasty appearance even after the cloth has been heavily calendered or Schreinered, to give a lustre to the unprinted portions. Naturally, the best contrast is obtained by printing zinc white on sateen cloth, and especially on mercerised sateen that is subsequently "lustred" in the Schreiner calender. Other patterns may, of course, be employed at will in place of stripes, and many beautiful brocade or damask effects are obtained by printing various patterns in zinc oxide colours on white or tinted grounds.

Zinc Oxide Printing Paste.

350	grms.	zinc oxide.
50	..	glycerin.
250	..	egg albumen 50 per cent. sol.
250	..	6 per cent. tragacanth thickening.
70	..	olive oil.
30	..	turpentine.
1000		

Grind the whole until it will pass easily through a straining cloth.

Print, steam in the rapid ager, and then finish without any further treatment. The above colour gives fine white damask effects on both white and tinted grounds.

For coloured effects of the same sort, an addition of any suitable colouring matter is made to the white paste. For this purpose any basic, direct, or pigment colour may be used, the quantity taken depending on the shade required. Generally, very light shades give the best results.

The majority of linings are printed on white or delicately tinted grounds, and when a dark colour enters into the pattern it is usually one of the ordinary "steam colours." The grounds are tinted with direct dyeing colours in the padding machine. Black, red, claret, brown, blue, and other dark ground linings are produced by any of the discharge or reserve processes already described—*e.g.* Aniline black, Para red, Para brown, Naphthylamine claret, Diaminogene blue, Sulphide colours, etc.

Besides zinc oxide, barium tungstate, barium sulphate, and lead sulphate are also used for damask effects. The tungstate of barium yields an exceedingly brilliant white, while the sulphates of lead and barium are only used for inferior and cheaper work. They (the two latter) are by-products from the preparation of aluminium acetate and sulphocyanide.

(8) METAL PRINTING.

The production of permanent metallic effects on textile fabrics is a problem which has occupied the attention of calico printers for a very long time.

Apart from the technical difficulties encountered in the printing of pastes containing a high percentage of metal in the form of a finely divided powder, it was impossible, until within recent years, to obtain solid-looking prints which were fast to washing and were unaffected by the action of impure air. At first sight it might appear that metallic powders could be treated like pigment colours, and fixed like, say, Chrome yellow with albumen. Such a process, however, does not yield satisfactory results; the prints are uneven, poor in colour and lustre, and lacking the body and the solidity so characteristic of the gold and silver woven and embroidered effects which first suggested the idea of applying metallic powders by printing. The heavy metallic powders settled in the colour box and stuck in the engraving and the chemical action of albumen, which contains sulphur, blackened the "gold" and "silver" powders, owing to the formation of copper and tin sulphides. The substitution of oil varnishes gave much more satisfactory results so far as regards brilliancy and permanency, but the method of printing mixtures of "gold" and "silver" and varnish with ordinary engraving left much to be desired in the way of solidity of appearance; in fact, the method was little used on this account. The most successful of the old processes of metal printing consisted in applying a sticky paste of glue and starch to the fabric, which was then passed directly, before the paste was dry, through a closed box, in which bronze powder was lightly brushed on the cloth. On leaving the "bronzing box," the cloth passed continuously through a series of closed boxes fitted with guide rollers and beaters, which latter, acting on the under side of the cloth, beat off all the "gold" powder not adhering to the printed parts. The goods were then hung in a dry, warm room in order to harden the glue vehicle, and, after a thorough brushing to remove all loosely adhering powder, were calendered to burnish the metal. In this way very effective and solid-looking metallic patterns were obtained, but unfortunately they were neither fast to washing nor to the blackening influence of impure air. Goods printed by this process were intended mainly for decorative hangings in theatres and the like, and consequently their liability to blacken in a gas-laden atmosphere was a serious drawback. With improved methods, however, many of the defects of earlier processes have been overcome; so much so, indeed, that even fine patterns are now printed on dress goods—patterns which retain their metallic lustre after washing and a long exposure to all sorts of air.

These improvements date from the introduction of the continuous stencilling machine patented by S. H. Sharp in 1894. Sharp's machine provided the first practicable means of producing fast, solid, metallic prints.

The metallic powder mixed with varnish was stencilled on the cloth, and the varnish was then dried by hanging the goods for several days in a warm, dry atmosphere; when quite dry and hard, the lustre of the metal was brought out by calendering. Prints executed in this way are remarkably permanent, and stand a severe soaping if the temperature is not too high; in the cold they are practically unaffected by strong caustic soda, a property which allows of them being "crimped," according to the methods to be described when dealing with the "Crimp or Crepon" style.

As Sharp's apparatus was patented, other methods were sought of producing similar results by means of the ordinary cylinder printing machine.

Previous attempts to print metallic varnishes with engraved rollers had given unsatisfactory work, but the problem was attacked afresh, and finally it was discovered that the cause of the earlier failures was due entirely to unsuitable engraving. The ordinary engraving of masses consists of a series of corrugations or furrows (the "ground"), which, although essential to the printing of starch, flour, gum, and albumen colours, are altogether inadequate to the production of first-rate metallic prints. The metal is not only apt to stick in and fill up the engraving, but even when a brush furnisher is used to keep the furrows clear of deposit, the amount of colour transferred to the cloth is insufficient to give a solid effect on calendering. The engraving adopted for metal printing is deep and smooth, without any furrows or other roughness whatsoever. Usually the pattern is etched out with nitric acid, and many worn-out copper rollers, useless for ordinary printing, can be utilised for metal printing by re-etching them deeply, so as to dissolve away most of what "ground" may still remain. From such deep, smooth engraving a heavy charge of "colour" is transferred to the cloth, and, with a brush furnisher, no difficulty is experienced in printing varnish mixtures containing as much as 25–30 per cent. of "gold" or "silver" powders.

A good quality of hard-drying copal varnish is the best medium to use for the printing and fixing of the various bronzes and "silvers." The metallic powders or "bronzes" consist of finely divided alloys of copper and tin, with sometimes zinc and lead; "silver" is either tin or aluminium, generally the latter. "Gold bronzes" vary in shade from the deep red of copper to the palest tint of gold; and, besides these and the "silver," there are a variety of crimson, blue, green, orange, olive, and other shades of so-called bronzes. Sometimes these coloured bronzes are mixed with aluminium powder to enhance their lustre.

The printing of bronze powders is carried out in the usual manner, but the goods are not passed through the drying apparatus; in fact, it is quite impossible to run them under and over a series of rollers, because the varnish, being sticky, would soil anything with which it came in contact. Instead of the ordinary drying, therefore, the printed cloth is drawn right over the drying machine and plaited down between "greys," the printed side to the "grey cloth." Some little "bronze" sticks to the grey, but the loss is too slight to affect the ultimate result to any appreciable extent. It is an advantage to employ damp "greys," since the presence of moisture prevents the varnish attaching itself to the "grey." From the printing machine, the goods are taken to a hot, dry hanging room, and there suspended until the "colour" is dry and hard; then, without further treatment, they are cold calendered and made up.

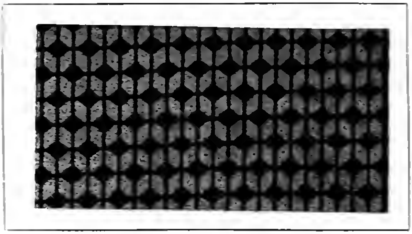
Gold Bronze.

250 grms. Bronze powder.
750 ,, copal varnish.
1000

"Silver."

100– 150 grms. aluminium powder.
900– 850 ,, copal varnish.
1000 1000

Other bronzes are prepared for printing similarly. Print: plait down between "greys": hang 3–6 days in a dry, warm ageing chamber; calender and finish.



Metal print.

Metal printing is confined to a very few styles It is not suitable for white or delicately tinted cloth, as the oil in the varnish spreads by capillary attraction beyond the edges of the pattern. On light grounds this causes an unsightly yellow stain all round the printed objects, whereas on dark grounds it is unnoticeable, though present. Moreover, dark blue, green, black, claret, purple, etc., contrast much better with gold and silver than pale pinks and the like. Again, very few colours are available for printing alongside "bronzes," because the lustre of the latter is impoverished by the acid fumes generated in the steamer. On blue grounds a Logwood iron black and green zinc oxide colour (see Linings) may be printed with good effects alongside a "gold" bronze, but as they cannot be steamed they are not fast, and are only suitable for temporary decorations, which are not expected to stand washing.

On goods already dyed, steamed, and finished, a cover pattern is often printed in "bronzes." In such cases a combination of steam prints with metallic effects is obtained, but the two patterns do not register with each other, and the steam or dyed colours can scarcely be said to have been worked in combination with the "bronze" cover print. Most of the metallic prints produced to-day are small spots, sprigs, and stripes on sateen cloth, previously dyed in various dark shades. They had a great run a few years ago, but never became, nor are likely ever to become, fashionable.

(9) CREPON OR "CRIMP" STYLE.

The characteristic feature of this style is the appearance of alternate plain and crinkled stripes in the fabric itself. Sometimes one, sometimes the other, and sometimes both of these two sorts of stripes are coloured; at other times they simply take the colour of the pattern over which they run.

The crinkled stripes, known as "crepon" and "crimp" stripes, are produced by a process based upon the property possessed by concentrated solutions of caustic soda, of causing cotton to shrink. Cotton cloth, printed in a stripe pattern with strong caustic soda, shrinks in the printed parts, and thus causes the unprinted parts to cockle or "crumple up." The greater the shrinkage or contraction of the printed parts, the more pronounced is the crepon effect obtained.

Coloured stripes are produced by the addition of direct-dyeing dyestuffs to the caustic soda or the paste used for printing the stripes to be "crimped" or "creponed."

Similarly, direct dyestuffs are employed for printing the patterns on cloth that is subsequently "covered" or otherwise treated in strong soda lye. But for this latter purpose any colours that are unaffected by caustic soda solutions—*e.g.* Aniline black, Indigo, and other vat dyestuffs, Sulphide colours, Para red, Naphthylamine claret, and even Victoria blue (basic colour)—may be employed, either alone or alongside the direct dyestuffs, so that the crepon style is capable of being applied to a great variety of purposes. In addition to the direct printing of multicolour patterns on white grounds, discharge and resist effects are easily obtainable on Aniline black by means of zinc oxide in conjunction with direct dyestuffs, or by Pluzanski's Azo colour resist process. The latter yields the fastest work; the former the greater variety.

There are two methods of producing crepons:—

(*a*) By the direct printing of caustic soda.

(*b*) By printing the parts of the cloth to be "crimped" with a gum resist, and afterwards padding the goods through caustic soda in a small padding machine.

By the first method it is impossible to print a design between the crepon stripes; that is, the plain stripe must always be white or a flat tint. By the second method any kind of pattern can be applied to the plain stripe, since the caustic soda treatment is a separate operation, and the goods can therefore be steamed or undergo any other suitable process before they are padded in caustic soda. In neither process of crimping is it usual to decorate the crimp stripes, not because it cannot be done easily enough by engraving for the purpose, but because the effect is bad. In some cases, however, the crepon or crimp stripe consists of several colours, arranged somewhat after the fashion of a continuous upright spectrum.

(*a*) Direct Process of Crimping.

In this process the cloth is printed with a thickened solution of caustic soda corresponding to between 60°-90° Tw. A pattern of any number of stripes may be employed, and by suitably distributing the caustic colours and the ordinary colours between the several rollers, either the plain or the crimp stripes, or both, may be produced in a variety of shades. Dark reds and clarets are obtained by printing Para red and Naphthylamine claret on naphthol-prepared cloth, along with caustic soda colours in the other rollers; such reds and clarets necessarily appear in crimped stripes only, since the addition of caustic soda to Azo colours would prevent their coupling with the naphthol. Aniline and other blacks, and dark colours generally, are unobtainable by the direct method of crimping, on account of the fact that the goods cannot be steamed with any degree of satisfaction. Apart from that, too, the "scumming" of the caustic soda influences them unfavourably. Some of the vat dyestuffs might possibly be applied successfully, as the "marking off" of the caustic soda on the rollers of the ager would not be likely to affect them prejudicially; this, however, is a point that remains to be tested.

I. Caustic Soda Printing Colour 64° Tw. (for Plain White Stripes).

6·400 litres caustic soda 100° Tw.
3·600 ,, gum Senegal 35 per cent. solution.
10 litres.

Add the soda to the gum gradually, stirring all the time.

II. Caustic Soda Printing Colour (for Plain Coloured Stripes).

6·4 litres caustic soda 100 Tw.

Add gradually to

3 litres gum Senegal 40 per cent.
250 grms. Direct dyestuff.
350 ,, water (boiling).
10 litres.

Mix the dyestuff with the water and then add the gum; heat till the dyestuff is dissolved.

For Pink take:—Erika B.N.
,, Yellow ,, Diamine fast yellow A.
,, Blue ,, Diamine sky blue F F.
,, Green ,, 2 parts blue; 7 parts yellow.
,, Violet ,, 2 parts pink; 1 part blue.
,, light shades, any of the above, reduced with caustic soda gum 64° Tw. as above.

If the crimp stripes are to appear in colours other than Para red and Naphthylamine claret, the direct dyestuffs are again employed, but made up in the following manner:—

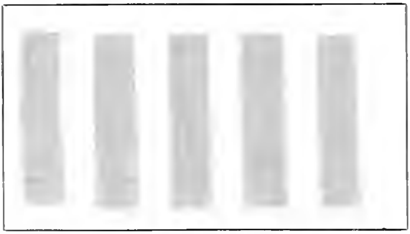
Colours for "Crimp" or "Crepon" Stripes.

25 grms. Direct dyestuff.
400 ,, water.
30 ,, phosphate of soda.

Dissolve, and stir into—

545 grms. 6 per cent. tragacanth thickening or starch paste.
1000

Heat the whole until the dyestuff is perfectly dissolved. and then cool down.



Direct Crimp.

According to this recipe, almost all direct dyestuffs may be employed. Light shades are obtained by adding extra thickening as required.

In order to obtain the best results as regards the prominence of the crepon stripes, the caustic colours should occupy at least half the surface of the cloth; indeed, the very best crepon effects are secured by printing the caustic colour in broad stripes, leaving only narrow stripes of unprinted cloth, or cloth printed in colours containing no caustic soda between each broad stripe. In this way the greater part of the cloth undergoes considerable shrinkage, thus causing the lesser part, which is not subjected to the action of the caustic soda, to crimp in the most pronounced fashion.

One example of the method of producing a four-colour pattern by the

"Direct Method of Crimping" will illustrate sufficiently the principle of the general *modus operandi.* For instance, to obtain an effect consisting of red, blue, and yellow crimp stripes, with broad white plain stripes between them, the cloth is first of all prepared in β-naphthol as usual.

It is then dried and printed for the colours in Para red, Diamine sky blue F.F., and Diamine fast yellow A., all thickened with tragacanth, starch, or British gum, and for the White, with caustic soda 64° Tw., thickened with either gum Senegal or tragacanth. After printing, the goods are run through the air for a short time with as little tension as possible, to allow the mercerised cloth to contract to the fullest extent; they are then passed through a hot air chamber and partly dried to prevent "marking off," and finally they are washed thoroughly in cold running water, soured in dilute sulphuric acid, washed again, and dried over cylinders or in hot air. In the wet state no more tension than is necessary should be put on the goods, otherwise they are liable to stretch, and so lose a good deal of their crepon effect.

Instead of printing the foregoing colours on white cloth, whereby stripe patterns only are possible, a good deal of variation can be obtained by printing them on cloth already printed in a multicolour floral or other pattern. In this case the previously applied pattern must, of course, be in colours that will withstand the action of caustic soda. Similarly, blotch patterns may be "crimped" with good effect; in fact, any suitably resistant colour may be utilised in this way to advantage. Amongst the colours that withstand caustic soda the following may be mentioned :—Azo reds and clarets, Victoria blue (tannate of antimony mordant), Silvertown blue dyed on iron mordant, Iron buff, Indigo, Thio-indigo, Brom-indigo, Vat red B., and the Ciba, Indanthrene, Helindone, Sulphide, and most of the Direct dyestuffs. Aniline black is also pre-eminently adapted to crimping after development.

(*b*) Resist Method of Crimping.

This process, which is due to John Mercer, is founded on the fact that thick solutions of gum Senegal, gum arabic, gum Gedda, or British gum, when printed on cotton cloth, form, when dry, efficient "resists" to the mercerising or shrinking action of caustic soda. They act mechanically by preventing the soda from coming into contact with the fibre during the subsequent crimping operation, which consists in padding the printed goods, through caustic soda, in a padding machine.

On the other hand, gum tragacanth, at the strength used for thickening colours, offers no appreciable obstruction to the absorption of caustic soda by the fabric, and therefore it can be used safely for the production of the plain stripes when these are required in colour, or when a plain white stripe is required to be decorated with a printed design.

By a plain stripe is understood a flat, uncrinkled stripe, irrespective of any pattern it may carry.

The same colours that are used for the "Direct Process" are used for the "Resist Process," but in the latter they are capable of being applied to a much wider range of patterns ; in fact any multicolour pattern containing a solid stripe can be executed by the Resist Crimp process as easily as by any other ordinary method of printing. All that is necessary is to use alkali resisting colours thickened with tragacanth in the plain, smooth stripes, and similar colours thickened with gum Senegal or British gum for the crimp stripe or stripes.

Apart from its wider scope, the "Resist Process" offers another great advantage over the Direct Process, inasmuch as the printed goods can be steamed before they are treated in caustic soda. This facility is not only of immense value as regards the better fixation of the colours, but it also makes possible the production of many crepon effects otherwise unobtainable. For instance, Aniline black may be employed as a part of a multicolour pattern that registers with the crepon stripe; or, again, resist effects on an Aniline black ground in combination with a white or coloured crepon stripe may be as easily obtained as by the usual Aniline black resist process. Neither of these styles are possible by the Direct Method of Crimping.

In practice, either gum Senegal or a "dark" British gum is used for printing the parts of the cloth to be "crimped."

The British gum is the cheaper, and for any but the most delicate shades quite as effective a resist as gum Senegal.

Gum tragacanth is employed solely for printing the "uncrimped" parts of the cloth, and for this purpose it has no competitor.

For convenience of description, colours thickened with dark British gum will be distinguished as "B.G. colours," while those thickened with tragacanth will be referred to hereafter as "G.T. colours." It may be well to note that "B.G. colours" may sometimes contain gum Senegal for the purpose of improving their working qualities; this, however, does not demand any modification of the nomenclature, since both gums play the same rôle.

The separate operations connected with the "Resist Crimp Process" are as follows:—

(1) Print the cloth with the required B.G. and G.T. colours.

(2) Dry and steam 3–60 minutes according to circumstances.

(3) Pad "straight through the nip" in caustic soda 50°–60° Tw. Allow to lie a short time, and then—

(4) Wash well in the rope form until the goods are free from soda.

(5) Sour in sulphuric acid ¼° Tw., wash, and dry.

If the patterns contain such colours as Benzopurpurine or Congo red, it will be necessary to treat them in dilute ammonia after the last wash out of "sours" in order to re-develop their bright red colour, which is turned blue by acid.

In the case of Aniline black resists, the printed goods are best steamed for 45–60 minutes after printing; they are then padded in Aniline Black P. or P.S. (see Black Discharges, pp. 513 and 514) in the usual manner; dried and steamed 3–4 minutes in the rapid ager 90°–94° C. The rest of the process is as above.

The following formulæ have given excellent results on the large scale:—

RESIST B.G. (FOR WHITE CRIMP STRIPES).

500 grms. dark British gum.
500 ,, water.

1000 Boil and cool. Best used slightly warm.

B.G. COLOURS FOR CRIMP STRIPES.

	RED B.G.	PINK B.G.	YELLOW B.G.	BLUE B.G.	GREEN B.G.
Congo red	50	...	...	...	...
Erika B.	...	25	...	...	...
Diamine fast yellow A.	...	...	25	...	...
Thioflavine S.	...	...	...	...	18
Diamine sky blue F.F.	...	...	...	25	6
Phosphate of soda	50	25	25	25	26
Water	475	500	500	500	500
Dissolve and add—					
Dark British gum	425	450	450	450	450
Heat together until the gum is dissolved, and cool.					
	1000	1000	1000	1000	1000

Paranitraniline red cannot be used with dark British gum. Other shades are obtained by mixing the above.

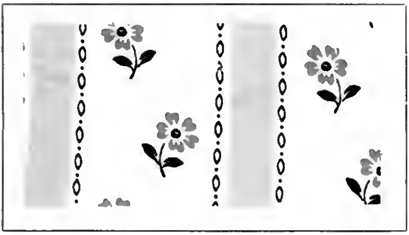
G.T. Colours (for Plain Coloured Stripes or for Patterns on Plain White Grounds).

Type:—

25 grms. Direct dyestuff.
25 ,, phosphate of soda.
475 ,, water.
475 ,, 6 per cent. tragacanth thickening.

1000 Boil and cool

For the various shades use the same dyestuffs as are used for B.G. colours. Instead of the Congo red, Para red (printed on naphtholated cloth) may be used for heavy plain stripes When Congo red is employed, the addition of albumen is beneficial in preventing it from "running."



Gum resist Crimp.

Examples:—

(1) *Pink crimp stripes with Three-colour pattern between them.*—Print the stripe with Pink B.G. and the pattern between with Blue G.T., Green G.T., Yellow G.T. Dry.

(2) *Pink crimp stripe and Green plain stripe.*—Pink B.G. and Green G.T.

(3) *White crimp stripe and Red plain stripe.*—Print Resist B.G. for the white and Para red (tragacanth thickening) for red on naphtholated cloth. Dry.

(4) *White crimp stripe on plain Black ground.*—Print Resist B.G. containing 30 per cent. acetate of soda on Aniline black padded cloth. Dry.

Nos. 1 and 2 may be steamed 45 minutes; No. 3 is not steamed at all; and No. 4 is steamed 3–4 minutes and then dried. All are then padded in caustic soda 63° Tw., washed well, soured, washed, and dried. In padding, the goods pass directly between the bowls of the padding machine; the bottom bowl is partly immersed in the caustic liquor, and supplies a sufficiently large charge of caustic soda to the cloth, without the risk of dissolving the "resist." Wherever the B.G. colours have been printed the cloth "cockles," and on washing out the resist it assumes the well-known appearance of the crepon effect.

The Aniline Black Resist Style in Crepons.—By combining the zinc oxide process of reserving Aniline black with the resist method of crimping, it is possible to obtain a great variety of coloured crepon effects, in which the "plain" stripe displays a floral pattern in several colours on a black ground, while the "crimp" stripe may be in white or colours according to the pattern in hand. The advantage of this method is that the crimp stripe is an integral part of, and "fits to" or registers with, the floral or other portions of the pattern.

With the exception of an addition of zinc oxide, the colours used are essentially the same as the B.G. and G.T. colours already given. They are prepared according to the following directions:—

(*a*) FOR CRIMP STRIPES.

B. RESIST WHITE B.G.

200	grms.	precipitated chalk.
50	,,	potassium sulphite 90° Tw.
50	,,	acetate of soda.
365	,,	water.
325	,,	dark British gum.
1000		

Beat the whole into a smooth paste and heat until the gum is dissolved, cool.

B. Resist White B.G. gives a better white under the black than zinc oxide. Zinc oxide, however, is to be preferred for colours, because it works better in printing and yields brighter shades. It is usually ground up with a little glycerin, and turpentine is added to minimise the tendency to froth.

Z. PASTE B.G. (FOR COLOURS) STANDARD.

200	grms.	zinc oxide.
170	,,	water.
25	,,	glycerin.

Beat into a paste, and add

200	grms.	dark British gum.
150	,,	gum Senegal 50 per cent. solution.
30	,,	turpentine.
775		

Heat to dissolve the gum, and then use warm or cold.

B. COLOURS B.G. (CRIMP STRIPES).

	B. RED B.G.	B. PINK B.G.	B. BLUE B.G.	B. GOLD B.G.	B. YELLOW B.G.
Congo red	50	...	..	...	...
Erika B.	...	25	...	...	...
Diamine sky blue F.F.	...	...	25	...	...
Diamine fast yellow A.	...	...	...	25	...
Thioflavine S.	..	...	...	...	25
Water	150	175	175	175	175
Phosphate of soda,	50	25	25	25	25
Dissolve and add—					
Z. Paste B.G. Standard	700	775	775	775	775
Albumen 40 per cent.	50	...	...	...	...
	1000	1000	1000	1000	1000

GREEN = 3 parts Yellow to 1 part Blue.
VIOLET = 2 ,, Pink ,, 1 ,, Blue.
OLIVE = 3 ,, Gold ,, 1 ,, Blue.
ORANGE = 6 ,, Gold ,, 1 ,, Pink.
SALMON = 3 ,, Gold ,, 1 ,, Pink.
FAWN = 14 ,, Pink, 5 parts Gold, 1 part Blue.

For lighter shades use the following reducing paste:—

Reducing Paste B.G.

775	parts	Z. Paste B.G.
225	,,	gum Senegal 30 per cent.
1000		

(*b*) For Colours in the Uncrimped Stripes on Black Ground.

B. Resist White G.T.

200	grms.	precipitated chalk.
50	,,	sulphite of potash 90° Tw.
50	,,	acetate of soda.
5	,,	Ultramarine blue.
345	,,	water.
350	,,	6 per cent. tragacanth thickening.
1000		

Grind well.

Z. Paste G.T. (Colours only) Standard.

200	grms.	zinc oxide.
25	,,	glycerin.
180	,,	water.
340	,,	6 per cent. tragacanth thickening.
30	,,	turpentine.
775		Grind well.

B. Colours G.T. (for Uncrimped Figured Resists on the Plain Black Ground).

Except that "Z. Paste G.T. Standard" replaces "Z. Paste B.G. Standard," these colours are identical with those immediately preceding, namely, the B. Colours B.G. Being thickened with gum tragacanth, they offer no resistance to the penetration of caustic soda into the cloth, and consequently they do not impede its mercerisation like the B.G. colours, which are thickened with British gum. Both groups of colours prevent the development of Aniline black by reason of the zinc oxide they contain.

A pattern consisting of alternate blue and white crimp stripes, having between each stripe a floral pattern in, say, red, pink, blue, yellow, green, and white, the whole being on a black ground, is produced by the following sequence of operations:—

(1) Print the blue and white stripes in B. Blue B.G. and B. Resist White B.G., and the rest of the pattern in B. Red G.T., B. Pink G.T., B. Blue G.T., B. Yellow or Gold G.T., B. Green G.T., and B. Resist White G.T. Dry.

(2) Steam for one hour. This may be omitted, but it improves the fastness of the colours. The steam must not be too moist.

(3) Pad through prussiate Aniline black in the usual manner for resist black styles. Dry quickly, but not too hard.

(4) Steam for from 2–4 minutes in the rapid ager, and pass through gaseous ammonia.

(5) Pad through caustic soda 63° Tw. Squeeze out excess of liquor and allow to lie a few minutes.

(6) Wash, in the rope form, in plenty of running water.

(7) Sour in sulphuric acid ¼° Tw. Wash in water.

(8) Wash in water containing a little ammonia; hydro-extract and dry up.

Goods printed according to Pluzanski's process of reserving Azo colours under Aniline black may be converted into "crepons" by running a stripe over them in thick British gum and, after drying, padding in caustic soda as above; or, more simply, by printing them directly with caustic soda. In neither case is it possible to obtain the crepon stripes in either white or colour, or in register with the reserve colours; they fall indiscriminately over pattern and ground, and take the colours of each. The same remarks apply to all styles in which the crepon stripes are printed as a "cover."

Other methods of producing direct colour resists under Aniline black for crimping are of little technical value: neither acetate of soda, acetate of zinc, acetate of magnesium, caustic soda, nor alkaline carbonates yield results at all comparable with the zinc oxide resists. In each case the colours are duller and weaker, no matter how they are applied.

"Crimped" metallic stripes are exceedingly effective so far as appearance is concerned, but they require care in their execution, otherwise the caustic soda is liable to saponify the oil and resin (varnish) with which they are fixed. To avoid this as much as possible, the printed goods are allowed to hang longer than usual in order to thoroughly harden the varnish; they are then calendered to burnish the metal, and finally padded through caustic soda and washed off without undue loss of time.

The best kind of fabric for "crepon printing" is one with more warp than weft, the most pronounced crimping of the stripes being the result of the contraction of the cloth in the direction of its length.

Some years ago the "Crepon" or "Crimp" style had a very successful run: at the present time, however, the production is limited, although it is capable of yielding some very fine effects.

PART VIII.

FINISHING OF PRINTED CALICOES.

FINISHING OF PRINTED CALICOES.

Finishing—the last stage in the production of a calico print—is a very important operation, since upon the quality of the "finish" depends in many cases the market value of the goods. The sole object of finishing is to give what is considered to be an attractive appearance and handle to the printed fabric. As to what constitutes an attractive appearance is a matter of opinion, and one better left undiscussed here; for many merchants require the same cloth, printed with the same pattern and in the same colours, to be finished in different ways, according to the individual taste of their customers in the various markets for which the goods are intended. Hence, taking into account the hundreds of different sorts of cloth in general use, it is obviously impossible, in a work of this size, to treat the subject of finishing on anything like definite lines; and it would be no less so even if a particular material were always given the same finish, because the methods and materials employed to attain identical results must be varied according to the condition in which the "finisher" receives the goods. For instance, goods printed in pigment colours, and "steam colours" thickened with starch or flour, are generally stiffer and harder than "dyed goods" and those that have been printed in gum-thickened colours. Consequently they must be treated differently in finishing if they are all to have the same ultimate "feel" and appearance. In some cases the stiffness, if undesirable, may be removed by re-soaping the cloth, or by steeping it in a weak infusion of malt for several hours, followed by a good washing; but this is not always feasible, especially if the colours are only moderately fast, and in such cases the finisher has to impart the necessary softness by other means. In like manner also the extra stiffening and other operations connected with the production of a particular kind of "finish" have to be modified in the course of working, in order to obtain uniformity in the "feel," gloss, weight, and appearance generally of the various lots of one cloth printed with the same, or same class of, pattern, but in an assortment of colours which have been applied by different methods and thickened with very different materials.

From the foregoing it will be evident that the business of the finisher can only be learned by experience, and that successful finishing can only be accomplished by employing such processes as experience, guided by the evidence afforded by a critical examination of the goods to be treated, shows to be best calculated to yield the required result. Moreover, finishing, although, like engraving, an integral part of calico printing, is yet a separate and distinct trade, with a literature of its own. Hence, more than a brief reference to and outline of the principal processes of finishing will not be attempted.

Finishing comprises the operations of stiffening, clearing, drying, stretching, calendering, embossing, measuring, and making up into attractive packages.

(1) **Stiffening** is effected by two different methods—

a. Padding in starch or other pastes.

b. Back starching.

Beyond the employment of suitable pastes, the first method is identical with the padding of dye liquors, and is performed in machines of similar construction.

In "back starching" the procedure is different in every respect, inasmuch as the goods do not pass through the stiffening paste, but have it applied to their unprinted sides by means of a roller, the lower half of which works in the paste, while the upper part comes into contact with the back of the cloth as it travels forward through the machine. Excess of starch is scraped off the cloth by a brass doctor placed immediately behind the starch roller. Fig. 79 will explain the mode of action of a "back starcher."

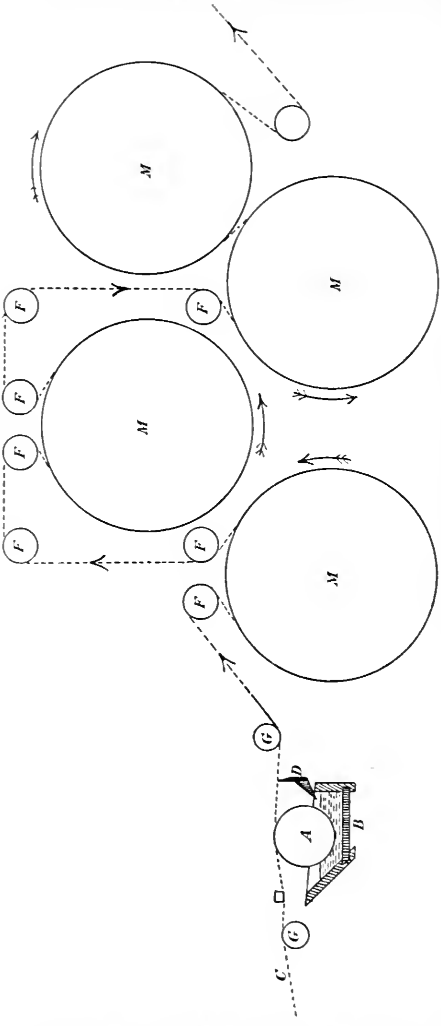


Fig. 79.—Section of back starching arrangement.

A is the starch roller, B the box containing starch paste, C the cloth, printed side uppermost, D the doctor, G G two adjustable guide rollers, F F skeleton guide rollers, M M large drying cylinders. The drying of the cloth is so arranged that the starched side does not come in contact with the cylinders until it is sufficiently dry not to "mark off." The brass doctor D is adjustable, so as to allow of a greater or less amount of starch remaining on the goods as required.

Most printed goods that are starched are treated on a "back starcher" in order that the brilliancy of the colours may not be impaired by the presence of a film of semi-opaque starch. For transparent finishes, they are usually padded in solutions of gum, soluble starch, or soluble salts.

A variety of starches are used, differing in the nature of the pastes they give when boiled. For some purposes a firm, stiff paste is best, whereas for others the softer and more gummy the consistency of the paste the better. By a suitable choice of starches all degrees between the two extremes may be obtained. As a rule, potato starch and sago flour are preferred, but wheat starch is also used, and besides pure starches there are many special "finishing starches" on the market.

For transparent finishes, the stiffening agents used are chiefly dextrine, soluble starch, common salt, and some "Epsom salts," the last chiefly in combination with other ingredients.

China clay is extensively employed in all branches of "starching" to increase the weight of the goods, and to fill up the interstices in low-grade fabrics. Far too much attention is paid to the "weighting" and "filling" of cotton fabrics, and, so far as the home trade market is concerned, it is a questionable policy to give the goods an appearance of solidity that they are far from possessing: the first wash removes the adulteration, and shows up the poverty-stricken quality of the cloth; and as no one wants to buy China clay and starch for calico, the exposure of the deception results in the loss of a customer if the goods have been originally purchased for the apparent quality of the material. In the case of goods that are not intended or expected to stand washing, "weighting" and "filling" may be used without drawback; and in certain styles of decorative work, such as temporary hangings and upholsterings, they are an advantage, since they allow of cheaper material being used for purposes which more expensive goods would serve no better. China clay is always employed along with starch and not with any other thickener.

Amongst the other adjuncts of the finisher are softening agents and various "blueing" substances. The former consist for the most part of soap, tallow, Turkey-red oil or glycerin, and sometimes glucose. Various hygroscopic salts —*e.g.* calcium chloride, magnesium sulphate, zinc chloride—and antiseptic bodies are also employed to impart softness and weight, and to prevent the formation of mildew. For "blueing" purposes artificial ultramarine is generally preferred, but occasional use is made of the soluble artificial dyestuffs of the basic and acid groups: the object of "blueing" is to neutralise the unpleasant yellow tint of "white grounds"—a tint that is always noticeable before finishing. The blue is applied in several ways according to circumstances. Sometimes it is mixed with the stiffening, sometimes with the "clearing liquor," and sometimes it is applied in a separate operation.

(2) **Clearing.**—This process simply consists in passing the goods through a dilute solution of bleaching powder and then, without washing, drying them directly over steam-heated cylinders. In some cases the goods are passed through a steam box before drying, but this is usually done before the "finisher" receives the goods. If the goods are only very slightly tinted, the bleaching liquor may, at times, be added to the starch paste used for stiffening.

(3) **Drying.**—After starching or otherwise stiffening, printed calico is usually dried over cylinders. If, however, it has lost too much width in process, it is dried a second time over a machine specially designed both to dry and stretch it out to the required width. This machine, known as a "stenter," consists essentially of a long horizontal frame of iron, along each side of which an endless chain constantly travels. On entering the machine, the cloth is gripped at the selvedges by pins or clips attached to the two endless chains, which, for a certain predetermined distance, gradually recede from each other, thus stretching the cloth breadthwise. At the same time the cloth is damped on the under side by

steam, so as to increase its elasticity. When the desired width has been reached the chains run parallel to each other; and the cloth, now held at the full stretch by the clips, and still travelling forward along the remaining length of the machine, is dried by the strong heat of a forced draught of hot air applied to its underside—a heat which not only dries but "sets" the cloth, and prevents its subsequent shrinking to the narrow width when it is finally released from the grip of the chain clips. The stenter used in finishing is similar to that shown on Plate VIII. p. 171, but it is longer and is provided with the damping and drying arrangements already referred to.

In certain styles, notably in muslins, the finish is almost, if not quite, as important as the cloth itself. Mercerised muslins are usually finished "soft," being as a rule simply passed through water containing a very little Turkey-red oil, then stretched and dried to width over the stenter, and finally calendered lightly to smooth them down. Starching is avoided as much as possible, as it tends to flatten the silky lustre of mercerised goods.

On the other hand, the characteristic "Batiste Finish" on muslins is obtained in quite another way, and depends upon the previous stiffening of the fabric, combined with a special method of stretching and drying. Starched muslin dried over any of the ordinary machines or "stenters" has a hard, "boardy" feel, is rigid, and inelastic and rough to the touch. In order to overcome these defects it is dried and stretched over a specially constructed "stenter" known as a "Jig Stenter." In this machine the clip chains travel forward along the frame with a "to and fro" movement in the direction of their length, each chain advancing and retreating in turn so that the cloth gripped between them is stretched by the constant backward and forward movement of its selvedges. The arrangements for damping and drying are exactly like those in the ordinary stenter; in fact the Jig Stenter is generally designed to work at will as an ordinary stretching machine, the Jig Motion being simply an extra movement. The effect of stretching and drying or Jigging the cloth in this manner is to cause the warp and weft threads to rub against each other, and thus to prevent them sticking together when the stiffening is dry. Batiste finished muslins have a soft, full, springy "feel," something like that of silk, but without its lustre; they are perfectly free from hardness, and possess a certain amount of elasticity which enables them to drape well without falling into clinging folds.

(4) **Calendering.**—A calender is a machine having heavy cylinders revolving when in work almost in contact with each other, so that cloth passing between them is smoothed and glazed by their pressure. The degree of glazing depends on the amount of pressure put upon the cloth.

Ordinary calenders consist of an iron bowl in the centre, with two paper or compressed cotton bowls above and below. The iron bowl is hollow, so that it can be heated by steam or gas, a contrivance which is required for certain finishes.

When a very high glaze is required, use is made of the "Friction Calender." This machine consists of one hollow chilled iron bowl, arranged to be heated by steam or gas, one paper bowl above it, and above that a second and smaller iron bowl, which works at a higher speed than the two lower ones, and thus causes friction. The action of the friction-bowl results in the production of an exceedingly brilliant glass-like glaze, which can be controlled either by reducing the speed of the bowl in question or by decreasing its pressure on the fabric.

In the embossing calender (for producing the *moiré* finish) a variety of figures are impressed on the cloth by an engraved steel roller working between two paper bowls under heavy pressure. The engraved bowl or roller may be heated from inside by gas or steam according to requirements.

The well-known "silk or Schreiner" finish is obtained by embossing

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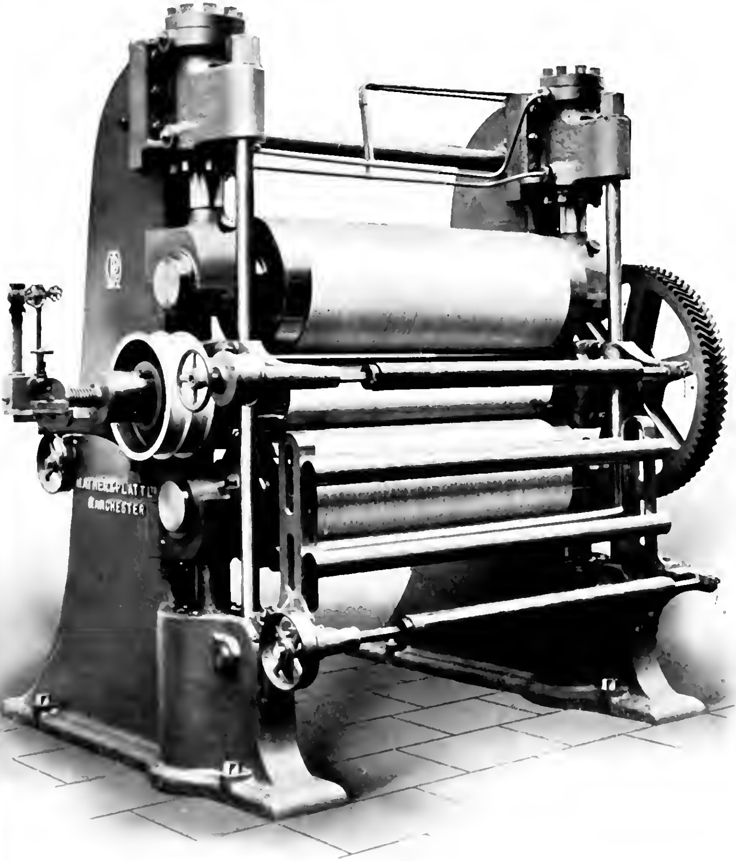

Schreiner Calender.

mercerised cloth with a series of fine oblique lines in a machine of this description. The engraved steel roller carries up to 256 lines to the inch, and when these are impressed on the cloth under great pressure they form thereon a multitude of minute and highly glazed ridges, from the sides of which a large amount of light is reflected. Embossed in this manner the fabric acquires a beautiful soft sheen, totally different from the brilliant glaze produced in the swissing or friction calender. Different qualities of sheen may be obtained by replacing the plain line pattern of the "Schreiner Finish" by various figured patterns such as moiré, watered, cross-hatched, honeycomb, and any other delicately engraved close-set designs.

For producing embossed patterns in higher relief than can be obtained by passing the goods between one dead smooth and one engraved cylinder, the cloth is passed between two engraved rollers, the one carrying the design in relief, the other with the design in intaglio. Either one or the other may be heated as required.

In addition to its employment for the "Schreiner Finish" and its allied styles, the finer and more delicate sort of embossing is largely used for the production of figured effects on heavily surface-starched bookbinding cloth. In this case the cloth is frequently weighted and filled with China clay or other plastic substances mixed with thick starch paste, which is coloured to the desired shade by the addition of dyestuffs. The coloured paste is applied either by printing or in a back starching machine, and, after drying, the goods are simply calendered and embossed without any further treatment for the fixation of the colour.

Watered or moiré effects on the back (or face) of various classes of calico may also be obtained by passing two pieces at once through the calender, back to back, or face to face, as the case may be. The rough surfaces presented by the warp and weft threads of each of the sides in contact act in much the same manner as engraved rollers towards each other, and, under the great pressure of the calender bowls, they mutually emboss each other, with the production of an ever varying "watered" or *moiré* effect. The cause of the "watering" is due to the crossing of the respective threads of the two pieces, whereby they become more flattened in some parts than in others, and consequently more highly glazed, in which condition they naturally reflect light unevenly. The same effect in a repeating pattern is obtained by engraving an embossing roller with two distinct series of fine lines, the one crossing the other at various angles according to kind of "watering" required.

In what is known as a "chesting calender" there are at least five cylinders or bowls, the middle one being of iron and hollow, so as to be heated by gas or steam, the extreme top and bottom bowls being also of iron, with a compressed paper bowl between each of them and the centre bowl. In "chesting," the cloth passes continuously between each pair of bowls, and instead of running out of the machine as it leaves the last, it is wound on the uppermost iron bowl, which is specially arranged to allow for the increasing pressure due to the increase in its size (or diameter) brought about by each additional thickness of cloth wound round it. When a sufficient quantity of cloth has been wound on, no more is fed into the machine, and the top bowl, with its load of cloth, is then revolved under constantly increasing pressure until the desired result is judged to be attained.

At this point the direction of the "chesting bowl" is reversed, and the cloth transferred from it to a batching roller; whilst batching, the pressure on the cloth is relieved, only sufficient being retained to prevent the chesting bowl from overrunning the batching apparatus. In modern machines a special brake motion is provided for this latter purpose. "Chesting" is never employed for printed goods, and therefore calls for no further description. Various types of calenders are illustrated in Plates IX., X., XI., and XII.

Another method of giving a gloss, and at the same time a thick, silky feel, to sateen cloth, etc., is that known as "Beetling." A great variety of "Beetle finishes" are produced, but they all depend upon the principle of giving heavy elastic blows to the "piece" with great rapidity. In order that each part of the cloth may be uniformly "hammered" the goods are beamed on heavy, slowly revolving rollers of iron, situated immediately beneath a row of beaters or "beetle hammers." In the old form of machine these beetles consist of stout balks of timber, raised and allowed to fall on the cloth by means of cams which alternately engage with and release a projecting peg fixed at the back of the hammer. In modern machines these simple appliances have been replaced by leather-faced "beetle hammers," actuated by steam power through the medium of cranks and connecting rods, and provided with springs to increase the elasticity of their blows. The massive iron "beams" or rollers upon which the goods are wound revolve slowly during the whole process of "beetling," so that every square inch of the cloth receives identical treatment. The various finishes are obtained by varying the duration of the hammering, the thickness of the stiffening mixtures previously applied to the fabric, and by other methods, such as winding on two pieces back to back, etc.

Plate XIII. illustrates Mather & Platt's Patent "Beetling Machine."

In all operations connected with starching, calendering, embossing, and beetling it is highly important that the cloth should pass through the processes at the full open width, without a crease. To ensure this condition brass expanding rollers, expanding cones, and corrugated brass or hard-wood scrimp tension rails are placed in front of all machines used in finishing. In starching and stiffening generally a crease or scrimp or double edge merely gives rise to unsatisfactory and irregular work, and is not, as a rule, likely to result in any damage to the fabric. But in calendering, embossing, and beetling, where the cloth is subjected to enormous and sometimes grinding pressure, the least crease constitutes a grave source of danger, and in the bulk of cases results in a more or less extensive tear. Apart from injury to the fabric, however, the presence of a crease or doubled-over selvedge invariably damages the delicately engraved rollers of the Schreiner calender; and as the re-engraving of these involves considerable expense, it is obvious that the utmost care should be taken to avoid exposing them to risks at the hands of careless or ignorant workmen.

After finishing, the printed goods are plaited in folds of a definite length on special Plaiting and Measuring Machines, which can be regulated to lay the cloth in regular folds of either a yard or a metre, or fractions of these standards. All that then remains to be done is to cut off a certain number of folds, make them up into attractive packages (in England generally containing 30 yards of cloth), arranged so that the quality of the article can be easily seen and examined, ticket the packages with distinguishing tickets denoting the pattern, quality, class, width, and length of the cloth, and any other particulars required by the market, and finally to bale them up and consign them to their destination.

For fuller particulars relating to the production of the scores of "finishes" in general use, the reader is referred to the standard works on the subject, namely:

Finishing of Cotton Goods; Depierre.

Chemistry and Practice of Finishing Cotton Goods; Bean and M'Cleary, 1905.

Finishing of Textile Fabrics; Beaumont, 1909.

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PART IX.

WOOL PRINTING.

WOOL PRINTING.

Compared with the printing of cotton, that of wool is a simple matter in so far as the fixation of dyestuffs is concerned. For most dyestuffs, the wool fibre has a much greater affinity than cotton, so much so indeed that by far the greater number of them are sufficiently fixed on wool without the employment of any mordant whatsoever. This is notably the case with the majority of the basic coal-tar colours, which, when applied to cotton, can only be fixed as tannin or chrome lakes, or by means of albumen. On cotton, too, the acid colours cannot be satisfactorily fixed at all, whereas for wool they constitute the most valuable group of colouring matters, since they yield exceedingly bright and, for most purposes, sufficiently fast colours. On wool, however, as on cotton, the fastest shades are produced by means of the mordant dyestuffs, which are applied in much the same way as to cotton. In wool printing the mordant colours are only used when fastness is of more importance than brightness, or when the shade required can be obtained from them more readily than from other classes of colouring matters. To some extent the direct colours are also printed on wool, but their application is limited, since they are inferior in brightness to the acid and basic colours. The chief use of direct colours in wool printing is for dyeing ground shades that are afterwards to be discharged with stannous chloride or hydrosulphite.

The natural affinity of wool for colouring matters is greatly enhanced by preparing it in tin salts, and by acting upon it with chlorine. This latter process was invented by John Mercer, who found that in "chlorinated" wool the depth of the colours was greatly increased, sometimes even to double that otherwise obtainable. Only by chlorinating the wool is it possible to bring about the full development of most colours, and thus to ensure the utilisation of the dyestuffs to the best advantage.

Before being printed, the woollen goods require bleaching in either sulphurous acid gas, bisulphite of soda, or hydrogen peroxide. The last two methods are most commonly employed in printworks.

In the "Bisulphite Process" the goods, after properly scouring in alkaline baths, are well washed and squeezed, and then passed alternately through baths of bisulphite of soda and hydrochloric acid; or they are slop-padded in bisulphite of soda, and then steamed for a short time. After bleaching, the goods are prepared in stannate of soda or chloride of tin, followed, except for very light patterns, by a run through a weak, acidulated solution of bleaching powder. They are then thoroughly washed, squeezed, and dried up ready for printing. There are several methods of both "chlorinating" and "preparing in tin," and sometimes the sequence of the operations is reversed. In some cases the tin preparation is omitted, and the pieces chlorinated and bleached in a continuous manner by being passed successively through baths of bisulphite of soda, bleaching powder, and sulphuric acid.

For delaines (*mousseline de laine*), which are the fabrics mostly used for printing, the following process of preparing the goods for printing has given good results:—

a. SCOURING.—(1) Wash the goods in the rope form in hot water (60° C.) for ½ hour.

(2) Soap with 10–15 per cent. (on the weight of the goods) Marseilles soap for ½ hour at 60° C.

(3) Wash well in water, hydro-extract, and bleach.

b. BLEACHING.—(1) Pass the goods in the open width through a solution composed of—

1 part peroxide of hydrogen (10 vols.);
4 parts water;
and sufficient ammonia to make slightly alkaline.

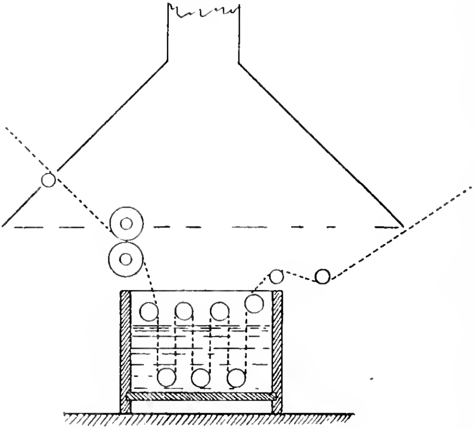


FIG. 80.—Chlorination beck.

After passing through this solution the goods are rolled up in the wet state and allowed to lie 24 hours; they are then washed and passed through a solution of bisulphite of soda, the concentration of which varies according to the discoloration of the material.

(2) BISULPHITE BATH.

1 part bisulphite of soda 70° Tw.
2–8 „ water.

Roll up again in the wet state and allow to lie a few hours; then pass directly through sulphuric acid 2°–2½° Tw., and finally wash thoroughly, hydro-extract, or squeeze out the excess of water.

c. CHLORINATING.—This process is carried out in a wooden or stone cistern furnished with guide rollers and squeezing bowls, and capable of holding about 2500 litres of liquor. Above the cistern or beck a hood is fixed to carry off the fumes of chlorine liberated during the operation. See fig. 80.

The chlorinating beck is charged differently according to the style of work in hand. Thus—

(1) For White Grounds.	For Dark Blotches.
2000 litres.	2000 litres water.
12 ,,	40 ,, bleaching powder sol. 11° Tw.
8 ,,	25 ,, hydrochloric acid 32° Tw.

The goods pass through these solutions in from 15–20 seconds, and for each piece the baths are replenished by adding—

For White Grounds.	For Blotches.
¾ litre.	2½ litres bleaching powder sol. 10° Tw.
4½ ,,	1½ ,, water.
½ ,,	1½ ,, hydrochloric acid 32° Tw.

(2) Wash well in plenty of water, and dry up through a dilute solution of glycerin on a stentering machine. The presence of a little glycerin enables the fibre to absorb the colour better, and is generally an advantage, especially during the subsequent steaming of the printed goods.

d. Tin Preparation.—(1) Pass the goods twice through stannate of soda at 10° Tw. Squeeze, and then pass at once through—

(2) Sulphuric acid 2° Tw., or hydrochloric acid 2° Tw.; wash well and dry.

Another method of preparing wool is first to pass through stannate of soda 10° Tw., then through hydrochloric acid 2° Tw., and finally through bleaching powder solution 1½° Tw., followed by a good washing and drying. The first method described, however, is generally considered to give the best all-round results.

If, during the course of "chlorinating," the wool is observed to turn yellow, its speed through the liquor must be increased, or the strength of the liquor must be diminished until the defect is rectified. It is necessary also to have always an excess of acid in the chlorinating liquor, otherwise apparently satisfactory goods will develop yellow stains, extending throughout their whole length, in the steaming process. To guard against any risk of this happening in the case of white ground prints, it is a common practice to prepare the goods in stannic hydrate only, omitting the chlorine treatment altogether. In most cases, however, it is usual to give the pieces a treatment in bleaching powder, whether for white grounds or not; and even when the "chlorinating," as such, is omitted, it is not unfrequently the custom to add about ½ litre of bleaching powder solution 4° Tw. to the acid bath used in the "tin preparation" (½ litre, that is, for every 50 yards passing through the acid).

The stronger the chlorination, the greater the affinity of the wool fibre for acid colours; but it is important to note that the stronger the treatment, the yellower in shade and the harder to the touch does it become. According to Pokorny (*Jour. Soc. Dyers and Col.*, 1908, p. 144), the chlorination of wool decreases its affinity for basic colours, whereas the treatment with strong bisulphite of soda increases the affinity of wool for these colours.

Printing and Steaming.—The printing of woollen piece goods is performed in the usual manner, either by machine or by block. Practically all wool colours are suitable for machine printing; but in block printing, care must be taken to use only such colours as require considerable heat for their fixation on the fibre, or of which the fixation can be retarded by the addition of certain ingredients, such as stannous chloride, stannic chloride, tungstate of soda, bisulphite of soda, and phosphate of soda. The less easily a colour dyes wool in the cold, the more likely is it to "equalise" well at the repeats of a block printed pattern in steaming. On the contrary, colours for which wool has great affinity are unsuitable for block printing, because they become fixed on the fibre at once almost, and thus render impossible the merging of the colour of one "repeat" into that of the repeat next applied. Such colours invariably yield uneven results, whereas those which are only developed and properly fixed in steaming produce the utmost degree of uniformity possible to block printing by hand. These remarks apply more particularly to the printing of "blotches" and large spaces of colour, —a style of work in which a smooth, level print is of the greatest importance. For small patterns in many colours, it is unnecessary therefore to pick and choose, since the repeats of such patterns are usually arranged to be invisible under any conditions.

With respect to machine printing, there are also several precautions to be observed if the best results are to be secured. For heavy patterns and all blotches the rollers must be deeply engraved, and, in general, delicate engraving of any sort is to be avoided. The cylinder of the printing machine ought to be "lapped" more thickly than for calico printing, and the blanket must be as soft and thick as possible. It is very important to dry the printed pieces at a moderate temperature, so that, as they emerge from the drying apparatus, they are only just dry, or better, just slightly damp. In some cases, even, the goods are plaited down between grey cloths, without any other drying than is obtained in this way, though usually they are passed through the ordinary hot-air apparatus, at a temperature adjusted to fulfil the required conditions, namely, gentle drying, with the retention of a trace of moisture.

In *steaming*, the presence of moisture is absolutely essential. The degree of humidity of the goods exercises great influence on the fixation, regularity, and brightness of the colours: if goods are not sufficiently damp, the fixation of the colours is imperfect, and they wash out a good deal, staining the surrounding parts of the cloth; conversely, if the fabric is too damp, the colours "run," and the sharpness of the impression suffers in consequence. In general, the required degree of humidity is obtained by wrapping the printed goods in damp "greys" containing from 5–15 per cent. of moisture, according to thickness or dryness of the woollen material to be steamed.

The steaming operation is usually effected, without pressure, in a "cottage steamer"; but a wooden box or a brick chamber may be utilised so long as the steam employed is moist. The moisture is introduced by blowing the steam through water contained in a small tank situated at the bottom of, or beneath, the steaming box, and suitable arrangements are made to prevent the pieces being splashed. The moister the steam, the deeper and brighter the resulting colours; too much moisture, however, is to be avoided, lest the colours run, and spoil the whole print. The pressure ought never to exceed that corresponding to a rise of 2–4 inches in a small water manometer attached to the steaming apparatus. The duration of steaming depends upon the weight, intensity, and nature of the colours printed; darker colours require a longer treatment than light ones. In some instances, notably for delicate floral patterns, the goods are steamed twice, being damped if necessary between the two operations.

The treatment of printed woollen fabrics after steaming is much simpler than that of calico prints. Patterns on woollen goods are always produced either by direct printing or by discharging dyed grounds, so that there are no dyeing, fixing, or clearing processes to complicate the after-treatment. The usual treatment after steaming is simply to wash the goods in the loose rope form in a copious supply of fresh running water.

The first wash may sometimes be followed by a second in warm water, but, generally speaking, a thorough wash in cold water is sufficient for most purposes.

During the washing, provision must be made against the fixation of loose colour on the white parts of the pattern. With cold, hard water this rarely occurs if the steaming has been properly carried out, but if warm water or very soft water is used it is advisable to add a little chalk to the water in the washing machines. This frequently precipitates the washed-off colour, and thus prevents its fixation on the cloth.

After washing, the goods are hydro-extracted, and finally dried on the stentering machine. Soaping is rarely employed for printed woollens, except where the whole of the colour combinations is got up in fast mordant colours.

The following are a few examples of various types of colours suitable for wool printing by machine: most of them have been found to stand a light soaping at 70° C.

(*a*) Acid Colours.

Scarlet :—	40	grms.	Ponceau F.R.R.R. (Cassella).
	500	,,	water.
	100	,,	acetic acid 9° Tw.
	160	,,	gum Senegal solution 50 per cent.
	200	,,	British gum.
	1000		

Violet :—As Scarlet, but use Formyl violet S. 4 B. (Cassella), and add 20 grms. of oxalic acid.

Yellow :—	40	grms.	Tartrazine O. (M., L. & B.).
	40	,,	tartaric acid.
	920	,,	gum Senegal or British gum thickening.
	1000		

Orange :—	40	grms.	Victoria yellow conc. (M., L. & B.).
	500	,,	water.
	80	,,	acetic acid 9° Tw.
	160	,,	50 per cent. gum Senegal solution.
	200	,,	British gum (dry).
	20	,,	oxalic acid.
	1000		

Navy Blue :— As Orange, but use Anthracene acid blue D.
Dark Blue :— ,, ,, Brilliant blue for wool B.
Bright Blue :— ,, ,, Patent blue V.

Navy Blotch :—	25	grms.	Chromotrope 6 B.
	12·5	,,	Patent blue V.
	2·5	,,	Acid violet N.
	0·5	,,	Victoria yellow conc.
	20	,,	oxalic acid.
	50	,,	sulphate of alumina.
	400·5	,,	water.
	499·0	,,	8 per cent. tragacanth thickening.
	1000		Boil together.

Chocolate :—	15	grms.	Acid violet N.
	16	,,	Victoria yellow conc.
	9	,,	Ponceau F.R.R.R.
	20	,,	oxalic acid.
	10	,,	glycerin.
	400	,,	water.
	520	,,	6 per cent tragacanth thickening.
	10	,,	turpentine.
	1000		

Red :—As Scarlet, but use Brilliant croceine 7 B.

Cyanol Blue (very pure and bright) :—

15	grms.	Cyanol extra.
150	,,	water.
10	,,	ammonia 25 per cent. Dissolve, and add—
660	,,	50 per cent. gum Senegal thickening.
115	,,	acetate of ammonia. Cool, and add—
25	,,	acetic acid 9° Tw.
25	,,	glycerin.
1000		

Green :—

40	grms.	Acid green extra conc.
500	,,	water.
100	,,	acetic acid 9° Tw.
160	,,	50 per cent. Senegal thickening.
200	,,	British gum (dry).
1000		

Olive :—

60	grms.	Naphthol green B.
465	,,	water.
200	,,	British gum powder.
125	,,	gum Senegal thickening 50 per cent. Dissolve and add—
30	,,	chlorate of soda.
60	,,	water. Cool, and add—
35	,,	acetic acid 12° Tw.
25	,,	pyrolignite of iron 24° Tw.
1000		

Brown :—

2–6	parts	Chocolate.
1–1	,,	Orange.

Black :—

75	grms.	Naphthol black B.
10	,,	Thiocarmine R. Paste.
250	,,	water. Mix well, and add—
250	,,	gum Senegal thickening 50 per cent.
200	,,	British gum powder. Boil, cool a little, and add—
17	,,	chlorate of soda.
50	,,	water. Cool, and add—
15	,,	sulphate of alumina.
15	,,	sulphuric acid 168° Tw.
118	,,	water.
1000		

Claret :—

75	grms.	Amaranth B.
400	,,	water.
235	,,	gum Senegal thickening 50 per cent.
150	,,	British gum. Heat to dissolve, cool, and add—
80	,,	acetic acid 12° Tw.
60	,,	water.
1000		

Most of the acid colours on the market may be applied like Amaranth B., or with a little oxalic acid in place of acetic acid; citric and tartaric acids are also used; and when the free acids precipitate the colouring matter in the printing paste they may be replaced with their respective ammonia salts, from which the acid is set free in steaming.

For block printing, sulphate of alumina, tungstate of soda, and stannic chloride are employed to retard the fixation; they act by converting the colouring matter into an extremely fine precipitate, which is fixed in steaming. Very insoluble acid colours require to be applied in neutral solutions, otherwise they both work badly and give "specky" prints. In such cases they are mixed with ammonium oxalate, which splits up in steaming, and supplies the acidity necessary to the full development of the colour on the fibre. Small amounts of ammonia are also frequently added to sparingly soluble dyestuffs, and they usually improve the levelling of the colour.

(*b*) BASIC COLOURS.

The employment of basic colours on wool is very limited, owing to the fact that they are much looser to light than on cotton, or than the acid colours. They are usually printed with acetic or other organic acids, and sometimes tannic acid is added for their better fixation.

PRINTING PASTE.	I.	II.
Basic dyestuff	25	25
Acetic acid 9° Tw.	100	100
Water	210	160
Tartaric acid	20	20
British gum	150	150
Gum tragacanth 6 per cent.	495	495
Boil, cool, and add—		
Acetic acid tannin sol. 50 per cent.	...	50
	1000	1000

These two recipes are suitable for all basic colours.

(*c*) EOSINES.

The following formulæ are all suitable for the printing of Eosines:—

	I.	II.	III.	IV.
Colouring matter	45	10	10	10
Water	380	280	100	100
Gum Senegal 50 per cent.	275	700	730	730
British gum	200	...	...	...
Acetic acid	100	...	...	...
Phosphate of soda	...	...	40	...
Acetate of soda	...	...	...	40
Soda ash	...	10	...	...
Stannous chloride	...	...	20	20
Water	...	...	100	100

The presence of stannous chloride produces yellower shades and acts favourably with regard to the "bleeding" of the colours. All brands of Eosine, Rose Bengale, Erythrosine, Phloxine, and Uranine, etc., are applicable by any of the above four recipes.

(*d*) DIRECT COLOURS.

The application of the Diamine colours will sufficiently illustrate the possibilities of the direct colours in wool printing.

They are distinguished by their fastness to washing, and even to milling, by their good levelling properties, and by the sharpness of the impression they give of the engraved pattern. The Diamine colours (and other direct dyestuffs) are printed with an addition of acetic acid, according to the following recipes. After printing, they are steamed, washed, and dried in the manner usual for wool, and they can therefore be employed in combination with any other wool colour:—

DIRECT COLOURS FOR WOOL PRINTING.

40–60	grms.	Direct colour.
300	,,	water.
300	,,	gum Senegal thickening 50 per cent.
200	,,	British gum. Boil, cool, and add—
90	,,	acetic acid 12° Tw.
70–50	,,	water.
1000		

Suitable for Diamine blues 2 B., 3 B., and Diamine sky blue, Diamine scarlet B. and 3 B., all of which are most useful for printing heavy patterns for dress goods. Other direct colours (Diamines included) are applied in a similar way, and various compound shades can be readily obtained by mixing.

(*e*) MORDANT COLOURS.

The vegetable extract colours are printed with exactly the same pastes as are used for cotton. The Alizarin colours, however, require the presence of acid or acid mordants to yield the best results, as for example:—

ALIZARIN RED.

30	grms.	Alizarin red 1 W.S. (M., L. & B.).
300	,,	boiling water.
450	,,	6 per cent. tragacanth thickening. Boil, cool, and add—
50	,,	sulphate of alumina.
25	,,	oxalic acid.
145	,,	water.
1000		

ALIZARIN BLUE.

40	grms.	Alizarin blue S.
430	,,	gum tragacanth 6 per cent.
30	,,	tartaric acid.
300	,,	water.
100	,,	acetate of chrome 30° Tw.
100	,,	starch paste 10 per cent.
1000		

Alizarin blue may be toned by the addition of acid colours such as Patent blue, Formyl violet S. 4 B., Fast acid violet A 2 R., Patent green O., and Acid green B.X. conc.

The mordant colours generally give somewhat dull shades, and are only used for the fastest work, such as the printing of flags and bunting.

Block Printing on wool requires the colours to be specially prepared with a view to preventing their fixation on the fibre in the cold. Frequently, too, the cloth undergoes a special preparation in tin, for the purpose of obtaining brighter colours than are otherwise obtainable.

The preparation is effected as follows:—The cloth, "chlorinated" as already described, is first well washed and squeezed, and then passed through a bath containing

200	litres	Tin Liquor W.B.
400	,,	water.

TIN LIQUOR W.B.

12	kilos.	oxalic acid.
120	,,	boiling water. Add, whilst stirring—
12	,,	stannate of soda.
120	,,	water (boiling). And when the mixture is clear add—
10	,,	Ammonia 25 per cent. Make up to 250 litres with water.

The goods pass through this bath in the open width, and on emerging excess of liquor is extracted by means of a pair of squeezing rollers; they are then allowed to lie in pile for 3 hours, and finally hydro-extracted and dried to width on a stentering machine, without washing.

This special tin preparation has not merely the advantage of giving brighter colours, but it also reduces their tendency to run during the time that they lie in the wet state on the printing table.

In the printing of wool by block, it is advisable to commence with the outlines (if there are any), and to print these in colours thickened with British gum and wheat starch. By proceeding in this manner, the possibility of the thinner and lighter colours running into each other, if not always prevented entirely, is reduced to a minimum. The spreading of a lighter shade into a dark blue, chocolate, or black outline is unnoticeable, whereas, if the reverse were to occur, the effect would be ruined.

The most important colours for block printing are those which level well during the steaming operation, and of these the following are amongst the best:—Brilliant cochineal 2 R. and 4 R., Amaranth, Ruby red A., Cyanol extra, Formyl violet S. 4 B., Naphthol black B., Auramine, Phosphine, Uranine, Tartrazine, Eosine, Croceine Orange C., Rose Bengale, Erythrosine, Quinoline Yellow, Palatine Scarlet, Scarlet, Alkali Blue, Flavazine and Sulphon-carmine C. Besides these, almost any wool colour suitable for machine printing may be employed for dark shades in block work.

The differences between the composition of block- and machine-printing colours relate mainly to the preparation of blotch colours; for floral and other light patterns, any of the printing colours used for roller printing are generally equally well adapted to block work, always provided that the "repeats" of the design show fully completed objects on the block.

The following typical recipes will serve as illustrations of the methods adopted in practice for the preparation of colours for block printing by hand.

DARK BLUE OUTLINE COLOUR.

45	grms.	Fast Blue B.D.
725	,,	water.
80	,,	wheat starch.
150	,,	British gum.
1000		Boil and cool.

Chocolate outlines are produced from a mixture of Orchil extract with a little of the above blue, and are similarly thickened.

BLACK BLOTCH.

80	grms.	Naphthol black B.
400	,,	water.
426	,,	gum Labiche 60 per cent.
2½	,,	Acid green extra conc.
1½	,,	Tartrazine O.
35	,,	water.
14	,,	sulphuric acid 168° Tw.
40	,,	water.
1000		

NAVY BLUE (BLOTCH).

220	grms.	Gallazine blue A. 15 per cent. (Durand and Huguenin).
220	,,	water.
45	,,	acetin.
7	,,	ammonia 25 per cent. Boil, and add—
{ 80	,,	China clay.
{ 40	,,	water.
45	,,	British gum.
333	,,	tragacanth thickening 6 per cent.
10	,,	chlorate of soda.
1000		Cool.

VARIOUS BLOTCHES.

	BLUE.	ROSE.	GREEN.	MAROON.	RED.	CLARET.
						grms.
Cyanol extra	16	...	...	...	...	...
Rose Bengale	...	25	...	...	...	...
Thioflavine T.	...	...	8	...	...	...
Brilliant green	...	...	2	0·5	...	...
Amaranth	...	...	...	42	...	55
Orange extra	...	...	...	7	...	3
Formyl violet S. 4 B.	...	...	...	0·5	...	0·5
Ruby red A.	...	...	...	...	40	...
Water	150	320	309	330	400	301·5
Gum Senegal 50 per cent.	660	600	600	600	500	500
Oxalic acid	...	...	...	10	...	...
Oxalate of ammonia,	...	...	...	...	...	15
Tartaric acid	...	...	8	...	30	...
Acetic acid 12° Tw.	25	...	...	...	...	...
Tungstate of soda	...	...	8	10	30	...
Stannic chloride 142° Tw.	...	...	25	...	...	25
Bisulphite of soda 90° Tw.	...	...	40	...	...	...
Ammonia	10	...	...	...	...	...
Acetate of ammonia solution	114	...	...	...	...	...
Glycerin	25	...	...	...	...	...
Acetate of soda	...	35	...	...	...	...
Stannous chloride	...	20	...	...	...	...
	1000	1000	1000	1000	1000	1000

In preparing the above colours, the colouring matter is first dissolved in a portion of the water, then added to the gum, and the whole warmed together. After cooling, the other ingredients, dissolved separately in the remaining water, are added to the gum colour paste, and, after well mixing and straining, the colour is ready for printing.

The above recipes may be employed for all members of the groups to which their respective colours belong.

Discharge Styles on Wool.—In common with most of the direct colours, the majority of acid Azo colours are readily dischargeable by reducing agents, such as stannous chloride, stannous acetate, hydrosulphite-formaldehyde compounds, and mixtures of zinc powder with bisulphite of soda, and this property is utilised in the production of an immense variety of discharge effects.

The following two lists of colours include respectively (1) those colours suitable for dyeing ground shades capable of being discharged in white and colours, and (2) those capable of resisting the discharge pastes, and therefore suitable for the production of coloured discharges.

(*a*) Ground Colours for White Discharges with "Hydrosulphite."

Flavazine.
Azo yellow.
Metanil yellow.
Milling yellow O.
Victoria yellows.
Brilliant orange.
Victoria scarlet.
Acid green.
Patent blue.
Ketone blue.
Naphthalene green.
Anthracene acid browns.
Acid magenta.
Victoria rubine O.
Naphthol red O.
Claret red.
Orange Extra
Brilliant cochineals.
Amaranth B.
Ponceau F.R., F. 3 R.
Lanafuchsine S.G., S.B.
Lanacyl blue B.
,, violet R., B.B.
Naphthol black B.
Naphthylamine blacks.
Diamine golden yellow.
,, scarlet B., 3 B.
,, rose B.D.
,, pure blue F.F.
,, brill. blue G.
,, green G. B.
Diaminogéne extra.

And similar colours which, while quite as suitable for the purpose, cannot be mentioned on account of space.

(*b*) Colours Suitable for Coloured Discharges.

(*With Stannous Salts.*)

Eosine.
Phloxine.
Erythrosine.
Rose Bengale.
Formyl violet S. 4 B.
Cyanol extra.
Thiocarmine R.
Aniline grey.
Methylene blue.
Brilliant green.
Malachite green.
Auramine.
Rhodamine 6 G.
Thioflavine T.
Acridine yellow.
,, orange.
Phosphine.
Methyl violet B.
Thionine blue G.O.
Safranine.
Magenta.
Quinoline yellow.

Coloured discharges are generally produced by the aid of stannous salts, but most of the recipes already given, in various parts of this volume, for coloured hydrosulphite discharge pastes may also be easily adapted to wool printing by leaving out the mordants (if desired), and by modifying the quantity of hydrosulphite according to the susceptibility of the ground colours to its action.

Except with the Diamine and other direct colours, tin discharges do not give very good whites, since the products of reduction are difficult to remove from the cloth; but for coloured effects they are excellent, and in many cases, too, they yield passable whites (on grounds of Azo acid blue, Victoria violet, Flavazine, and blue shades of Victoria scarlet). The best and most reliable whites, however, are given by hydrosulphites, with or without the addition of zinc oxide.

The "Zinc Bisulphite" discharge is practically obsolete. It was always a difficult process to work, by reason of the fact that the zinc powder was exceedingly liable to stick in the engraving of the rollers, and thus give rise to imperfect discharges. It was really a "hydrosulphite discharge," and since the introduction of the soluble and stable "hydrosulphite-formaldehydes" (sulphoxylates) its application has become unnecessary.

As a rule, discharge effects on wool come out best on "chlorinated" material, especially in dark shades. When the ground colour levels easily, it can be dyed on such material to considerable advantage—amounting in some cases to a saving of 25 per cent. of dyestuff. On the other hand, colours that require careful attention to obtain level shades are better dyed on untreated wool, and treated in chlorine afterwards. Most of the acid colours given in the first list above withstand the run through the "chlorinating baths" without undergoing very much alteration in shade, and they may therefore be used for the production of compound shades with colours that do not dye up well on chlorinated cloth (Anthracene acid browns, Lanacyl blue R., etc.). Although the "chlorination" is not absolutely essential, it offers undoubted advantages in most cases.

(1) Tin Discharges on Woollen Fabrics.

The wool fibre resists the destructive action of acid stannous salts much better than the cotton fibre, and consequently it is possible to use more concentrated discharge pastes, with a corresponding gain in the purity of the "whites" and discharge effects generally.

In addition to stannous chloride, the following ingredients are used in tin discharges: tartaric, citric, and oxalic acids; acetin; and for coloured discharges, acetate of soda and sulphocyanide of ammonia.

Whilst coloured discharges are easily obtainable, it is always difficult to obtain pure whites with "tin discharges," owing to the formation of coloured reduction products, which resist all efforts at removal. For this reason white discharges with stannous salts are rarely attempted, except on light grounds of acid colours, and medium grounds of Diamine and other direct dyeing colouring matters. When mixed effects in white and colours are required, the former is preferably obtained by printing hydrosulphites, although, if the white object be small, stannous chloride may be employed, as in such a case the white shows up well by contrast with the ground and neighbouring discharge colours.

The recipes given below will illustrate the preparation of white and coloured stannous chloride Discharges.

Discharge White (Stannous Chloride).

	I.	II.	III.	IV.
				grms.
Acid starch paste 12½ per cent.	500	500	500	...
British gum paste 25 per cent. .	150	75	50	...
Stannous chloride	250	250	250	350
Acid starch paste 20 per cent. .	...	...	...	525
Acetate of soda	...	125	...	90
Sulphocyanide of ammonia .	...	...	85	...
Citric acid (powder) . . .	...	...	50	35
Water	100	50	65	...
	1000	1000	1000	1000

After printing, steam 10 minutes without pressure, wash and dry. For prolonged steaming the following is suitable:—

White Discharge S.A.

800	grms.	acetate of tin 28° Tw.
150	,,	starch.
50	,,	dextrin.
1000		Boil and cool.

Print, steam 1 hour without pressure, wash well and dry.

Coloured Discharges (Stannous Chloride).

	Red.	Yellow.	Blue.	Green.	Violet.	Pink.
						grms.
Eosine G.G.F.	75	...	...	...	...	...
Quinoline yellow O.	...	50	...	...	...	...
Phloxine S.	25	...	...	...	...	30
Victoria blue B.	...	...	20	...	...	..
Brilliant green	...	...	...	7½	...	...
Thioflavine T.	...	...	...	22½	...	...
Methyl violet	...	...	...	...	10	...
Boiling water	175	150	180	170	190	170
Acid starch paste	...	500	500	500	500	...
Citric acid	25	25	25	25	25	25
Gum Senegal 50 per cent.	250	...	...	...	..	300
British gum	100	...	...	...	...	100
Acetate of soda	75	75	75	75	75	75
Stannous chloride	200	200	200	200	200	200
Water	75	...	...	..	...	100
	1000	1000	1000	1000	1000	1000

Print, steam about 10 minutes without pressure, wash well and dry. For easily dischargeable colours and light shades the above quantity of stannous chloride must be reduced, otherwise the impression of the pattern will appear clumsy after steaming, owing to the "running" of the stannous chloride. The above recipes represent the application of acid and basic colours, and any other members of these two groups that will stand reducing agents may be employed in the same manner.

Very fine red and blue styles are produced by first dyeing the wool in a dischargeable acid red and then printing over it a blotch pattern in a discharge navy blue; red and dark green may be obtained by the same method. The following are examples of this style.

Ground Shade.—Dye "chlorinated" wool (delaine) in 2½ per cent. Brilliant cochineal 2 R., with addition of acetic acid and Glauber salt. Wash, dry, and print Discharge blue or green.

Discharge Blues and Green.

	Blue R.	Blue G.	Green.
			grms.
Formyl violet S. 4 B.	25	25	...
Acid green extra conc.	25	35	. .
Naphthalene green V.	...	...	50
Water	250	240	75
Acetic acid 9° Tw.	...	...	175
Acetate of tin 28° Tw.	500	500	500
British gum	100	100	100
Starch	75	75	75
Citric acid	25	25	25
	1000	1000	1000

After printing, steam ¾–1 hour without pressure, wash well and dry.

(2) Hydrosulphite Discharges.

The hydrosulphite-formaldehyde compounds produce much purer whites than tin salts, and many of the colours that withstand the action of the latter are readily discharged by the former. Hence the hydrosulphites are used chiefly for white discharges on dark grounds. For coloured discharges they may be associated with certain of the Eosines, basic colours, and mordant colours, like Modern violet, Blue 1900, and Modern yellow. The recipes already given for these colours, under the heading "Discharging of Insoluble Azo Colours," are equally suitable for the production of discharge effects on wool colours: in the case of coloured discharges with basic dyestuffs the tannin is usually omitted, but its presence is sometimes an advantage in fixing the colour more permanently.

Hydrosulphite White.

{ 100 grms. zinc oxide.
} 100 ,, water.
250 ,, hydrosulphite N.F. conc.
550 ,, British gum thickening.

1000

Heat to dissolve the hydrosulphite.

After printing, steam 3–4 minutes at 102° C., wash and dry. Rongalite C. and Hyraldite A. conc. are similarly employed. Hyraldite W. already contains zinc oxide, and merely requires thickening for use. The addition of zinc oxide is not essential to the production of a complete discharge, but it enhances the brightness of the white considerably by covering the fibres with a white coating, a large part of which remains after washing.

The hydrosulphite discharges are applicable to all the ground colours dischargeable by stannous salts, and in addition to many others which effectually resist these latter.

In both tin and hydrosulphite discharges it is always preferable to use, whenever possible, acid or mordant colours. When basic colours are employed, extra precautions have to be taken in the washing operations to prevent the discharged colours from being soiled by the dyestuff washed out of the ground shade.

Heilmann and Battegay (*Journ. Soc. Dyers and Colourists*, 1906, p. 234) have pointed out the suitability of sulphite of potash for the production of discharges on woollen goods, and their experiments prove that certain acid colours are extremely sensitive to the action of this reagent.

They find that sulphite of potash discharges, amongst others, the following colours: Azo acid red, Domingo blue, Scarlet 5 R., Tartrazine, Half-wool scarlet 4 B., etc.

By a short run through the rapid ager, Domingo blue yields half-discharge effects, but perfect whites are obtained by prolonging the steaming for 30 to 45 minutes without pressure.

Various effects are obtained by dyeing the wool with mixtures of dischargeable and non-dischargeable colours, and also by the direct printing of coloured sulphite of potash pastes.

The following examples are typical of these "Sulphite Discharges":—

White:—700 grms. Sulphite of Potash 90° Tw.
200 ,, British gum paste.

Heat, cool, and add—

50 grms. acetate of soda.
50 ,, water.

1000

COLOURED DISCHARGES.

	YELLOW.	RED.	BLUE.	GREEN.	VIOLET.
Milling yellow O.	50	...	...	30	...
Rhodamine 4 G.	...	35	...	...	...
Safranine O.	...	15	...	...	...
Cyanol extra	...	..	12	10	...
Formyl violet 4 S. B.	...	...	...	...	10
Water	250	250	288	260	290
British gum	200	200	200	200	200
Sulphite of potash 90° Tw.	500	500	500	500	500
	1000	1000	1000	1000	1000

On an experimental scale the above colours have given satisfactory results on grounds dyed with the acid colours mentioned above. Great care, however, is needed in steaming, since, if the printed sides of the cloth happen by any means to come in contact with each other, the sulphite of potash "marks off" and partly discharges the colour of those parts of the cloth which ought to remain untouched.

Printing of Half-Wool or Union Goods.

Goods consisting partly of wool and partly of cotton are bleached and "chlorinated" in much the same way as all-wool goods. They are first well scoured at 40°–45° C. in a bath containing 3 grms. of soap and 5 grms. of ammonia soda per litre; then thoroughly washed until every trace of soap is removed, and finally bleached either by the peroxide of hydrogen process or by being "stoved" with sulphurous acid gas. The combined "Peroxide and Bisulphite" process, as described for pure wool, may also be employed with advantage. The "chlorination" and the preparation in tin salts is carried out in the usual manner. Sometimes half-wool goods are prepared with phosphate of tin. For this purpose they are padded in a cold solution of stannic chloride 4° Tw. (or oxymuriate of tin); allowed to lie, rolled up for two or three hours, and then passed, without washing, into a cold or tepid 5 per cent. solution of sodium phosphate; finally, they are well washed and dried.

For the most part only the acid, basic and direct colours are used in half-wool printing; the mordant colours find only a limited application, and then chiefly in combination with basic dyestuffs, for the double purpose of increasing their brightness and their covering quality. The direct colours are useful for direct printing, and also for the dyeing of ground shades intended for subsequent discharging.

After printing, the treatment of the goods is in most respects identical with that of all-wool fabrics. If, however, they contain a large amount of cotton they are damped, and then steamed in *dry* steam without pressure for $\frac{3}{4}$ to 1 hour; then washed and dried. Basic colours printed with tannin have to be run through tartar emetic (1 per cent. solution) to fix the colour on the cotton fibre.

PRINTING.—The cloth prepared as above is printed with colours prepared according to the following directions: the recipes are typical of those suitable for the different groups of dyestuffs usually employed:—

BASIC COLOURS.

20	grms.	basic colour.
75	,,	acetic acid 9° Tw.
125	,,	water.
20	,,	tartaric. Dissolve, and add to—
710	,,	starch-tragacanth or gum Senegal thickening.
50	,,	50 per cent. sol. of tannic acid in acetic acid.
1000		

Suitable for all basic dyestuffs. Methylated spirits may replace wholly or in part the acetic acid if the colours are at all difficult to dissolve.

Direct Colours.

25	grms.	direct dyestuff.
350	,,	water.
100	,,	British gum.
350	,,	6 per cent. tragacanth thickening.
40	,,	phosphate of soda.
135	,,	water.
1000		

For all Diamine, Titan, Mikado, Dianil colours, and for Erika, Chicago blue, Geranine, and most other direct dyestuffs.

Acid Colours.—The acid colours used for half-wool are identical with those employed for pure wool. Having no affinity for the cotton fibre, their fastness on half-wool depends upon the amount of pure wool present in this mixed fabric.

Blacks and Dark Outlines on Half-Wool.

Blacks and dark colours generally are obtained with Logwood, and mordant colours toned with basic colours containing tannin.

Black.—Logwood with iron and chromium mordants.

Chocolate.—Persian berries, Magenta, and Methyl violet or Brilliant green, with tannin and chrome mordant.

Dark Navy.—Logwood (a little), Methyl violet, and Brilliant green, with chromium acetate and tannin.

Bright Navy.—Marine blue with a very little Brilliant green.

The direct colours are also used at times for other dark shades, but usually they are reserved for medium and light colours.

Discharging on Half-Wool.—Discharge effects on half-wool materials are obtained by printing tin or hydrosulphite discharges on colours dyed with direct dyestuffs.

The best and surest method of securing level ground shades is that of padding the goods through a padding machine containing dye liquors prepared on the following types:—

Padding Liquors for Direct Colour Dyeing.

	Light Blue.	Dark Blue.	Navy.	Pink.	Yellow.	Brown.
Diamine sky blue F.F.	10	...	...	...	...	...
Dianil blue R.	...	...	50	...	...	...
Titan pink or Erika	...	..	...	25	...	...
Dianil yellow R.	...	...	...	...	10	...
Chicago blue	...	25	...	...	...	...
Dianil brown 2 G.	...	...	..	...	...	15
Water	920	885	860	885	920	915
Phosphate of soda	20	40	40	40	20	20
6 per cent. tragacanth	50	50	50	50	50	50
	1000	1000	1000	1000	1000	1000

Heliotrope = Mixtures of Pink and Blue.
Green = „ „ Yellow and Blue.

Pad, dry, and print with discharge colours as under:—

Discharge White.

600	grms.	acid starch-tragacanth paste.
200	„	stannous chloride.
20	„	citric acid.
180	„	ammonium sulphocyanide.
1000		

Discharge Red.

25	grms.	Rhodamine 6 G. extra.
10	„	Safranine A.N. extra.
150	„	acetic acid.
200	„	water.
150	„	light British gum.

Boil, cool, and add—

80	grms.	Persian berries extract 50° Tw.
50	„	sulphocyanide of ammonia.
200	„	tin crystals ($SnCl_2$).
75	„	acetic acid tannin solution 50 per cent.
60	„	glycerin and water 1 : 1.
1000		

Bright Blue.

20	grms.	Thionine blue G.O.
150	„	acetic acid.
15	„	citric acid.
100	„	water.

Dissolve, add—

290	„	water.
120	„	wheat starch.
25	„	glycerin.

Boil, cool, and add—

80	grms.	ammonium sulphocyanide.
200	„	stannous chloride.
100	„	acetic acid tannin solution 50 per cent.
1000		

This last recipe serves for Rhodamine, Auramine, Thioflavine T., Brilliant green, Malachite green, Methyl violet, Methylene blue, and mixtures of these and of all other basic dyestuffs, so that all varieties of compound shades are easily obtainable.

For dark blue blotches on red grounds the cloth is dyed and printed as under:—

(1) Dye the goods with 2 per cent. Diamine scarlet B. with an addition of phosphate of soda and Glauber salt; wash well, dry, and—

(2) Print with the following blue:—

Dark Blue S.D.

30	grms.	Methyl violet B.
25	,,	Victoria blue B.
10	,,	Brilliant green.
175	,,	acetic acid 9° Tw.

Dissolve, and add—

400	grms.	gum Senegal solution 50 per cent.
50	,,	British gum.

Boil, cool, and add—

30	grms.	Persian berries extract 50° Tw.
60	,,	ammonium sulphocyanide.
150	,,	stannous chloride.
30	,,	tannic acid.
30	,,	acetic acid 9° Tw.
10	,,	glycerin.
1000		

After printing on half-wool cloth dyed with direct colours, all the foregoing discharges are steamed for 3–4 minutes in the rapid ager. The goods are then passed in the open width through a 1 per cent. solution of tartar emetic, well washed and dried. If the discharge is imperfect, a second run through the ager is usually sufficient to rectify it.

The same hydrosulphite discharge process that is employed for all-wool fabrics is equally suitable for half-wool materials, with the subsequent employment of the tartar emetic bath.

PART X.

SILK AND HALF-SILK PRINTING.

SILK AND HALF-SILK PRINTING.

In so far as its behaviour towards colouring matters is concerned, the silk fibre so closely resembles the wool fibre that the printing of silk fabrics presents but little variation from the printing of woollen fabrics. The main difference between the two processes lies in the preparation of the cloth, which, in the case of silk, consists only of mordanting the goods in stannic chloride or phosphate. The chlorination of silk does not increase the affinity of the fibre for colouring matters as it does in the case of wool.

The printing of silk, like that of wool, is restricted to the production of direct-printed and discharge and resist styles. The application of thickened mordants, followed by ageing, dunging, and dyeing, is inadmissible, on account of the staining of the silk fibres in the dye bath.

In addition to the basic, acid, phthalem, direct, and mordant colours, all of which are suitable for silk printing, certain others, such as Aniline black, Nitroso blue, and Dinitroso-resorcin brown are also applicable, both for direct, discharge, and resist prints. The insoluble Azo colours produced on the fibre are never employed, since they cannot be obtained sufficiently fast to "rubbing."

Multicolour patterns, especially if they be heavy, are usually printed by block. Machine printing on silk is chiefly confined to single-colour patterns; for although silk has a greater affinity for most colouring matters than wool, it does not absorb thickenings so easily, and, consequently, these latter remain more or less on the surface of the cloth, and are extremely liable to smear during their passage under several rollers in quick succession. For this reason block printing is preferable to roller printing for patterns of two or more colours. Colours printed by block remain untouched by the application of subsequent colours, and therefore they are free from the tendency to smear and streak that is so much more troublesome in the printing of silk by machine than in that of other textile fabrics.

Nevertheless, many multicolour patterns on silk are printed by machine, and, with care, good results are obtained.

Whatever method of printing be adopted, the production of bright level colours depends upon the proper cleansing of the fibre. In order to ensure this, it is always advisable to scour the pieces before printing, however clean they may appear to the eye.

For this purpose they are soaped for 1–1½ hours at 35°–40° C. with 10 per cent. of their weight of neutral olive-oil soap; then thoroughly washed and mordanted with tin. In the soaping, care must be taken to avoid the presence of free alkali, which would tend to injure the fibre.

Preparation in Tin.—Pad the goods, in a beck holding 1000 litres, with the following:—

$$\left\{\begin{array}{ll} 50 \text{ litres} & \text{stannic chloride } 140^\circ \text{ Tw.} \\ 950 \quad ,, & \text{water.} \end{array}\right.$$

After padding, wind the cloth on a wooden centre in the wet state, and allow to lie thus for 4 hours; then wash well, and dry on a stentering machine. Sometimes the tin is precipitated as phosphate before washing, in which case the padded goods are passed through a 5 per cent. solution of sodium phosphate and allowed to lie again for 2 hours, and finally thoroughly washed and dried.

When the silk is of a yellow tinge, it must be bleached before preparing with stannic chloride or any other tin salt. A good bleach is the following:—

After scouring in soap as above, work the pieces, in a stone pit, until saturated, in hydrogen peroxide liquor, and then allow to lie in the liquor until sufficiently white.

HYDROGEN PEROXIDE LIQUOR.

{ 50 litres hydrogen peroxide 10 vols.
{ 200 ,, water containing a little ammonia.

The bleaching will be effected in about 5 hours, after the lapse of which time the goods may be washed and treated in stannic chloride.

Printing.—In view of the fact that practically all wool colours are equally suitable for silk, it is unnecessary to give more than types of formulæ for the preparation of printing pastes. The following will be found to answer most purposes:—

DIRECT COLOURS.

25 grms. colouring matter.
675 ,, water.
250 ,, British gum.
Boil, cool, and add—
50 grms. acetic acid 9° Tw.
———
1000

ACID COLOURS.

25 grms. dyestuff.
300 ,, water.
25 ,, glycerin.
525 ,, 6 per cent. tragacanth thickening.
Boil, cool, and add—
{ 100 grms. water.
{ 25 ,, tartaric acid.
———
1000

Suitable for acid colours in general.

BASIC COLOURS.	I.	II.
Basic dyestuff	25	25
Water	275	225
Acetic acid 9° Tw.	100	100
Glycerin	25	25
6 per cent. tragacanth thickening	500	450
Tartaric acid	25	25
Water	50	50
Acetic acid tannin solution 50 per cent.	...	100
	1000	1000

These recipes are suitable for all basic dyestuffs. Usually the addition of tannin can be dispensed with, but its presence renders the colours faster.

The mordant colours of the Alizarin and vegetable groups generally are printed with the addition of 1 to 2 per cent. of tartaric or oxalic acid to the printing colours used for cotton. But this addition is by no means necessary, as, in practice, cretonne patterns have been printed for years with the identical mordant colour and basic colour printing pastes employed for cotton sateens; indeed, the silk and cotton fabrics have been sewn end to end and printed one after the other without any change of colour, and without stopping the machine. Alizarin reds and pinks for silk printing (and also for cotton) are usually brightened by the addition of 3–8 grms. of Rhodamine 6 G. extra per kilogramme of standard colour; and the silk pieces are previously padded in Turkey-red oil (1¼ per cent. fatty acid). The use of too much Turkey-red oil should be avoided, as it detracts somewhat from the lustre of the fibre.

Silk goods printed with mordant colours—*e.g.* Alizarin red, pink, blue, bordeaux, green, etc., and Logwood, Persian berries extract, etc.—and basic colours containing tannin are steamed for an hour in the usual way, but preferably with slightly damp steam; they are then fixed in tartar emetic, well washed, soaped at 60° C. in the open width, washed again and dried. Most silk fabrics are, however, printed in acid colours and basic colours without tannin, and these, after steaming, are simply washed in water and dried at once.

The best thickening agents to employ for silk printing are those which wash out very easily, namely, gum Senegal, gum Arabic, gum tragacanth, and well torrefied British gum. All these yield level shades; and tragacanth is especially to be recommended for dark blotches, as it gives colours faster to washing than the other gums: for pale blotches, gum Senegal stands alone; and though it is expensive, it gives shades unsurpassed for purity and uniformity. Starch and flour are quite useless in silk printing, except for the finest stipple work, and sometimes for outlines and Aniline blacks.

A good Aniline black on silk is made up according to the directions given below:—

ANILINE BLACK.

100	grms.	starch.
423	,,	water.
150	,,	6 per cent. tragacanth thickening.
80	,,	British gum.
25	,,	Turkey-red oil 25 per cent.
2	,,	Methyl violet (for sightening).
50	,,	chlorate of soda.

Boil, cool, and add—

100	grms.	aniline salt.
20	,,	aniline oil.

Stir till dissolved, and immediately before use add—

50	grms.	copper sulphide 25 per cent. paste.
1000		

After printing and carefully drying, the goods are aged at 30°–33° C. until the black is developed; they are "chromed" at 60° C. in a 1 per cent. solution of bichromate of soda, and finally washed, soaped at 60° C., washed again, and dried.

Dark blues are often produced on silk fabrics with Nitroso-blue, which is applied in the same way as to cotton goods, but with an excess of oxalic acid, or otherwise without the addition of sodium phosphate.

The production of discharge and resist effects also constitutes an important branch of the silk-printing industry.

The majority of printed silk neckties, handkerchiefs and mufflers are executed by one or other of these processes, and both are capable of being applied to a variety of styles.

(*a*) Discharge Styles.

The material is dyed with any of the acid colours or direct colours that are easily dischargeable on wool, and then printed with tin, hydrosulphite, or sulphite of potash discharges. Nitroso-blue and Dinitroso resorcin brown are also dischargeable on silk with tin or sulphite pastes, and give excellent dark effects.

The hydrosulphite discharges are employed more extensively than the tin discharges, since the latter are apt to injure the fibre during steaming. At the same time stannous chloride, used with judgment and care, gives very satisfactory results, and is applicable to a wider range of colours than the more powerful reducing agent, hydrosulphite-formaldehyde.

(1) TIN DISCHARGES.

The preparation of these colours differs little from that of those given for wool. Usually they contain a smaller proportion of tin crystals, and are steamed rather longer in consequence, but in other respects they are practically the same, as the following recipes will show.

WHITE DISCHARGE FOR SILK.

200	grms.	6 per cent. tragacanth thickening.
445	,,	acetic acid starch paste 15 per cent.
20	,,	citric acid.
125	,,	stannous chloride.
60	,,	sulphocyanide of ammonia.
150	,,	water.
1000		

COLOURED DISCHARGES ON SILK.

	RED.	PINK.	BLUE.	YELLOW.	GREEN.	VIOLET.	ORANGE.
Rhodamine 6 G. 100 per cent.	20	10	...	...	...	...	5
Auramine conc.	5	...	...	25	22·5	...	20
Cyanal extra	...	...	15	...	...	...	...
Formyl violet S. 4 B	...	...	...	...	...	20	...
Brilliant green	...	...	...	...	7·5	...	...
Water	180	180	180	170	175	180	170
Gum Senegal 50 per cent. sol.	675	675	675	675	675	675	675
Stannous chloride	85	95	95	95	90	90	95
Sulphocyanide of ammonia	25	25	25	25	20	25	25
Citric acid	10	15	10	10	15	10	10
	1000	1000	1000	1000	1000	1000	1000

Any of the other colours mentioned as suitable for coloured discharges on wool are equally suitable for silk.

(2) HYDROSULPHITE DISCHARGES.

The alkaline salts of sulphoxylic acid formaldehyde compounds, such as Rongalite, Hyraldite, and hydrosulphite N.F., have replaced almost entirely the mixtures of zinc powder and bisulphite of soda that were formerly used as alternatives to stannous chloride or acetate for the production of discharge, and especially white discharge, effects on dyed silk fabrics. They not only give a pure white, but have the advantages of working better than zinc powder pastes, and of not attacking the fibre, like stannous salts, at the strength required to yield a satisfactory white. For coloured discharges they may be mixed with any dyestuffs that resist their reducing action, and that, at the same time, are suitable for silk. Amongst these the following give good results:—Thioflavine S., Eosine, Rose Bengale, Phloxin, Erythrosine, Quinoline yellow, Victoria scarlet, Victoria violet, and all the basic colours enumerated in previous chapters dealing with hydrosulphite discharges. For the same purpose Modern blue, violet, and yellow, and Persian berries extract, may be employed with chrome mordants.

WHITE DISCHARGE ON SILK (HYDROSULPHITE).

200	grms.	hydrosulphite N.F., Rongalite C. or Hyraldite (concentrated brands).
200	,,	water.
600	,,	gum Senegal 50 per cent. or British gum paste.
1000		

COLOURED DISCHARGES (HYDROSULPHITE).

25	grms.	colouring matter.
350	,,	water.
225	,,	British gum. Boil, cool, and add—
{ 150	,,	hydrosulphite N.F. conc.
{ 200	,,	water.
50	,,	citrate of ammonia 20° Tw.
1000		Suitable for basic and acid colours.

The foregoing tin and hydrosulphite discharges are printed on silk goods dyed with the same colours as are used for similar discharge effects on wool, and which, therefore, need not be enumerated again. Acid and basic colours are dyed with an addition of acetic or sulphuric acids, and direct colours with either acetic acid or soap, to the dye bath, according to their several requirements.

After printing and drying, the goods are steamed without pressure, allowed to air a short time, and then well washed and dried. Tin discharges are steamed from 5 to 45 minutes according to the amount of stannous chloride they contain; hydrosulphite discharges are steamed 3–4 minutes at 102°–103° C.

(*b*) Resist Styles.

For these styles, stannous chloride, hydrosulphite, and resin, fat, and wax resists are used; the two first mainly for resists under "cover" prints, the last for resists under dyed grounds.

The tin and hydrosulphite resists are made up like "discharges," with sometimes an addition of zinc oxide or China clay, and are first printed on the silk, which is then "covered" with another pattern in acid or direct colours. The goods are then steamed and washed as usual.

Resin, fat, and wax resists are printed hot, as when cold they set hard. Either block or roller machine may be used, and there is no reason why stencilling should not be employed for certain styles. Coloured resists with resin, etc., are obtained by first printing in the colours by block, and then, after drying, printing the whole pattern again with the same set or a similar set of blocks in the resisting mixture. In this way any desired colours may be resisted during the subsequent dyeing of the ground shade; and as the resists act in a purely mechanical manner, the dyed shade and the resisted colours need not be specially selected for their respective dischargeable and resisting properties. Hence any silk colour is equally applicable to either the reserved pattern or the dyed ground.

The resin mixtures are known as "Mastic Resists." The following two recipes will illustrate the composition of these mixtures :—

MASTIC RESISTS.	I.	II.
Resin	600	300
Beeswax	100	60
Swedish Pitch	...	100
Stearin	...	40
Benzene or Petrol	300	...
Naphtha	...	500
	1000	1000

After printing, the resists are dusted with talc powder or French chalk to prevent them from "marking off" or "sticking" together, and the goods are then dyed in the cold. When sufficiently dyed, the wax and resin are removed by working the silk in a bath of benzene or naphtha, neither of which dissolves the colours.

For the production by the "Mastic Process" of a so-called bandana handkerchief in red, yellow, blue, and white on a dark green ground the following sequence of operations may be carried out:—(1) Block print the white silk with thickened pastes of Victoria scarlet, Victoria yellow, Cyanol extra; (2) Steam for $\frac{1}{2}$–1 hour without pressure; (3) Wash and dry to width on a "stenter"; (4) Print the mastic reserve over the previously printed red, yellow, and blue, and on the parts of the silk cloth where the white, omitted in the first printing, is to appear; (5) Dye in the cold, or at 20°–25° C., in the following:—

2 per cent. Methylene green.
$\frac{3}{4}$ per cent. Auramine O.
10 per cent. acetic acid.
10 per cent. Glauber salt.

Work in the dye liquor until the required depth of shade is obtained, rinse in water, hydro-extract, hang up to dry, and (6) Wash in benzene or carbon tetrachloride until the mastic reserve is entirely removed. After the solvent has evaporated from the goods, the fastness of the ground shade may be increased by a second steaming for $\frac{1}{2}$ hour, but this is rarely necessary. Instead of the colours used above, any others suitable for silk may be employed in like manner.

Printing of Satins.

The printing of satin goods is carried out in exactly the same manner as that of cotton goods, so that, with the exception of vat dyestuffs and Madder colours, all the colouring matters used for cotton may be employed in precisely the same way for half-silk goods containing cotton. The presence of the latter requires the addition of tannin and chromium acetate to the basic and Eosin colours respectively, otherwise they would wash out at once in the first wash.

On account of the silk contained in the fabric, the Azo colours—Para red, etc.—are unsuitable for satin, as they cannot be obtained free from the defect of "rubbing off."

The Aniline black given for silk is equally adaptable to satin, and Paramine brown also serves as a suitable ground and outline colour.

The colours used in the direct printing of satin being for the most part fast, will stand soaping, and can therefore be thickened sometimes with starch; as a rule, however, it is better to use gum Senegal, gum tragacanth, or British gum, since they wash out very easily, leaving the lustre of the silk unimpaired.

Starch may be employed for dark outlines, but for blotches and other masses of colour, whether dark or light, the gums give by far the best results, especially in the case of fabrics one side of which is almost pure silk, such as the furniture satins with a cotton back and silk face.

Apart from furniture cretonne patterns, the most important branch of half-silk printing is that connected with discharge and resist styles.

Aniline black and Paramine brown discharge styles are carried out exactly as described for cotton.

The Browning process, as might be expected, gives the most lustrous, if not the brightest, colours on Aniline black, and is perhaps, on the whole, the most suitable, but other processes give satisfactory results, and even the presence of zinc oxide (Kay's process) is unobjectionable in fine discharge patterns, which, while they lose somewhat in lustre, gain more in brilliancy of colour.

The purest whites are obtained by the resist method, especially those produced under Nitroso-blue, in what is known as the "Foulard Blue Style."

The application of Nitroso-blue to half-silk is similar to its application to cotton, but both printing and slop-padding colours require an increased quantity of acid to yield the best results.

The following process for producing white resists under Nitroso-blue is recommended by the Farbwerke Höchst, the patentees of the colour:—The goods printed with the resist paste are thoroughly dried, then padded in Nitroso-blue M.R., and finally steamed, fixed in tartar emetic, washed, soaped, and dried.

WHITE RESIST.

170	grms.	British gum.
195	,,	water.
130	,,	glue solution 1 : 2.
85	,,	acetic acid 12° Tw.
250	,,	stannous chloride.
170	,,	tartaric acid.
1000		

Print, dry, and pad the goods in—

BLUE M.R.	I.	II.
Nitroso-base M. 50 per cent.	50	50
Hydrochloric acid 36° Tw.	16·7	16·7
Water	140	170
Tannoxyphenol R.	...	63
Resorcin	33	...
Hot water	85	85
Tannin solution 50 per cent.	100	...
Oxalic acid 10 per cent.	420	420
6 per cent. tragacanth thickening	100	100
Make up with water to	1000	1000

Pad, dry carefully in hot air, steam at 100° C. without pressure for 5-15 minutes, pass through a 1 per cent. solution of tartar emetic, wash, soap, and dry as usual.

The same process may be applied to pure silk.

The printing of wool and silk fabrics is carried out exactly as for pure wool, and calls for no special description.

ADDENDA.

1. CIBA YELLOWS.

The range of the Ciba series of vat dyestuffs has been extended recently by the introduction of two new colours—Indigo yellow 3 G. Ciba and Indigo yellow G. Both colours may be fixed in calico printing either by the glucose-alkali or the hydrosulphite-formaldehyde process. The latter process admits of the use of carbonate of potash, whereby the disadvantages attendant on the use of strong caustic alkali are avoided.

Indigo yellow 3 G. Ciba gives pure greenish-yellow shades, fast to light, washing, and chemicking. In combination with Ciba and other vat blues it yields good medium shades of green and olive. Being tinctorially weak, however, it is unsuitable for dark shades; and, for the same reason, medium shades cannot be reduced, since the effect of the yellow is weakened more than that of the blue.

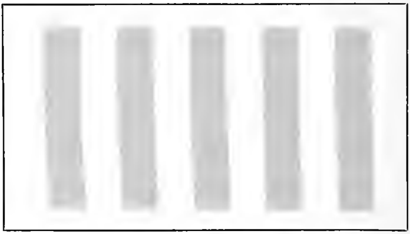
The following recipe illustrates the application of Indigo yellow 3 G. Ciba:—

300	grms.	dyestuff.
250	,,	British gum.
50	,,	glycerin.
130	,,	water.
150	,,	carbonate of potash.

Heat to 50° C. for 10 minutes; then cool and add

50	grms.	Rongalite C.
50	,,	water.
20	,,	olive oil.
1000		

Print, dry, steam for 2–3 minutes at 102°–104° C., develop in boiling soap (or chrome, cold), and finally wash well.



Indigo yellow 3 G. Ciba.

Indigo yellow G. is applied in the same way, but gives a redder shade.

2. HYDRON COLOURS.

The three Hydron blues and a Hydron violet, recently brought out by the firm of Leopold Cassella & Co., are the first members of an entirely new series of vat dyestuffs. They are derived from carbazol and its analogues, whereas the other well-known classes of vat colours are derivatives of either Indigo, Indirubin, or anthraquinone.

A desire has long existed among calico printers for a colour which, while possessing the depth and fastness of Indigo, would be capable of being applied in such a way as to obviate the disadvantages entailed by the necessity for printing Indigo in a strongly alkaline medium. The Hydron blues more than fulfil these conditions, for they are faster even than Indigo, and are applied with *weak* alkalies, such as the carbonates of soda or potash.

Hydron blue R. gives deep full shades of Indigo; Hydron blue G. yields lighter and greener shades, rather brighter than light Indigo; and Hydron deep blue G. a very dark colour, chiefly used for shading purposes. All three brands are not only fast to soaping, acids, and alkalies, but also to light and "chemicking," which cannot be said of even medium, not to speak of pale, shades of Indigo.

Hydron blues, whether printed or dyed, may be resisted by the usual resists (zinc and copper salts, Leukotropes, etc.) used for other vat colours, but once dyed they cannot be discharged by any known process; hence their application is, at present, restricted to direct printed, cover and pad, and "dipped" styles, so that Indigo still holds its own for discharged styles.

The Hydron blues may be mixed with other vat colours for the production of compound shades, worked along with them in multicoloured patterns, and generally applied to the same purposes, their mode of application being practically identical.

Hydron blue R. may, if desired, be printed by any of the methods employed for Indigo, but Hydron blue G. is best suited to the hydrosulphite-carbonate process which, in fact, yields the most satisfactory results with both colours. Hydron deep blue G. is not, as yet, much used in printing.

The following recipe is recommended by the makers for the preparation of the printing colours:—

50	grms.	Hydron blue R. or G. 40 per cent. paste.
50	,,	glycerin.
210	,,	water.
30	,,	soda ash.
60	,,	glucose.
50	,,	dissolving salt B. (benzyl-sulphanilate of soda).
50	,,	Hyraldite C. extra 50 per cent. solution.

Heat to 140° F. for $\frac{1}{4}$ hour: cool a little, and add

500	grms.	thickening H.
1000		

Lighter shades are obtained by adding more thickening.

Thickening H.:—

150	grms.	wheat starch.
550	,,	water.
300	,,	gum tragacanth, 6 per cent.
1000		

Print, dry, and steam for 4–5 minutes at 104° C. in steam as free from air as possible; then sour lightly with the addition of a little bichromate of soda (5 grms. sulphuric acid and $2\frac{1}{2}$ grms. bichromate per litre), wash well, soap, wash, and dry.

Brighter results are obtained with Hydron blue G. by replacing the souring by a treatment in perborate of soda ($1\frac{1}{2}$ grms. per litre) at 105°–120° F.

Resist Printing.

For imitations of the Indigo-dipped styles the Hydron blues may be resisted by the usual Indigo resists composed of copper, lead, and zinc salts, and also for "batticks" with the customary wax resists. The dyeing may be done in the "dipping vat," or on a padding machine; and as Hydron blues dye much more readily than Indigo the latter method is frequently adopted.

For padding, the liquor is made up as follows:—

Light Blue.		Medium Blue.		Dark Blue.		
10	grms.	10	grms.	10	grms.	Hydron blue G. 40 per cent. paste.
—	,,	10	,,	20	,,	Hydron blue R. 40 per cent. paste.
10	,,	20	,,	30	,,	caustic soda 77° Tw.
10	,,	20	,,	30	,,	hydrosulphite concentrated powder.
2½	,,	2½	,,	2½	,,	Turkey-red oil 40 per cent.
1000	,,	1000	,,	1000	,,	water.

First mix the caustic soda and Turkey-red oil with the dyestuff, heat up to about 50° C., and then add gradually the hydrosulphite dissolved in cold water, stir until the liquor is quite yellow, and finally add the remainder of the water. Use at 25° C.–32° C.

The goods printed with the resist, and well dried, are run through the above solutions at the temperature indicated. If more than one run is required they are exposed to the air for a short time between the runs. After the final padding the goods are well aired as for Indigo, soured, well washed, and dried.

If the resists show any sign of slipping in the warm dye liquor the padding may be done cold, but usually they withstand a run equivalent to about one minute's immersion in the warm liquor.

Hydron violet B. possesses the same properties as the blues. For printing, however, the makers recommend the use of caustic soda in place of soda ash. This means that, if the colour will not work to advantage with soda ash, it will deteriorate on standing, owing to the small content of caustic soda becoming converted into carbonate.

Hydron Violet B.

50	grms.	Hydron violet B. 40 per cent. paste.
50	,,	glycerin.
220	,,	hot water.
20	,,	caustic soda 77° Tw.
60	,,	Hyraldite C. extra 50 per cent. solution.
50	,,	glucose.
50	,,	dissolving salt B. Heat to 50° C. for ½ hour: then add—
500	,,	starch-tragacanth thickening.
1000		

After printing and drying treat as described for Hydron blues.

3. LEUKOTROPE RESISTS UNDER VAT COLOURS.

Although zinc chloride is an effective resisting agent under many Vat and Sulphide dyestuffs, its hygroscopicity presents certain disadvantages in practice, and its substitution by the Leukotropes is, therefore, of interest to calico-printers.

The Society of Chemical Industry in Basle were the first to notice that Leukotrope printing pastes, containing *no* hydrosulphite-formaldehyde, were capable of preventing the fixation of Vat dyestuffs afterwards printed over them; but they failed, at the same time, to observe that the presence of strong caustic alkalies was equally unnecessary, and, consequently, their process is of much less practical value than that of E. Bentz and the Calico Printers Association,[1] in which caustic alkalies are absent altogether.

This latter process consists essentially of printing one of the Leukotropes, suitably thickened, on white cloth, and then over-printing suitable Vat colours (made up in the customary manner) with either a pad or cover roller. The Vat colours are fixed in the usual way by a run through the rapid ager, followed by a treatment in bichromate of soda or perborate of soda.

Example:		
	150 grms.	Leukotrope O.
	850 ,,	British gum thickening.
	1000	

Print, dry, and over-print Hydron blue G. (*q.v.*), dry, and run through the rapid ager, etc.

Amongst the colours suitable for over-printing may be mentioned Ciba violet B., Helindone brown 2 R., Alizarin indigo G., 3 R. and 7 R., Thio-indigo scarlet 2 G., Hydron blue R., Thio-indigo orange R., Immedial brilliant green G. G., Helindone red 3 B., and Ciba grey.

Another advantage of the process is that coloured resists may be obtained by adding a sufficiency of Leukotrope to colours, such as Alizarin red, α-Naphthylamine claret, and certain other colours, and then printing suitable Vat colours over them as above.

In the same way Leukotrope may be associated with mordants, and the goods afterwards dyed up in any suitable mordant dyestuff.

Reserve salts O. and W. (Kalle) behave similarly to the Leukotropes. They are specially adapted to resisting printed Indigo, under which they yield fine sharp impressions.

4. PROCESS FOR PREVENTING THE TENDERING OF GOODS DYED WITH SULPHIDE COLOURS.

It has long been known to dyers and calico-printers that goods dyed with Sulphide colours are liable, sooner or later, to lose considerably in tensile strength. This may occur during any of the various processes immediately following the dyeing operation, or it may not take place until the goods have been stored many months. Sometimes no "tendering" at all takes place; while, on the other hand, cases are frequently cited where goods have left the works in perfect condition, and have been found to have become quite "tender" on arrival at their destination in some far eastern port.

The cause of "tendering" has been fully investigated by J. E. Pilling,[2] who came to the conclusion that it was due entirely to the presence of sulphuric acid; and, further, that this sulphuric acid was formed not necessarily by the

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[1] English Patent No. 16,389, 1910.

[2] *Journal of Society of Dyers and Colourists*, Feb. 1906.

oxidation of sodium sulphide, or polysulphides (often present in the dyestuff), but by the oxidation of the colour-molecule itself, or by the oxidation of sulphurous acid to which mixed goods are subjected in the stoving (sulphuring) process, and which is always present in the atmosphere of manufacturing districts.

Most of the methods recommended for overcoming the tendering action of Sulphide dyestuffs depend either upon the use of oxidising agents (to further the oxidation of the dyestuff during process), or upon an after-treatment with salts capable of neutralising free mineral acids.

In this latter connection the following compounds have been recommended: soap, sulphite of soda, carbonate of soda, and the formates and acetates of lime and soda. Up to a certain point these salts are undoubtedly efficient, but they possess the disadvantage of being soluble, and, consequently, when the goods are washed they are removed from the fibre and become inoperative.

The employment of bichromates and acetic acid with the idea of completing the oxidation of the colouring matter at once has not been found to attain its object with any degree of certainty.

In the process of G. E. Holden[1] the drawbacks connected with the application of soluble neutralising salts are obviated by the fixation on the fibre of an insoluble calcium salt which reacts quantitatively with the sulphuric acid as it is produced, and in that way provides a permanent and effective method of preventing the "tendering" of the dyed goods.

The process, which is very simple, consists in treating the dyed goods in a 1 per cent. solution of tannic acid at 40° C., squeezing, passing through lime water, and finally washing.

Goods dyed with a number of representative Sulphide blacks, blues, browns, etc., when treated in this way and exposed, along with untreated samples, to a temperature of 120° C. for twenty hours, retained their original strength unimpaired, whilst the untreated samples all became tender, and many of them quite rotten.

In addition to preventing a loss in tensile strength, this process has other advantages, namely: (*a*) in some cases it *increases* the tensile strength of the fibres; (*b*) in the case of blacks especially it improves the depth and tone so as sometimes to allow of 10 per cent. less dyestuff being used to produce a given shade; (*c*) it adds to the weight of the goods; and (*d*) it is said to increase the power of the goods to absorb starches (in finishing).

Equally good results are obtained by replacing lime water by any other suitable salt of calcium, barium, or strontium; and soda ash may be used in place of tannic acid, although the tannates have been found to yield by far the best results.

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[1] *Journal of Society of Dyers and Colourists*, April 1910.

5. COMPARISON OF THE THERMOMETER TABLES OF CELSIUS (OR CENTIGRADE), FAHRENHEIT AND RÉAUMUR.

Degrees.			Degrees.			Degrees.		
Celsius.	Fahrenheit.	Réaumur.	Celsius.	Fahrenheit.	Réaumur.	Celsius.	Fahrenheit.	Réaumur.
0	32·0	0·0	34	93·2	27·2	68	154·4	54·4
1	33·8	0·8	35	95·0	28·0	69	156·2	55·2
2	35·6	1·6	36	96·8	28·8	70	158·0	56·0
3	37·4	2·4	37	98·6	29·6	71	159·8	56·8
4	39·2	3·2	38	100·4	30·4	72	161·6	57·6
5	41·0	4·0	39	102·2	31·2	73	163·4	58·4
6	42·8	4·8	40	104·0	32·0	74	165·2	59·2
7	44·6	5·6	41	105·8	32·8	75	167 0	60·0
8	46·4	6·4	42	107·6	33·6	76	168·8	60·8
9	48·2	7·2	43	109·4	34·4	77	170·6	61·6
10	50·0	8·0	44	111·2	35·2	78	172·4	62·4
11	51·8	8·8	45	113·0	36·0	79	174·2	63·2
12	53·6	9·6	46	114·8	36·8	80	176·0	64·0
13	55·4	10·4	47	116·6	37·6	81	177·8	64·8
14	57·2	11·2	48	118·4	38·4	82	179·6	65·6
15	59·0	12·0	49	120·2	39·2	83	181·4	66·4
16	60·8	12·8	50	122·0	40·0	84	183·2	67·2
17	62·6	13·6	51	123·8	40·8	85	185·0	68·0
18	64·4	14·4	52	125·6	41·6	86	186·8	68·8
19	66·2	15·2	53	127·4	42·4	87	188·6	69·6
20	68·0	16·0	54	129·2	43·2	88	190·4	70·4
21	69·8	16·8	55	131·0	44·0	89	192·2	71·2
22	71·6	17·6	56	132·8	44·8	90	194·0	72·0
23	73·4	18·4	57	134·6	45·6	91	195·8	72·8
24	75·2	19·2	58	136·4	46·4	92	197·6	73·6
25	77·0	20·0	59	138·2	47·2	93	199·4	74·4
26	78·8	20·8	60	140·0	48·0	94	201·2	75·2
27	80·6	21·6	61	141·8	48·8	95	203·0	76·0
28	82·4	22·4	62	143·6	49·6	96	204·8	76·8
29	84·2	23·2	63	145·4	50·4	97	206·6	77·6
30	86·0	24·0	64	147·2	51·2	98	208·4	78·4
31	87·8	24·8	65	149·0	52·0	99	210·2	79·2
32	89·6	25·6	66	150·8	52·8	100	212·0	80·0
33	91·4	26·4	67	152 6	53·6			

To convert
F° into C° subtract 32, multiply by 5, and divide by 9.
F° ,, R° ,, 32, ,, 4, ,, 9.
C° ,, F° multiply by 9, divide by 5, and add 32.
C° ,, R° ,, 4, ,, 5.
R° ,, F° ,, 9, ,, 4, and add 32.
R° ,, C° ,, 5, ,, 4.

6. HYDROMETER TABLES.

Comparison of Hydrometer Degrees Twaddle and Baumé with the Specific Gravities for Liquids heavier than Water.

Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees Baumé.	Specific Gravity.	Degrees Twaddle.	Degrees Baumé.	Specific Gravity.
1	0·7	1·005	58	32·4	1·290	116	53·0	1·580
2	1·4	1·010	60	33·3	1·300	118	53·6	1·590
4	2·7	1·020	62	34·2	1·310	120	54·1	1·600
6	4·1	1·030	64	35·0	1·320	122	54·7	1·610
8	5·4	1·040	66	35·8	1·330	124	55·2	1·620
10	6·7	1·050	68	36·6	1·340	126	55·8	1·630
12	8·0	1·060	70	37·4	1·350	128	56·3	1·640
14	9·4	1·070	72	38·2	1·360	130	56·9	1·650
16	10·6	1·080	74	39·0	1·370	132	57·4	1·660
18	11·9	1·090	76	39·8	1·380	134	57·9	1·670
20	13·0	1·100	78	40·5	1·390	136	58·4	1·680
22	14·2	1·110	80	41·2	1·400	138	58 9	1·690
24	15·4	1·120	82	42·0	1·410	140	59·5	1·700
26	16·5	1·130	84	42·7	1·420	142	59·9	1·710
28	17·7	1·140	86	43·4	1·430	144	60·4	1·720
30	18·8	1·150	88	44·1	1·440	146	60·9	1·730
32	19·8	1·160	90	44·8	1·450	148	61·4	1·740
34	20·9	1·170	92	45·4	1·460	150	61·8	1·750
36	22·0	1·180	94	46·1	1·470	152	62·3	1·760
38	23·0	1·190	96	46·8	1·480	154	62·8	1·770
40	24·0	1·200	98	47·4	1·490	156	63·2	1·780
42	25·0	1·210	100	48·1	1·500	158	63·7	1·790
44	26·0	1·220	102	48·7	1·510	160	64·2	1·800
46	26·9	1·230	104	49·4	1·520	162	64·6	1·810
48	27·9	1·240	106	50·0	1·530	164	65·0	1·820
50	28·8	1·250	108	50·6	1·540	166	65·5	1·830
52	29·7	1·260	110	51·2	1·550	168	65·9	1·840
54	30·6	1·270	112	51·8	1·560	169	66·1	1·845
56	31·5	1·280	114	52·4	1·570	170	66·3	1·850

Comparison of Hydrometer Degrees Baumé with the Specific Gravity of Liquids lighter than Water.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
11	0·993	16	0·960	21	0·930	26	0·901
12	0·987	17	0·954	22	0·924	27	0·896
13	0·980	18	0·948	23	0·918	28	0·890
14	0·973	19	0·942	24	0·913	29	0·885
15	0·967	20	0·936	25	0·907	30	0·880

7. WEIGHTS AND MEASURES.

Metric System.

1 gramme (grm.) = 15·43 grains (grs.).
1 kilogramme (kilo.) = 1000 grms. = 15,430 grs. = 2$\frac{1}{5}$ lbs. nearly.
1 cubic centimetre (c.c.) = 17 minims = $\frac{1}{284}$th gill.
1 litre = 1000 c.cs. = 35 ozs. nearly = 3½ gills nearly.
1 metre = 100 centimetres (cms.) = 1·093 yards.

English System.

1 ounce (oz.) = 28·35 grms.
1 pound (lb.) = 16 ozs. = 453·6 grms. = 0·4536 kilo.
1 gill = 2 noggins = 10 ozs. = 0·284 litre.
1 pint = 4 ,, = 20 ozs. = 0·567 ,,
1 quart = 8 ,, = 40 ozs. = 1·135 ,,
1 gallon = 4 quarts = 8 pints = 16 gills = 32 noggins = 10 lbs. = 4·543 litres.
1 inch (″) = 2·54 centimetres (cms.).
1 foot (′) = 12″ = 30·48 cms.
1 yard = 3′ = 91·4 cms. = 0·914 metre.

8. PRICE LIST OF DRUGS.[1]

Acids—Acetic, 40 per cent.	12s. 6d. per cwt.
Citric	1s. 4d. per lb.
Formic, 90 per cent.	33s. per cwt.
,, 45 per cent.	18s. per cwt.
Lactic, 50 per cent.	21s. per cwt.
Muriatic (Tower Salts 30° Tw.)	2s. per carboy.
,, (Cylinder ,,)	3s. 3d. per carboy.
Nitric, 89° Tw.	1¾d. per lb.
Oxalic	2¾d. per lb.
Sulphuric (Pyrites 168° Tw.)	£3, 2s. 6d. per ton.
,, (,, 145°–148° Tw.)	£1, 10s. per ton.
,, (,, free from Arsenic, 145° Tw.)	£1, 15s. per ton.
Tannic, 82 per cent.	1s. per lb.
,, Levissimum	1s. 9½d. per lb.
,, (ordinary)	8½d. per lb.
Tartaric	1s. 0½d. per lb.
Albumen, Egg	1s. 6d. to 2s. 6d. per lb.
,, Blood	6d. to 8d. per lb.
Alum	£6 and £6, 10s. per ton.
Aluminium, Acetate (Red Liquor)	5d. to 7½ per gallon.
,, Sulphate	£5, 5s. per ton.
,, Sulphocyanide	2s. to 3s. 6d. per gallon.

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[1] Taken mainly from the *Journal of the Society of Dyers and Colourists*, June 1912.

Aluminate of Soda	£29 to £34 per ton.
Alumino Ferric (slabs)	£3, 5s. per ton.
Ammonia, 20 per cent. S. G. 0·915	2d. per lb.
,, 33 per cent. S. G. 0·880	2¾d. per lb.
Ammonium Chloride (Sal Ammoniac)	1sts, £42 ; 2nds, £40 per ton.
,, Sulphate	£14, 5s. per ton.
Antimony Fluoride (double)	5½d. per lb.
,, Oxalate	6d. per lb.
,, Salt (65 per cent.)	5½d. per lb.
,, Tartrate (Tartar Emetic 28 per cent.)	5¼d. per lb.
,, Tartrate (Tartar Emetic 44 per cent.)	8½d. per lb.
Arsenic, White, Powdered	£12, 10s. per ton.
Arseniate of Soda 60 per cent.	£25, 10s. per ton.
Binarseniate of Soda 65 per cent. As_2O_5	£27 per ton.
Barium, Sulphate	£2 to £3, 10s. per ton.
,, Sulphocyanide	3¾d. per lb.
Beeswax	£5, 10s. per cwt.
Bleaching Liquor, 28° Tw. 6 to 7 per cent.	£3, 15s. per ton.
,, Powder 35 per cent.	£4, 10s. per ton.
Borax	£16, 10s. and £17, 10s. per ton.
China Clay	35s. to 43s. per cwt.
Coal Tar Products—	
Alizarin Red, 20 per cent.	7d. per lb.
Aniline Oil (pure)	5d. per lb.
,, Salt (pure)	4¾d. per lb.
Anthraquinone, 30 per cent. paste	10d. per lb.
Benzole, 90 per cent.	10½d. per gallon.
,, 50/90	10d. per gallon.
Carbolic Acid (cryst.) 39–40° C.	8½d. per lb.
Cochineal	1s. 6d. to 2s. per lb.
Copperas (Green)	22s. per ton.
Copper Sulphate	£24 per ton.
Chalk	32s. per ton.
Chrome Alum	£16 per ton.
Dyewoods—	
Bark (Baltimore)	£5, 15s. per ton.
Barwood	£6 per ton.
Camwood	£16 per ton.
Fustic (Jamaica)	£5, 10s. per ton.
Limawood, Peachwood	£10 per ton.
Logwood (Jamaica)	£5 per ton.
,, (St Domingo)	£4, 10s. to £5 per ton.
,, (Honduras)	£6, 15s. per ton.
Extracts—	
Bark liquor	21s. per cwt.
,, extract	16s. to 24s. per cwt.
Myrobalan, 50° Tw.	9s. per cwt.
Sumach Extract	14s. to 16s. per cwt.
Orchil	25s. to 30s. per cwt.
Peachwood	11s. per cwt.
Persian berries	36s. per cwt.
Logwood	20s. to 30s. per cwt.
Hematein Paste	25s. to 30s. per cwt.
,, Crystals	50s. to 60s. per cwt.
Flavin	1s. 6d. to 2s. 9d. per lb.

Glycerin	£95 to £100 per ton.
Hydrogen Peroxide (12 vols.)	1s. per gallon.
Indigo—	
Bengal	2s. 10d. to 5s. per lb.
Oude	2s. 6d. to 4s. per lb.
Kurpah	1s. 9d. to 3s. 4d. per lb.
Artificial (20 per cent. paste)	8d. per lb.
Iron liquor, Black, 24 per cent. Tw.	5d. per gallon.
,, Red	2s. 6d. per cwt.
Lead, Sugar of (White)	£26 per ton.
,, ,, (Brown)	£22, 10s. per ton.
,, Nitrate	£26 per ton.
Lime, Acetate (Grey)	£12 per ton.
,, ,, (Brown)	£7, 10s. per ton.
Litharge	£17 per ton.
Magnesium Chloride	£3, 10s. per ton.
,, Sulphate (Epsom Salts)	65s. per ton.
Methylated Spirits, 61° O.P.	2s. 3d. per gallon.
Oils—	
Castor	£33 per ton.
Cocoa Nut	£42 per ton.
Cotton Seed	£25, 10s. per ton.
Gallipoli	£50 to £55 per ton.
Linseed Oil (East Indian)	£37 per ton.
Lubricating	1s. to 1s. 6d. per gallon.
Olive	£40 to £44 per ton.
Palm (Lagos)	£30 per ton.
Rape Seed	£33 per ton.
Tallow (Australian)	£32 to £37 per ton.
,, (Home Melted)	£36 per ton.
Paraffin Wax	2d. to 2½d. per lb.
Potash—	
Bichromate	3½d. per lb.
Binoxalate	4½d per lb.
Carbonate, 90/92 per cent.	£18 per ton.
Caustic, 75/80 per cent.	£21 per ton.
Chlorate	3¾d. per lb.
Ferricyanide (Red prussiate)	9½d. per lb.
Ferrocyanide (Yellow prussiate)	4¾d. per lb.
Permanganate	37s. per cwt.
Prussian Blue (paste)	8½d. per lb.
Resin (common)	10s. 6d. per cwt.
Resin Spirits	17s. to 20s. per cwt.
Soap, White Curd	£29, 10s. per ton.
,, Soft Gallipoli	35s. per pack.
Soda—	
Acetate	£15 per ton.
Bicarbonate	£6, 15s. per ton.
Bichromate	3d. per lb.
Bisulphite, 50° Tw. 15/20 per cent. SO_2	3s. 3d. per cwt.
Carbonate (Soda Ash) 48 per cent.	£3, 15s. per ton.
,, ,, ,, 58 per cent.	£3, 15s per ton f.o.r.
,, (Crystal Carbonate)	7s. 6d. per cwt., in bags.
,, (Soda Crystals)	£2, 7s. 6d. per ton in barrels, and £2 per ton in bags, f.o.r.

Soda (*contd.*)—	
Caustic, 70 per cent.	£9, 12s. 6d. f.o.r.
Caustic, 78 per cent. to 79 per cent.	£10, 15s. f.o.r.
Chlorate	3¾d. per lb.
Chloride (Common Salt)	19s. per ton.
Ferrocyanide (Prussiate)	3d. per lb.
Hydrosulphite	10¼d. per lb.
Nitrate (95 per cent.)	11s. 3d. per cwt.
Nitrite (96/98 per cent.)	£27 per ton.
Peroxide	1s. per lb.
Phosphate	£9, 15s. per ton.
Silicate, 140° Tw.	£4, 7s. 6d. per ton.
Stannate (40 per cent.)	£4 per cwt.
Sulphate (Salt Cake)	42s. 6d. per ton.
,, (Glauber's)	45s. per ton.
Sulphide (concentrated)	£8 per ton.
,, (crystallised)	£5, 10s. per ton.
Sulphoxylate formaldehyde	1s. 7½d. per lb.
Starch (American)	£10 per ton.
,, (Farina)	£12, 10s. per ton.
,, (Dextrin)	£16 per ton.
Sulphur (recovered)	£6 per ton.
Talc (French Chalk)	£3, 10s. to £6 per ton.
Tannins—	
Cutch	20s. to 40s. per cwt.
Gambier (Block)	28s. per cwt.
Divi-divi	8s. to 12s. per cwt.
Myrobalans	5s. 6d. to 7s. 6d. per cwt.
Sumach—PTT	10s. 6d. per cwt.
Tartar—Brown and White	70s. to 90s. per cwt.
Tin (English Ingots)	£190 per ton.
,, Crystals	1s. 1½d. per lb.
Titanium Potassium Oxalate	£4, 15s. per cwt.
Titanous Chloride	£4 per cwt.
,, Sulphate	£3, 2s. 6d. per cwt.
Zinc Powder	£24 per ton.
,, Chloride 96° Tw.	£6, 10s. per ton.
,, Oxide	£27 per ton.
,, Sulphate	£7, 10s. per ton.

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