THE CHEMISTRY
AND
TECHNOLOGY OF PAINTS

By MAXIMILIAN TOCH

AUTHOR OF "MATERIALS FOR PERMANENT PAINTING," ETC., ETC.

WITH 83 PHOTOMICROGRAPHIC PLATES
AND OTHER ILLUSTRATIONS

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PREFACE TO FIRST EDITION

THE difficulty which I encountered in writing this book was not how much to write but how much to omit, for I found on compiling my notes that I could very easily have made two volumes, each larger than the present one, and still would not have covered the ground thoroughly. It is for this reason that I have omitted many of the pigments which are rarely used, and have paid no attention whatever to the pigments which have gone out of use.

I have not considered it desirable to use any space in this book with extended repetition of matter that can be found in other books of reference, for I have so much matter which is the result of original research that very few references are cited.

This being the first book ever written on the subject of mixed paints, I am cognizant of the fact that there are many matters in it which I shall have to alter in future editions, and many subjects upon which I shall have to enlarge. It must be borne in mind that mixed paint is demanded by a progressive civilization and that there are no two manufacturers who make identically the same mixtures. As time changes, the progressive manufacturer alters his formulas, and an indication of this is that the original mixed paints were mostly emulsions and soap solutions, whereas today the tendency is toward purity and improvement, and one manufacturer tries to outdo the other in making a paint that will last, the ideal paint, however, being never reached.

This volume is intended for the student in chemistry who desires to familiarize himself with paint, or the engineer who desires a better knowledge of the subject, or for the paint manufacturer and paint chemist as a work of reference. It is not intended for those who have no previous knowledge or training in the subject.

Some of the chapters in this book are taken from my lectures delivered at various universities, and others are extracts from lectures delivered before scientific bodies. One of the objects which I have had in view during the entire time I have been writing this book is to familiarize the student in chemistry, or the post-graduate, with the science and technology of modern paints, so that in a very short time the chemist unfamiliar with the subject may obtain sufficient knowledge to make a reasonable examination of paint.

The chapter on linseed oil illustrates this, and my researches and theories on the difference between raw and boiled linseed oil are here published for the first time. From the formulas and disquisition on the subject it can be easily seen that if raw linseed oil be taken as a standard nearly all comparisons fail if boiled linseed oil is under examination.

320 Fifth Avenue
New York, 1907

PREFACE TO SECOND EDITION

Since the first edition of this book was published the efforts of a large number of technical men working in this field have resulted in very important advances both in the production of new pigments, oils and special paints and in the scientific elucidation of many obscure phenomena in paint technology. Improvements have also been made in the method of manufacture as well as in the quality of many of the older pigments. Advances have also been made in the discovery and utilization of a number of oils which have not heretofore found extended use in the paint trade.

These important advances have necessitated rewriting most of the book and the addition of new matter to the extent of doubling its size. Some of the important additions which may be worthy of mention are, standard specifications for pigments and oils; new special paints and driers; the theory of corrosion of iron and steel and its prevention as well as the action of fungi on paints; the important subject of the hygiene of workmen; detailed methods of analysis of paints and paint materials as well as tables of constants of such materials.

Undoubtedly the chemical manufacturer and the chemical student who intends to become proficient in paint chemistry will find it essential to read a great deal of the past as well as the current technical literature of the subject, but it is the hope of the author that this book will give the student a comprehensive survey of the progress already made and furnish a foundation for further improvement.

MAXIMILIAN TOCH

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THE CHEMISTRY
AND
TECHNOLOGY OF PAINTS

INTRODUCTION

THE manufacture of mixed paints is essentially American, having been accredited to some enterprising New Englanders who observed that when a linseed oil paint was mixed with a solution of silicate of soda (water glass) an emulsion was formed, and the paint so made showed very little tendency to settle or harden in the package. Several lay claim to this discovery. The first mixed paint was marketed in small packages for home consumption and appeared about 1865.

The addition of silicate of soda is still practised by a few manufacturers, but the tendency is to eliminate it as far as possible and to minimize as much as possible the use of an alkaline watery solution to keep the paint in suspension. The general use of zinc oxid has had much to do with the progress of mixed paint, for it is well known that corroded white lead and linseed oil settle quickly in the package, while zinc oxid keeps the heavier lead longer in suspension. Where only heavy materials are used, manufacturers are inclined to add up to 4 per cent of water. Under another chapter on "Water in the Composition of Mixed Paints," page 254, this subject will be fully discussed.

To the pigments are added many materials possessing but little body, hiding or covering property, which are known as inert fillers, and some of these, particularly the silicates of alumina and the silicates of magnesia, the various calcium carbonates, and silica itself, are used to counterbalance the heavy weight or the specific gravity of the metallic pigments; and whereas these inert fillers were formerly regarded as adulterants and cheapening agents, they are now looked upon as necessities, and the consensus of opinion among practical and many scientific investigators is that a compound paint composed of lead, zinc, and a tinting pigment, to which an inert material has been added, is far more durable than paint made of an undiluted pigment. The consuming public and the painter himself have not been sufficiently educated as yet to understand the merits of these diluents, and the paint manufacturer has been reticent in his statements regarding the use of various fillers.

These facts account to a large degree for the opposition to the use of such materials. When it is taken into consideration that within forty years the sale of mixed paints in the United States has grown to almost sixty million gallons per year (and the outlook is for a larger increase in the use of mixed paints), it is obvious that the demand is healthy, even though the manufacture of mixed paints has been directed or based largely upon empirical formulas.

One of the railroads of the United States buys at this writing upward of one million dollars' worth of paint material per year, a large share of this being mixed paints, or paint ready for the brush. Nearly all of the large manufacturing industries which use large quantities of paint are gradually altering their methods, so that their paint comes to them ready for application. In no case, to the best knowledge of the author, does a single one of these industries prescribe a single pigment with linseed oil for general purposes, for it has been shown that a mixture of several pigments and a filler is superior from the standpoint of lasting quality and ease of application to a mixture of a single strong pigment and the vehicle.

The structural iron industry, which has reached an enormous development in the United States, uses paints ready mixed with the one exception of red lead, which, in the old prescription of thirty-three pounds of red lead to one gallon of oil, cannot be prepared ready for the brush, for reasons which will appear in the proper chapter.

The manufacture of agricultural implements, wagons, and wire screens can be cited as industries in which manufacturers have within a very few years adopted the use of ready-mixed paints for their products. These paints are not brushed on, but are so scientifically made, and the relation between a vehicle and a pigment is so carefully observed, that large pieces of their products can be dipped into troughs and the paint allowed to drain. The surface is more evenly coated and the work done in far less time than would be required were it applied by means of the brush, as in former years.

In view of all these facts, the prejudice on the part of the general public and the trepidation of the manufacturer are to blame for the unheralded knowledge of the constituents of mixed paints. There are many cases where materials which were once despised are regarded now as essential to the life and working quality of paint, and the attitude of the paint manufacturer must in the future be a frank and open admission of the composition of his materials. If a paint is composed of a mixture of white lead, zinc oxid, and barytes, and it has been proved that a mixture of these three will outlast a mixture of either of the other two, there is no reason why a manufacturer of mixed paints shall not so state.

New materials have come into use which have taken the place in a large degree for many purposes of the time-honored and useful white lead, and many mixed paint manufacturers have already begun to educate the public to the superiority of one material over another. It stands to reason, however, that the manufacturer of a raw material which has been in use for a very long time is going to refute as much as possible the statement made with regard to newer materials, and these discussions tend to do good rather than harm.

In the case of one of the large railroads, the specifications for a certain paint demand the use of over 70 per cent of inert filler, and if these inert fillers had no merit no railroad or large corporation would permit their use. These large corporations support chemical laboratories and employ the best talent which they can engage. They continually experiment, and in their specifications the results of their experiments are obvious, and therefore if a large corporation can state publicly not only what the composition of these paints shall be, but conclude that such compositions are based upon the results of scientific investigation, the paint manufacturer can do likewise and stand back of his products, provided they be mixtures of various materials which time, science, and investigation have proved to be superior.

Unfortunately, however, there are some manufacturers who have "hidden behind a play of words" and permit chicanery and finesse to enter into the description of their products; but fortunately some of them have seen the errors of their way, and already there is a tendency toward openness and candor with regard to their wares. There was a time, and it still exists in a measure, when substitutes for white lead were very largely sold, and misleading labels appeared on the packages; for instance, a man would make a mixture of 80 per cent barytes and 20 per cent white lead, and would print on the label—"The lead in this package is guaranteed absolutely pure," followed by a commendation and guarantee that certain sums of money would be paid if the lead were not found to be pure. This, of course, is a moral fraud and an unfortunate play on the ambiguity of the language, and many of the manufacturers, in view of such unfortunate misstatements, are altering the names of their paste products, or lead substitutes, omitting the word "lead" entirely.

Another unfortunate mistake is made when a manufacturer makes a mixed paint and states on the label, "This paint is composed of pure lead, pure zinc, pure linseed oil, pure drier, and nothing else." The analyses of the paint have proved that in addition to the "pure" products mentioned three gallons of water were added to every hundred gallons of paint in order to keep the paint in suspension, and that it had not been strained and therefore contained a large amount of dirt and foreign matter. Ethics would clearly indicate that no manufacturer has a moral right to label his paint as being entirely pure and composed of four materials, when as a matter of fact an excessive quantity of water was added which destroyed in a large degree the value of the other materials. In another chapter the question of the percentage of water which may be contained in any paint will be thoroughly discussed. Three per cent is entirely excessive in an exterior linseed oil paint, and a manufacturer has no right, either morally or legally, to hide behind a misrepresentation of his paint when the paint is largely adulterated for the purpose of overcoming his ignorance in the manufacture.

CHAPTER I

THE MANUFACTURE OF MIXED PAINTS

THE modern methods of making mixed paint are divided into two classes, which depend upon the specific gravity and fineness of the raw material.

One of the methods employed is to mix the raw material with sufficient linseed oil to form a very heavy paste, the proper tinting material being added during the process of mixing. This paste is then led down from the floor on which it is made into a stone mill and ground. Even when the mill is water-cooled, the mass frequently revolves at such a speed that the paste paint becomes hot. It is then allowed to run from the mill into a trough called the "cooler," or is stored in barrels to be thinned at some later time. In case the operation is continuous and the paste is thinned at once, it passes from a stone mill to a mixer below which contains the requisite quantity of thinning material composed of oil, volatile thinner, and drier, where it is intimately mixed by means of paddles. It is then compared with the standard for shade, and if the tone should not be identical with the former mixing, either tinting material or pigment is added in sufficient amount to produce the proper shade. From the last mixer, known as the "liquid mixer," the paint is drawn off and filled into packages, the final operation before allowing it to enter the package being to strain it. This method has been used ever since mixed paints have been made. The majority of white paints, or paints of heavy specific gravity, are made in this manner.

The paints of lower specific gravity, varnish and floor paints, are made differently. This method is really the reverse of the old-fashioned method, in that the liquid and pigment are placed in a mixer on an upper floor in the amounts necessary to produce the correct consistency. The paint is run down in a thin stream to the floor below into a mill known as the "liquid mill." The liquid mills revolve very rapidly, the stones being flat.

According to the best practice of making paste paints a grinding surface is supposed to be conical, although there is much difference of opinion on this subject. When the paint has run through the stones of a liquid mill, it comes out of a spout and is then ready for packing, due precaution being taken, however, to strain it twice, once as it passes down into the liquid mill and again as it flows out. There is much difference of opinion among paint-making mechanics as to the proper surface which a grinding surface shall present; for instance, the first depression in the stone of a mill is deep, tapering toward the edge, and is known as the "lead." From the end of this "lead" fine lines radiate toward the "periphery" of the stone. These are called the "drifts," and the paints containing silica wear off the surface of even the hardest flintstone mills, so that in well-regulated factories a man is always employed sharpening the mills, and by the term "sharpening" is understood cutting out the "drifts" and "leads."

Not so many years ago paint mills were composed of either iron or steel, but in modern paint practice mills of this character have been abandoned, except for use as filling machines. They grind fairly fine when sharp, but inasmuch as all silicious paint materials are harder than steel or iron they become dull in a very short time. Then again, the attrition grinds off small particles of iron, which affect all delicate tints more or less.

The arrangement of the tanks and mills in the factory is of the greatest importance. Taking up first the second method of mixing paint already described, the liquid and white base are mixed in large, heavy cast-iron mixers, which are located on a platform high enough to discharge into a liquid mill. (See Fig. 1, Heavy Mixers.)

The mixed material is ground through this mill and discharged from it into storage tanks situated conveniently on a platform below the floor on which the mill is located, these storage tanks holding from 1500 to 2000 gallons of the ground product. From the storage tanks a pipe-line with its various branches carries the paint to tinting tanks placed at convenient distances from the storage tanks, the latter being high enough to allow the paint, by gravity, to flow through pipes to the tinting mixers. This pipe-line is made of wrought iron, the usual diameter of which is 4 inches, the joints being all flanged so that the pipes may be easily taken apart and cleaned.

Underneath the storage tanks and close to the outlet is a master valve, so that the product in the tank may be shut off at any time and the flow cut out from the system of pipes. Opposite each tinting tank (these tanks should be in parallel rows and numbered to correspond to the tints that are to be made) a 2-in. branch pipe is connected to the 4-in. main, and each of these branches is furnished with a valve to control the discharge into the tinting mixers. The cast-iron mixers already mentioned should be so arranged that two mixers work in conjunction with one mill. The mill is of stone and known as a liquid or incased mill, the usual diameter being 30 to 36 inches.

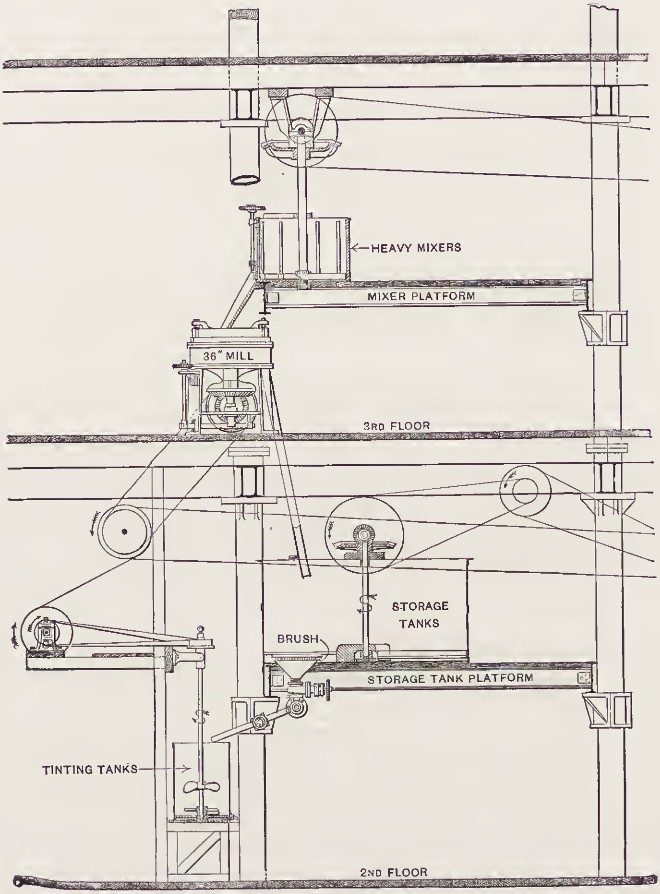
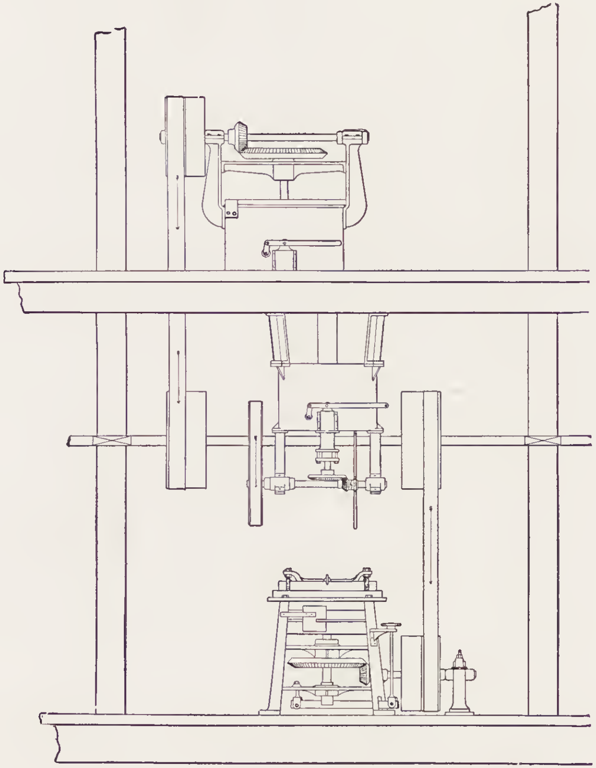
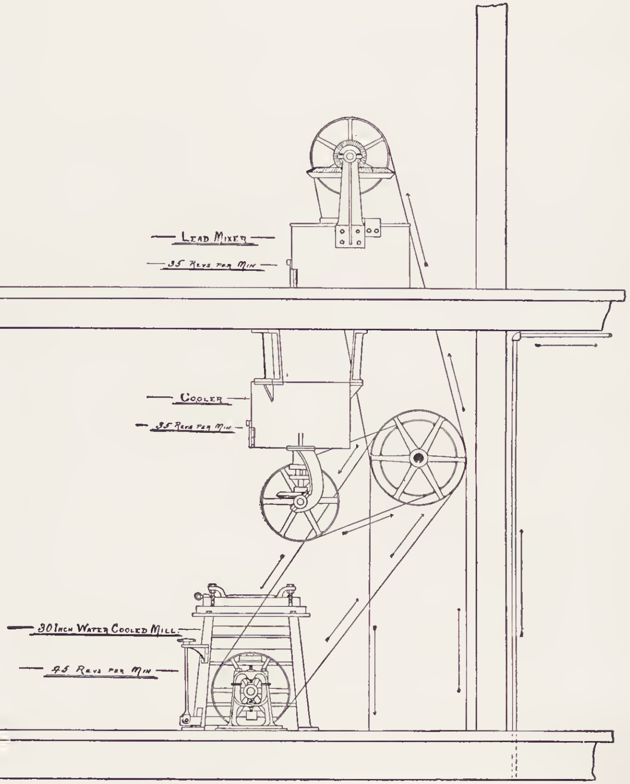


FIG. 1—HEAVY MIXERS

The storage tanks are made of sheet metal with heavy sheet-steel bottoms, and are furnished with a slowly revolving stirrer to keep the ground liquid agitated. The outlet of these tanks is of generous size and covered with a steel wire screen to prevent any foreign

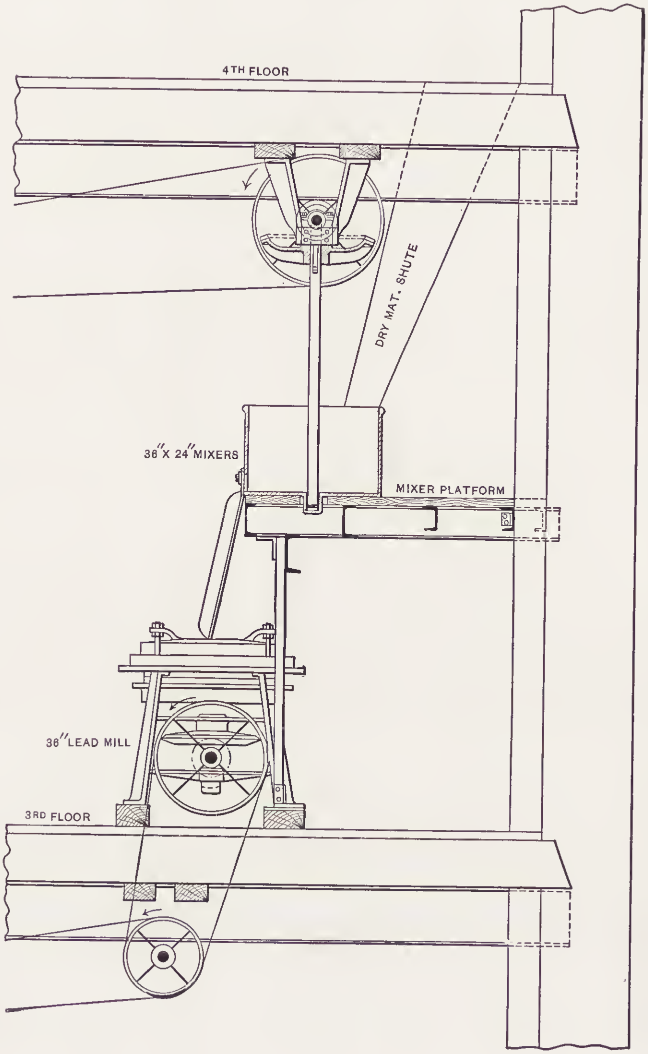



Lead Mixer
35 Revs per Min
Cooler
35 Revs per Min
30 Inch Water Cooled Mill
45 Revs per Min

matter such as chips of wood or like material from getting into the supply pipes. Fastened to the stirrer of these tanks is a wire brush which scrapes the surface of the screen in its rotation around the tank, thus keeping the holes of the screen free for the proper flow of the liquid. The tinting colors used in this process are usually ground through small stone mills of 15 in. or 20 in. diameter, and are stored in convenient portable receptacles.

This method of liquid paint-making reduces the handling and labor cost to a minimum, the hardest work being done on the mixer platform where the dry pigment and the proper amount of liquid are first mixed. In a factory where the floors are not arranged so that the method already described can be carried through by gravity alone, it is possible and practicable to introduce a force pump, preferably of the rotary type, to make up for this deficiency. When this latter method is used, the cast-iron mixer and mill should remain in the same relative position as before, but the storage tank could be placed in any other part of a building and on the same floor as the liquid mill, but high enough to discharge by gravity into the tinting mixers. The ground pigment would then be discharged into a small tank situated at the foot of the mill, to which the rotary pump is attached. As this tank is filled with the ground product, the pump would force it through the proper pipe connection to the storage tank, the connection from the storage tanks to the tinting mixers being the same as in the first described process.

The other method in use is to mix and grind the pigment in paste form, using the same style of mixer; but instead of a liquid mill a paste mill is used. Situated at the back of this paste mill, and close to the discharge scraper, is a steel tank of generous dimensions (usually


4TH FLOOR
DRY MAT. SHUTE
36" X 24" MIXERS
MIXER PLATFORM
36" LEAD MILL
3RD FLOOR

500 gallons), into which the ground pigment is discharged. This steel tank is provided with a stirrer for mixing the ground pigment with the oil and other thinners that are added to it, in order to reduce it to a liquid form. It is then carried to the tinting tanks by a pipe-line on the same general plan as that heretofore described.

One of the advantages of this plan is that this outfit can be used in a dual capacity, i.e. it can be used for the mixing of liquid paints after the plan described and, by changing the scraper from the back to the front of the mill, the outfit can be changed into a paste-grinding plant.

THE PIGMENTS

CHAPTER II

THE WHITE PIGMENTS

THE white opaque pigments used in making mixed paints are white lead, zinc oxid, sublimed white lead, leaded zincs, lithopone, and other zinc and lead pigments.

Among the white leads there are several varieties; the principal ones, however, are the old Dutch process lead and the quick process lead, both of which are hydrated carbonates of lead.

There are many varieties of zinc oxid made in the United States, depending largely upon the raw material. The grade made principally from spelter, according to the French process, is known in America as "Florence Red" and "Green Seal Zinc." The seals on zinc indicate the whiteness of color, the green seal being the whiter. In Germany the colored seals extend to a greater range than in America, the green seal being the whitest, the red next, the blue next, the yellow next, and then the white.

The New Jersey zinc oxids are made direct from the ore and are almost as pure as the zincs made from the metal, but they have a totally different tone, being much more of a cream color than the so-called French zincs.

The Mineral Point zincs made in Wisconsin contain a varying percentage of sulphate of lead. The leaded zincs of Missouri are analogous in composition to those of Mineral Point, but the percentage of sulphate of lead is much higher.

The standard zinc lead white of Colorado contains 50 per cent oxid of zinc and 50 per cent sulphate of lead. Sublimed white lead is made in Joplin, Missouri, from Galena mineral, and will average 95 per cent oxysulphate of lead and 5 per cent zinc oxid. This material has been largely superseded by a white known as Ozark White, which is described under that heading.

Lithopone is a double precipitate of sulphide of zinc and sulphate of barium.

These are the opaque white pigments used in the manufacture of mixed paints. It is not within the power of any man to say which one of these is the best, because under certain circumstances one material will outrank another, and long practice has demonstrated that no single white pigment material is as good as a mixture of various white pigments for mixed paint. The differences of opinion and conflicting reports that one hears concerning these raw materials are largely due to competition among manufacturers. Whenever a new material is exploited a manufacturer of a tried and staple pigment naturally finds the defects in the new material and informs his salesmen to this effect. And so when a material finally succeeds and takes its place among the recognized list of pigments it has gone through all the hardships and vicissitudes possible.

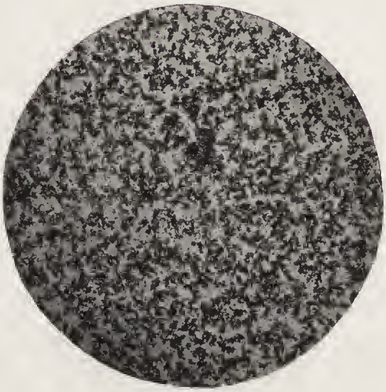
For two thousand years, more or less, there was no other white pigment than white lead. Within the lifetime and memory of many a paint manufacturer in the United States all the pigments described in the beginning of this chapter have been born and have prospered. The great competitor of white lead is zinc oxid, and the weakness of white lead is the strength of zinc oxid, and vice versa. White lead, for instance, is a soft drier and zinc oxid is a hard drier. White lead finally becomes powdery; zinc oxid in its eventual drying becomes hard, and it is for these reasons that a mixture of zinc oxid and white lead forms such a good combination. On the other hand, it is regarded as a fact that a paint composed of an opaque white pigment in a pure or undiluted state should not be used, for experience and chemistry have both shown that an inert extender added in moderate proportions to the solid white pigment increases its wearing power, and when the surface finally needs repainting it presents a better foundation for future work. Taking all of these facts into consideration, a paint manufacturer who combines experience with the teaching of chemistry is quite likely to produce a material that will add both to his reputation and his income. He certainly has a great advantage over the man who works entirely by rule of thumb.

WHITE LEAD

Formula, $2PbCO_3 \cdot Pb(OH)_2$; Specific Gravity, 6.323 to 6.492

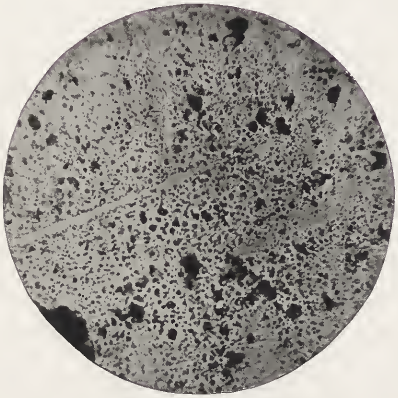
White lead is the oldest of all white paints, and prior to the middle of the last century it was the only white pigment in use with the exception of a little zinc and bismuth. Within half a century quite a number of other white pigments have come into use, and only gradually have the defects of white lead become known. However, paint manufacturers in the United States are very large users of dry white lead, which, together with zinc, asbestine, and other inert materials, forms the bases or pigments of the mixed paints. There seems to be an antagonism against the use of white lead which apparently is unfounded, for, although white lead may have its defects, there is no other white pigment which is 100 per cent perfect, and therefore it is only fair to give that time-honored material its proper due. White lead as a priming coat on wood, particularly when it contains more oil than should normally be used, cannot be excelled.

The history of this pigment, its method of manufacture, and the general uses to which it has been applied are so well known, and are generally given even in elementary text-books on chemistry, that it is not the author's purpose to take up much space for this subject. Briefly stated, however, there are two processes for the manufacture of white lead. One is called the Dutch process, which takes about ninety days and is a slow corrosion of a buckle of lead in an earthenware pot in the presence of acetic acid. Carbonic acid from fermenting tan bark acts on the lead, converting the material into hydrated carbonate of lead. In the other, which is called the quick process, the acetic acid solution is directly acted upon by either carbonic acid gas or an alkaline carbonate salt. The old Dutch process is still much more largely used than the quick process, the resulting product being much more desirable from the practical standpoint. There are a number of other processes under a variety of names, but none of them differ very much from the so-called "quick process."



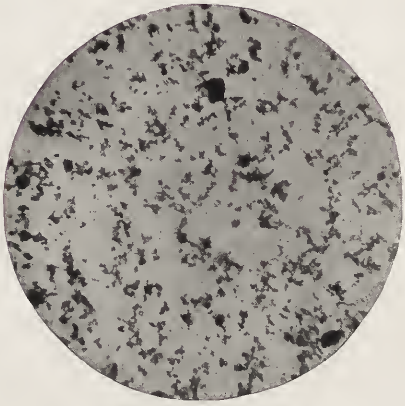
No. 1. CORRODED WHITE LEAD — Photomicrograph ×250, of known purity and composition.

White lead is in great favor with the practical painter, not for its wearing quality, but principally for the freedom with which it is applied. Although white lead is generally spoken of as a carbonate of lead, it is composed of approximately 69 per cent carbonate of lead, $PbCO_3$, and 31 per cent of lead hydroxid, $Pb(OH)_2$. It is this lead hydroxid which combines quite rapidly with oil and forms an unctuous substance sometimes known as "lead soap." White lead is variable in composition, the amount of hydroxid ranging from 15 to 30 per cent. In addition to this, during the process of manufacture of the old process lead, and after its final washing, it is mixed with linseed oil while still in the wet state. The oil having a greater affinity for the white lead than the water has, the latter is displaced. A small percentage of moisture adds to the free working quality of the paint made from white lead. (See "Water in the Composition of Mixed Paints," page 255.)



No. 2. Old Process White Lead — Photomicrograph ×250.

White lead is regarded as a poisonous pigment, and so it is, but this property should not condemn it for application to the walls of a house or for general paint purposes, because its toxic effect cannot be produced from a painted surface. Its poisonous quality is manifest to the workmen in the factories where white lead is made, and also to the painter who is careless in applying it. The unbroken skin does not absorb lead very rapidly, but the workman inhaling lead dust, or the painter who allows a lead paint to accumulate under his finger nails, is likely to suffer from lead poisoning. In one or two factories where much white lead is ground, a small percentage of potassium iodide is placed in the drinking water. This overcomes any tendency toward lead poisoning, by reason of the fact that the soluble iodide of lead is formed in the system and the lead is thus flushed out through the kidneys. Charles Dickens, in one of his short stories called "A Bright Star in the East," comments on the misery produced in a certain white lead factory in London, and expressed the hope that American ingenuity would overcome the dangers which beset the men. In one of the largest white lead works in New York City lead poisoning does not occur, owing to the ingenuity and care exercised by the management.



No. 3. WHITE LEAD (new process) — Photomicrograph ×250.

The ratio of oil necessary to reduce white lead to the consistency of paint can by no means be given in exact figures. The old Dutch process lead will take four and a half gallons of linseed oil to one hundred pounds of white lead ground in oil, in order to obtain a paint of maximum covering property. The new process lead will take more oil than this, and in many instances up to six gallons to the one hundred pounds of white lead paste, which contains approximately $1\frac{1}{10}$ gallons of linseed oil. On a mixed paint basis, 60 pounds of dry white lead will take 40 pounds of linseed oil to produce the correct ratio, but in addition four pounds of volatile thinner, such as benzine or turpentine, can be added to increase the fluidity and assist in the obliteration of brush marks. No general rule can be given for the percentage of oil necessary, as temperature has much to do with this, but the difference in the amount of oil necessary to produce a good flowing paint during summer or winter can be approximately given as 10 per cent, less vehicle being necessary in summer than in winter.

White lead when exposed to the elements becomes chalky after a while and assumes a perfectly flat appearance which resembles whitewash, and comes off very readily on the hand. As long as there was no remedy for this there was no comment on the subject, but at the present time investigators have improved paint mixtures so that this defect is not so palpable as it was in former years. From many experiments made by the author the causes of the chalking of white lead may be summarized as follows:

First. The action of the carbonic acid in rain water.

Second. The action of sodium chloride (salt in the air).

Third. The catalytic action of white lead itself in being a progressive oxidizer of linseed oil.

First. If white lead be treated with water containing carbonic acid, it is found that the same solvent action takes place upon carbonate of lead as takes place upon calcium carbonate.

Second. If white lead be treated with a sodium or ammonium chloride solution, a solvent action is apparent, and as sodium chloride is always present in the air at the seashore, and carbonic acid is everywhere present in the atmosphere and is readily taken up in a rain storm, the chalking of white lead can be attributed to these causes.

Third. This cause is, however, problematical and cannot at this writing be stated with any degree of positiveness. It is quite true that white lead and linseed oil do not attack each other so readily on an interior wall as they do on a wall exposed to the elements.

One of the defects mentioned by many writers on white lead is its susceptibility to sulphur gases. In nature these sulphur gases are generated in two places; namely, in the kitchen of every house, and in and around stables and outhouses. In kitchens the cooking of vegetables liberates hydrogen sulphide to a great extent, the odor of which is familiar to everybody who comes into a house where either cauliflower or cabbage is being cooked. But, inasmuch as undiluted white lead is not often used for interior painting, the defect is not so noticeable. A few stables or outhouses are painted pure white, and when they are painted white the painter generally has sufficient knowledge of the subject to use zinc oxid instead of white lead.

It cannot be denied that the ease of application of white lead, as well as its enormous covering property, has had much to do with the preference for it as a paint. With the exception of lithopone, it has a greater hiding property, volumetrically considered, than any other white paint; on the other hand, gravimetrically considered, it has less body than any of the lighter paints.

The addition of an inert filler, such as artificial barium sulphate, silica, and barytes, improves white lead considerably. These inert fillers, which will be considered under their proper chapters, are not affected by chemical influences in the slightest degree, and where they are used in the proper proportions additional wearing quality, or "life," as the painter calls it, is given to the paint. The percentage of inert fillers which can be added to white lead varies up to 50 per cent. More artificial barium sulphate than natural barium sulphate can be added. If a comparative exposure test be made, both on wood and metal, of undiluted white lead and white lead containing an inert extender, it will be found that at the end of eighteen months the paint which contained the filler is in a better state of preservation than that which did not contain it. Generally considered, white lead is an excellent paint, more particularly when added to other materials.

Sulphate of Lead

Formula, $PbSO_4$; Specific Gravity, 6.2 to 6.38

It must be borne in mind that the sulphate of lead of commerce, which is not so frequently met with nowadays as formerly, is a very poor paint material, and it must not by any means be confounded with sublimed white lead, which is at times erroneously called lead sulphate.

The lead sulphate of the paint trade is a nondescript article which was sold as a by-product by the textile printers who used acetate of lead as a mordant, and to this liquid sulphuric acid was added and the precipitate was sold to the paint trade under the name of lead bottoms or bottom salts. Occasionally this material is still met with, and wherever it is used in a mixed paint it does more harm than good. It is likely that the pure neutral lead sulphate, which is a good oxidizing agent, dries well, and covers fairly well, could be used for ordinary light tints if diluted with the proper inert materials, but the lead sulphate which is sold by the textile printers is always acid and is sometimes coarse and crystalline, though at other times quite fine. The chemist, the paint maker, and the engineer must never confound this lead sulphate with the lead sulphate contained in sublimed lead, zinc lead, or leaded zincs.

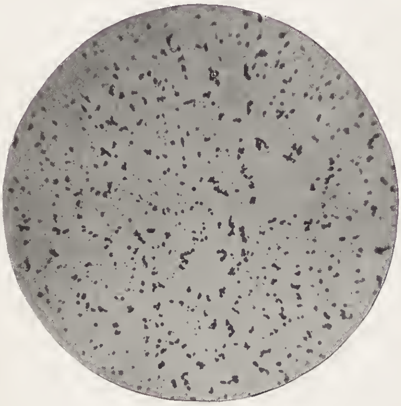
Sublimed White Lead

Specific Gravity, 6.2

Sublimed white lead is an amorphous white pigment possessing excellent covering and hiding power, and is very uniform and fine in grain. It is a direct furnace-product obtained by the sublimation of Galena, and within the last ten years it has come into great prominence among paint makers, now being regarded as a stable, uniform, and very valuable paint pigment. The author has examined a great many paints containing sublimed lead. Among one hundred reputable paint manufacturers in the United States sixty-five used sublimed lead. About eight thousand tons were used in the United States in 1905. Considering the fact that sublimed lead as a pigment is about twenty-five years old, it is very likely, judging from its qualities, that it will be used more universally and in larger quantities in the future.

When mixed with other pigments, such as zinc oxid, carbonate of lead, and the proper reducing materials added, such as silica, clay, barium sulphate, etc., it produces a most excellent paint, and at the seashore its wearing quality is superior to that of carbonate of lead. In composition it is fairly uniform. From the analyses of thirty-four samples of sublimed lead its composition may be quoted as 75 per cent lead sulphate, 20 per cent lead oxid, and 5 per cent zinc oxid, although each of these figures will vary slightly either way. Corroded white lead also varies in its percentage of hydroxid, but for analytical purposes a constant must be admitted which will fairly represent the composition.

The question has arisen of late years whether sublimed lead is a mixture of the three components just cited, or whether it is a combination of lead sulphate and lead oxid with the mechanical addition of zinc oxid. Inasmuch as all the lead oxids that are known in commerce or in chemistry are yellow, red, or brown it is held by many that the lead oxid of sublimed lead is really an oxysulphate, or, in other words, a basic sulphate of lead. A mixture of precipitated lead sulphate, litharge, and zinc white in approximately the proportions found in sublimed lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed lead when ground in raw linseed oil takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for repainting in twelve hours, because lead sulphate is a fair drier and lead oxid a powerful one. Yet the oxysulphate, having the same composition, behaves totally differently from the mixture and in addition is of a different color.



No. 4. Sublimed White Lead — Photomicrograph ×250, showing great uniformity of grain.

Under the microscope sublimed lead shows the absence of crystals and remarkable uniformity of grain. Being a much more inert chemical body than the other lead paints, it does not react on linseed oil, and therefore makes a much more durable paint compound. It has been urged that sublimed lead is not as susceptible to sulphur gases as white lead, but this the author has not been able to substantiate, for while it may take hydrogen sulphide a longer time to discolor it, it is simply a question of degree and it is acted upon by sulphur gases, although not as quickly as white lead.

Sublimed lead can be determined in a white mixed paint without any difficulty, owing to the established ratio between lead oxid and lead sulphate. The percentage of free zinc sulphate in sublimed white lead varies from a trace to a half per cent, and many times a chemist will report more zinc sulphate than is actually present, because in washing or boiling a dry or extracted sample the lead sulphate may interact with the zinc oxid and show a larger percentage of zinc sulphate than is really present in the dry products before analysis.

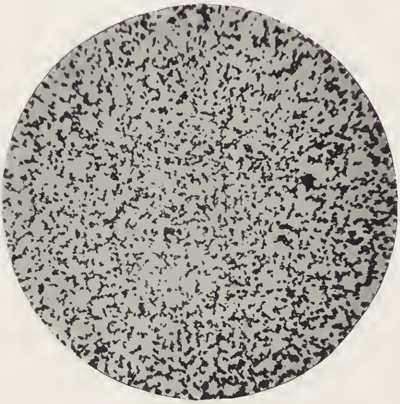
Sublimed white lead as a marine or ship paint is of much value, owing to its hardness of drying and imperviousness of film.

Standard Zinc Lead White

The ores utilized in the manufacture of this material are what are known in mining parlance as "Low Grade Complex Ore," originating in and about Leadville, Colorado; Low Grade, inasmuch as the gold, silver, and copper are present in quantities too small to warrant the excessive cost of refining. Naturally this ore contains varying percentages of zinc blende or sphalerite and Galena or native lead sulphide, and in order to furnish the product with the proper proportions of lead and zinc the ores are first analyzed, then mixed in their proper proportions, and volatilized at a heat of from 2200 to 2500° F. In the volatile state it is carried to the combustion chamber, where the chemical transformation of the product, due to oxidation, completes itself. The white fume is collected in woolen bags, further oxidized on open-hearth furnaces, whitened, and then bolted.

The pigment carries approximately 50 per cent pure zinc oxid and 50 per cent lead sulphate, which have combined at an intense heat in vapor form, the union being far more intimate than anything that could be obtained by mechanical means.

This pigment was first put upon the market twenty-four years ago, and had been popular in the mixed paint trade for a period not exceeding ten years, and within the last eight or ten years it had become more uniform and was regarded as a valuable paint material by a great many mixed paint manufacturers. However, this material is at present not manufactured, but has been largely superseded by a white known as Ozark White, which will be described under that heading.



No. 5. Standard Zinc Lead White — Photomicrograph ×250.

The color, while it is not as white as zinc oxid, is about the same shade as the average corroded white lead. The pigment can be used to great advantage in combination leads, graded leads, primers, floor paints, and ready mixed paints. Its specific gravity is approximately 5.5, and its composition theoretically 50 per cent pure zinc oxid and 50 per cent lead sulphate. The pigment generally contains a trace of silica, iron, and alumina. A very small portion of the lead is in the form of a basic lead sulphate, and the pigment undoubtedly takes up a little moisture on standing. Its average analysis shows the following composition:

$PbSO_4$	50.00 per cent
ZnO	49.55 per cent
$ZnSO_4$	0.40 per cent

The percentage of zinc sulphate will vary slightly, but under normal conditions it will seldom average higher than ½ of 1 per cent, and where it does average more than this it is frequently due to long-continued boiling in the flask, which causes a reaction between lead sulphate and zinc oxid.

Analyses of Standard Zinc Lead White

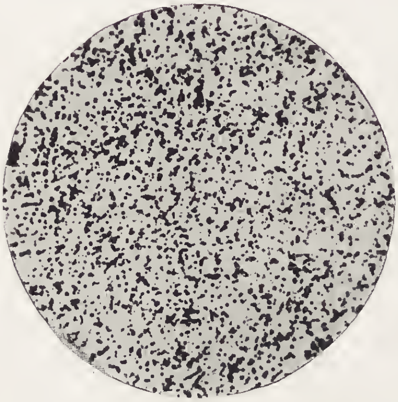
$PbSO_4$	48.90	50.00	49.22	49.80	50.15	48.87
ZnO	50.50	49.55	50.41	49.90	49.25	50.82
$ZnSO_4$	0.25	0.40	Trace	0.20	0.12	Trace

Photomicrographs of zinc lead show a uniformity of grain, and microscopic investigations fail to show anything but a homogeneous product. It is very stable. When exposed to the air in a thin film, mixed with a proper proportion of linseed oil and drier, it retains its gloss longer and chalks less than a similar film containing a mixture of 50 per cent corroded white lead and 50 per cent zinc oxid. Like white lead, it whitens on exposure, but holds up in suspension better, as indicated by its low specific gravity. When a paint is made on a zinc lead base ground in pure linseed oil it will not separate, form a cake, or yield a sediment; neither will it peel, chalk off, or turn yellow.

OZARK WHITE

Ozark White is a very desirable pigment and has all of the good qualities of Standard Zinc Lead White and

Sublimed White Lead. It is very largely used in the manufacture of mixed paint. In many respects it is superior to the old Standard Zinc Lead White, because its approximate composition is 60 per cent of zinc oxid and 40 per cent of lead sulphate.



No. 6. Ozark White—Photomicrograph ×300.

The process is so highly perfected that the manufacturers can control the composition so as to insure a variation of not over 2 per cent, and with rare exceptions the material does not vary 1 per cent from the composition given. To attain this degree of uniformity, a complete analysis of every car of ore is made as soon as it is received before passing it to the mechanical mixers. At the mixers another analysis is made, and an ore higher in zinc or lead added, as the case may require, in order to have the proper metal constituents. The ore, after being mixed with the proper proportion of coal and antifluxing material (crushed silicious rock or mine screenings), is charged into furnaces which have previously been bedded with a sufficient amount of coal to start combustion. The furnaces are then sealed, allowing the temperature to rise to about 2300° F., at which point it is held until the zinc and lead pass off together in the form of fume, which is conducted by means of suction fans through pipe-lines for a distance of about 500 feet, where it enters large brick bag houses. The fumes have by this time lost considerable of the heat, so that they may be gathered into fabric bags, where the gases pass out and the pigment is collected. From the bag house the pigment is conveyed to an automatic packer and placed in barrels of suitable weight, and is then ready for the consumer.

An actual chemical analysis of an average type of Ozark White shows the following:

ZnO	59.32	per cent
$PbSO_4$	39.05	" "
$ZnSO_4$	0.78	" "
SO_2	0.05	" "
H_2O	0.66	" "
As_2O_3	0.12	" "
Total	99.98	per cent

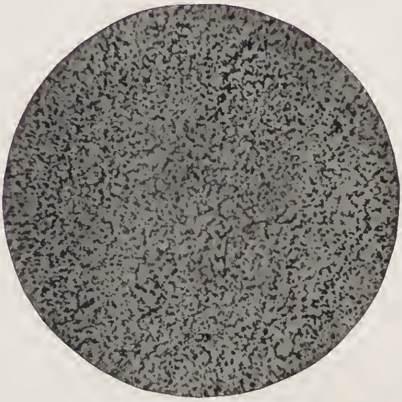
Zinc Oxid

Formula, ZnO; Specific Gravity, 5.2

Zinc oxid as a paint pigment is only sixty years old, and when it is taken into consideration that in that short space of time its use has grown until in 1905 nearly seventy thousand tons were used in the paint industry in the United States, it speaks for itself that the material must be of exceptional merit to have advanced so rapidly. At the same time, although it is impossible to obtain any exact figures on the subject, it is probable that more than one half of these seventy thousand tons was used in connection with other materials.

The discovery of zinc oxid by Le Clair in France and Samuel T. Jones in America is sufficiently well known, and has been quite thoroughly written up in other books. The former made zinc oxid by subliming the metal; the latter made it by subliming Zincite and Franklinite ores. The specific gravity of zinc oxid will average 5.2, and fifty pounds will take fifty pounds of linseed oil; in other words, to produce the proper mixed paint it will require a far greater proportion of linseed oil than white lead will take. It is generally stated in text-books that zinc oxid is not affected by sulphur gases and therefore will not turn color. This statement is not exactly correct; the author always contended that zinc oxid is not *visibly* affected by sulphur gases, but there is no doubt, as any chemist will admit, that zinc oxid is affected by sulphur gases, although not to the same extent as white lead. As zinc sulphide, zinc sulphite, and zinc sulphate are white products, the absorption is not evident to the eye, and hence the erroneous statement has crept into use that zinc oxid is not affected by sulphur gases.

When mixed with linseed oil and the proper amount of drier, it sets and dries much more slowly than white lead. Nevertheless this drying continues in the form of progressive oxidation until the surface becomes very hard. A comparison between zinc-oxid and white-lead paints will show that the progressive oxidation which takes place when white lead dries produces a chalky mixture, while the reverse is true of zinc oxid, which will produce a hard and brittle vitreous surface which is somewhat affected by temperature changes. Owing, therefore, to the diverse effects of the two pigments, a combination of lead and zinc is often well recommended. The hard drying zinc has not, however, been very well understood. Fifteen years ago the author undertook a series of experiments and found that the drier was very largely responsible for the hardening action of zinc. If the linseed oil be prepared with litharge (PbO), the resulting zinc paint will last far longer and be much more flexible and consequently not readily cracked when exposed to a variation of temperature of even 130° F., such as we have in this climate. If, however, a drier is used in which manganese (MnO_2) and red lead (Pb_3O_4) have been cooked with the oil, the action of the manganese continues until a vitreous surface is the result. It is owing to the result of these investigations that the use of American zinc oxid made from Franklinite ore has become so general for the manufacture of white table oilcloths. (See Journal of Society of Chemical Industry, No. 2, Vol. XXI, Jan. 31, 1902.)



No. 7. American Zinc Oxid — Photomicrograph ×300, very pure and very uniform in grain; this oxid is made direct from the ore.

When enamel paints are made of an oil varnish and zinc oxid, and the drier in the varnish is composed of manganese and lead, the enamels eventually become hard, evidently through the catalytic action of the manganese. It is desirable to omit the manganese in high grade enamels, or, where manganese must be used in order to obtain a rapid setting, the borate of manganese should be employed, but only in very small quantities.

The American zincs are:

First. The Florence Red and Green Seal zincs, which are made by the sublimation of the metal and are practically pure and equal in all respects to those made in France and Belgium.

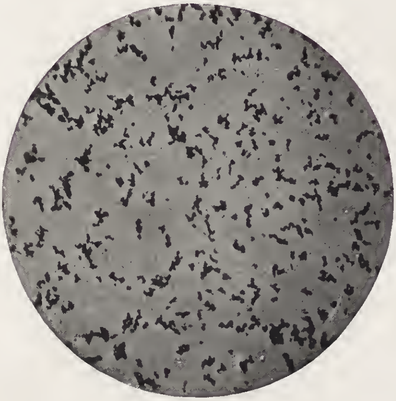
Second. The New Jersey zinc oxids, which are made from Franklinite ore and are free from lead and frequently run over 99 per cent ZnO.

Third. Mineral Point zinc, which is made at Mineral

Point, Wisconsin, and contains from 2 to 4 per cent of lead sulphate.

Fourth. The leaded zincs made in Missouri, which contain from 4 to 10 per cent of sulphate of lead.

Zinc oxid chalks to some extent in the same manner as white lead, but only if the atmosphere is charged with carbon dioxid or salt. The same experiment which was carried out with white lead in order to show its solubility in a solution of carbon dioxid was carried out with zinc oxid and the same result obtained. Much weight cannot be given to these experiments, because these chemicals are not always present in the atmosphere. They are merely chemical results which demonstrate both the cause and effect, but it is of some interest to know why the paint films perish. The zinc oxids made from western ores are slightly more permanent than those made from the New Jersey ores, and as paint materials they possess the advantage of containing a larger quantity of lead sulphate.



No. 8. French Green Seal Oxid — Photomicrograph ×300, much whiter than the American zinc made from the metal, but coarser in grain.

Nearly all zincs contain a small percentage of zinc sulphate. Much unnecessary trouble has been caused by the criticism against zinc sulphate. Where a paint contains moisture or where water is added in a very small amount to a heavy paint in order to prevent it from settling, and not more than one per cent of actual water is contained in the paint, zinc sulphate forms an excellent drier, particularly where it is desirable to make shades which contain lampblack. The outcry against zinc sulphate is unwarranted, because as much as 5 per cent is used in making a patent drier. The amount of zinc sulphate, however, in most of the dry zinc pigments probably decreases with age. Zinc oxid or other zinc paint which will assay 1 per cent of zinc sulphate will, when kept in storage for six months, show a decrease in the zinc sulphate to one half of 1 per cent.

In the enamel paints the presence of zinc sulphate is not a detriment, and in floor paints it might be considered as a slight advantage, for it aids in the drying and hardening. However, too much of the soluble salt is never to be recommended.

ZINOX

This is a hydrated oxid of zinc not manufactured in this country, but made and used almost entirely in France. It is not yet sold dry, but generally sold either in the form of a ready mixed enamel or in a semi-paste form, and is presumed to possess advantages over zinc oxid. From experiments which the author made it has been found that the hiding power and working quality are practically the same as that of zinc oxid. It possesses, therefore, no marked advantage over a zinc oxid enamel, although it is stated that it remains in suspension longer than any other pigment. The zinc oxid enamels all remain in suspension a very long time, and even though they settle they do not settle very hard and can be very easily stirred. In thinner media, such as are used for the manufacture of flat wall paints, the hydroxid of zinc has some advantage over the oxid, as it produces a paint that remains in suspension longer and is more ready for use than that made from the oxid.

LITHOPONE

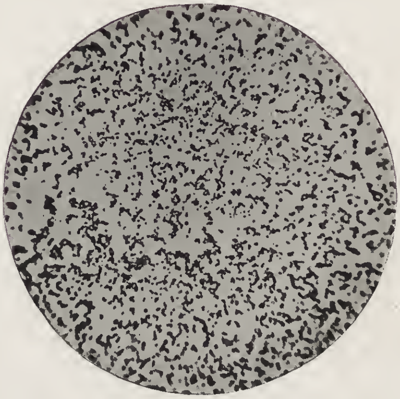
Synonym: Oleum White, Beckton White, Charlton White, Ponolith, Jersey Lily White, Orr's White

Chemical Formula, $ZnS + BaSO_4$; Specific Gravity, 4.2

When solutions of zinc sulphate and barium sulphide are mixed together in molecular proportions a heavy flocculent precipitate is formed according to the following reaction: $ZnSO_4 + Aq + BaS + Aq = ZnS + BaSO_4 + H_2O$. The theoretical percentage will be about 29½ per cent zinc sulphide and 70½ per cent barium sulphate. This precipitate as such has no body or covering power, and when washed and dried is totally unfit for paint purposes; but John B. Orr, of England, in 1880 discovered that when it is heated to dull redness, suddenly plunged into water, ground in its pulp state, thoroughly washed and dried, its characteristics are totally changed, and it makes a very effective and durable pigment for paint purposes. In the first place, it is then a brilliant white; in the second place, it is extremely fine in texture; and in the third place, it has more hiding power than pure zinc oxid. Owing to its chemical composition it is stable in every medium known for paint purposes, excepting those which are highly acid. It took several years to perfect the manufacture of lithopone, but it may be easily said that at the present time lithopone is made with great uniformity and has valuable properties, as will hereinafter be shown.

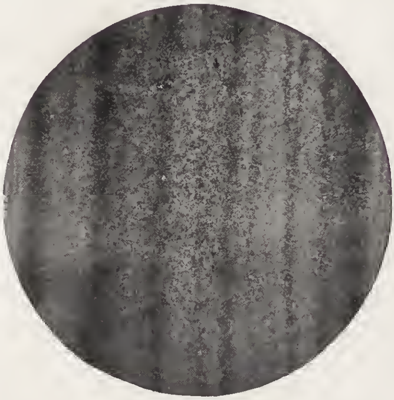
The method of manufacture is quite simple, success depending very largely on the purity of certain materials. It is worthy of mention, however, that the average chemist unfamiliar with both the theory and practice of its manufacture cannot make it successfully. In the first place, solutions of barium sulphide and zinc sulphate of known composition must be made. The fact that they are impure has no effect on the ultimate product, provided the chemist knows the impurities he has to deal with and the simple methods for their elimination. For instance, the zinc sulphate must be free from iron or a yellowish product is the result. The solutions must be standardized for each batch. The impurities can be eliminated during the process of manufacture, or, more properly speaking, before they are pumped into the precipitation tub.

The barium sulphide, however, is quite pure, for the reason that metals like copper, iron, and manganese which are likely to be present, form insoluble sulphides. Barium sulphide is made by heating barytes ($BaSO_4$) to dull redness with coal, petroleum residuum, pitch, sawdust, or other materials having a high percentage of carbon. The resulting reaction may be represented by the following equation: $BaSO_4 + 4C = BaS + 4CO$, although under many circumstances the reaction is more slightly complicated. After the reaction is completed and before the air can have any influence on the sulphide, the mass is digested in vats and filtered; when the solution reaches a density of 17°, Baumé long, yellowish, needle-shaped crystals separate from the mother liquor. These crystals are almost chemically pure barium sulphide.



No. 9. LITHOPONE (dry) — Photomicrograph ×250, exceedingly fine and uniform in grain.

With the proper concentration of the solutions, proper temperature and speed at which the two solutions are poured together, the resulting precipitate will be of such physical characteristics that it can be most easily filtered and dried. It is then placed in muffles and heated above 920° Fahrenheit, suddenly plunged into water, again ground, washed, and dried. It is then ready for the market. The overheating of the precipitate decomposes some of the zinc sulphide and converts it into zinc oxid. All of the earlier manufacturers overheated their product, and that is the reason why lithopone formerly contained from 5 to 10 per cent zinc oxid, whereas theoretically it should have contained none. The manufacturers of the present day, however, have overcome all these difficulties, so that a remarkably uniform product is obtained, the percentage of zinc oxid being small indeed.



No. 10. LITHOPONE (ground in oil) — Photomicrograph ×250, exceedingly fine grain.

We have here an excellent example, as has been stated under another chapter, of a pigment containing 70 per cent barium sulphate, which may be regarded as perfectly pure and normal, and yet twenty-five years ago any pigment containing far less barium sulphate than lithopone would have been regarded as adulterated. No man can reasonably state that barium sulphate is an adulterant to lithopone, for the obvious reason that it is a constituent part of the pigment.

Lithopone has gone through many vicissitudes; no pigment has been blackguarded quite as much as this, and yet no pigment has survived its condemnation as well as this. Almost every paint manufacturer in the United States finds some excellent use for it. Within the last seven or eight years lithopone has come into its own, and today there is no paint manufacturer in the United States, to the best of the author's knowledge, who does not use this material. Ten years ago very few paint manufacturers used it at all.

Since 1906 many chemists, including such capable men as Professor Ostwald, have attempted to find the cause of the darkening of lithopone in sunlight. When night comes a change takes place, and the following morning lithopone is as white as it ever was. This property is called the "photogenic" quality. This photogenic action goes on continually, and there have been a large number of investigators who have attempted to overcome this, and a review of the literature shows that most of the methods, with two or three exceptions, have been empirical. It has remained, however, for Professor W. D. Bancroft of Cornell University to delegate one of his students, W. J. O'Brien, to make these investigations, and the full account is recorded in Volume XIX of the Journal of Physical Chemistry, 113–44 (1915); an extract is herewith given of the phenomenon.

That the darkening in sunlight is due to the formation of zinc from zinc sulphide was shown by the fact that the dark product reduced ferric alum, as shown by the appearance of a blue color with potassium ferricyanide, and that it is readily soluble in acetic acid, in alkalies, and in solutions of sodium chloride and sodium sulphate. The zinc is a direct product of the action of light on zinc sulphide. The results of the investigation are summarized as follows: Quenching in water prevents further oxidation of the red-hot zinc sulphide. It also disintegrates the semi-fused mass and dissolves out most of the soluble salts. Heating the barium sulphate-zinc sulphide precipitate is necessary to dehydrate the zinc sulphide and to change its physical condition, so that it forms a dense mass with good body which can be ground more readily. The yellow color produced on overheating is due to an oxid film, as was shown by Farnau. The darkening of lithopone is not due to impurities such as iron, lead, cadmium, etc. The presence of salts which form soluble zinc salts, such as sodium chloride, sodium sulphate, etc., accelerates the darkening of the lithopone. These salts dissolve away the zinc oxid film. This is similar to the behavior of magnesium in water. Magnesium does not decompose water very readily at ordinary temperatures. In the presence of magnesium chloride, however, the action takes place vigorously. The presence of salts which form insoluble zinc salts, such as the alkaline phosphates, bicarbonates, ferrocyanides, and borates, retards or prevents the darkening of lithopone. The action of light on the zinc sulphide is a reducing one, hydrogen sulphide and metallic zinc being formed. The reaction is not a reversible one; the metallic zinc formed is oxidized to zinc oxid; barium sulphate is not necessary for the darkening of the zinc sulphide. Heating the zinc sulphide is not necessary to get it to darken, although heating makes the zinc sulphide more sensitive to light, probably because the reducing atmosphere and the sodium chloride used remove the zinc film more readily. The zinc oxid film can be removed by boiling in a concentrated solution of zinc chloride. The zinc sulphide so treated will darken in the presence of a reducing agent. When barium sulphate is precipitated with the zinc sulphide, it aids the darkening, due to the fact that it adsorbs the zinc sulphide, thereby giving increased surface exposure of the zinc sulphide. It probably also adsorbs the metallic zinc. The zinc sulphide will darken without the presence of a reducing agent if it is precipitated with barium sulphide and boiled in a concentrated solution of zinc chloride. The barium sulphate probably adsorbs metallic zinc as well as zinc sulphide, thus making the latter sensitive to light. The patented processes for the prevention of the darkening of lithopone depend upon the formation of an insoluble film around the zinc sulphide. It is impossible to make a lithopone that will not darken unless there is a film protection of some kind over the zinc sulphide. A lithopone of good quality that would not darken was made by producing an oxid film on the zinc sulphide and keeping the oxid content above 3 per cent and below 5 per cent. Aluminium oxid can be substituted for the zinc oxid. A film of sulphur protects to some extent; no experiments were made to determine the maximum efficiency possible.

From the above we can readily see that the theory is a tenable one, and that the action of light on zinc sulphide is a reducing one, sulphuretted hydrogen and metallic zinc being formed. Metallic zinc is again converted into zinc oxid, and the color of the metallic zinc mixed with the other bases gives the gray shade that is apparent. The manufacture of a lithopone, therefore, that would not darken, by producing an oxid film and keeping the oxid content above 3 and below 5 per cent, would have its disadvantages, for in a rosin varnish or an acid resin varnish livering would eventually take place, and one of the principal features of lithopone has been that an acid resin or rosin varnish could be used and no chemical reaction would take place.

The large use of lithopone today is for flat wall paints, for it can be mixed with the China wood oil-rosin varnishes without the danger of livering or hardening, and it has every advantage as far as hiding power and freedom from mechanical defects that white lead and zinc oxid have, with the added advantage of being non-poisonous (although the danger of using a poisonous material on a wall is largely overestimated). Lithopone is likewise very largely used in the cheaper grades of enamel paints.

As an interior white, a first coat white, or as a pigment in the lighter shades for floor paints, lithopone cannot be excelled for its body, durability, hardness, fineness of grain, and ease of application. It does not oxidize progressively, and this single feature has made it invaluable to the table oilcloth and floor oilcloth industry throughout the world. Its indiscriminate use, however, is not to be recommended, and the paint chemist should be permitted to decide when its value is the greatest. As a marine interior paint, either as a first coat or for making neutral paints where other whites would be necessary, it is found to outlast both zinc oxid and lead carbonate.

CHAPTER III

THE OXIDS OF LEAD

THE oxids of lead used in making mixed paints are principally litharge, which is PbO, and red lead or orange mineral, Pb_3O_4.

LITHARGE

Chemical Formula, PbO; Specific Gravity, 9.2 to 9.5

Litharge is the first oxid of lead; that is to say, when lead is melted and heated in a current of air the first oxid produced is the PbO, yellow in color, and known as litharge. Very pure litharge has the color of pale ochre.

Litharge in the manufacture of preservative paints has excellent protective qualities, because it is basic and resists corrosion. Furthermore, litharge and linseed oil make a very hard cementitious film which withstands abrasion, but unfortunately litharge combines with linseed oil so rapidly that when used in mixed paints to any great extent it tends to "liver" and saponify. On the other hand, a number of black paints which are composed of lampblack, carbon black, charcoal, or a mixture of these, are held together by the use of litharge, and where these paints are used within a month or two after they are made they serve their purpose perfectly.

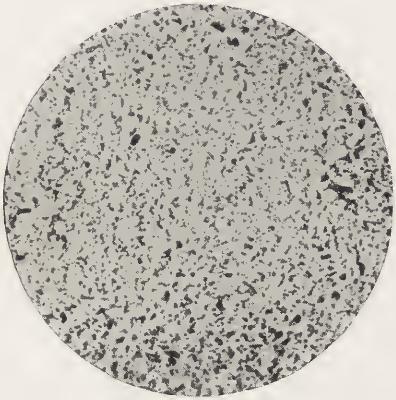
Litharge is soluble in acetic acid, and the other impurities in it are generally insoluble, so that a very rapid test can be made from the paint manufacturer's point of view by simply boiling in acetic acid. Litharge varies in texture under the microscope, as is shown in the accompanying photomicrographs.

Flake litharge is generally used by varnish makers or oil boilers for making drying oil, but the more finely powdered forms of litharge have a peculiar construction, and when the litharge is impure and contains metallic lead and red lead it is distinctly noticeable under the microscope.

RED LEAD

Chemical Formula, Pb_3O_4; Specific Gravity, 9.0

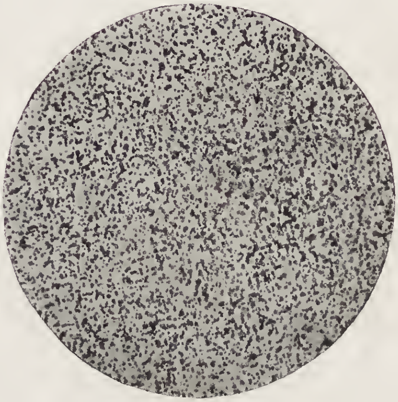
Red lead is a very heavy orange-red pigment, more or less crystalline in structure. It is prepared by heating litharge to a temperature of 600° to 700° F.



No. 11. LITHARGE—Photomicrograph ×100.

Owing to the conditions under which it is made it contains from a trace to an appreciable percentage of litharge (PbO), and when used for paint purposes it cannot be said that a small content of litharge does any harm. When prepared in linseed oil it must be freshly used, otherwise it forms a distinct combination with linseed oil and becomes hard and unfit for use. In its physical characteristics it can be compared with plaster of paris. It acts very much like plaster of paris when mixed with water. Once set, it may be reground and will never set again. Its use as a priming coat for structural steel has been enormous, but engineers who have studied the subject have come to the conclusion that there are other materials just as good, or better, which are easier to apply and do not possess the characteristic difficulties of application. The author has made many investigations on this subject, and for further detail would refer the reader to the Journal of the Society of Chemical Industry, Vol. XXI, January, 1902, and Vol. XXIV, May, 1905.

There are some manufacturers in the United States who make red lead from litharge and use nitrite of soda as an oxidizing material, and in the manufacture of this type of red lead carelessness in manufacture will result in a fairly large percentage of caustic soda remaining in the red lead. Caustic soda finds its way frequently into litharge when it is made by what is known as the nitrate process, in which nitrate of soda and metallic lead are fused together, yielding an oxid of lead, PbO, and nitrite of soda, $NaNO_2$.[1] Red lead manufactured by this process will usually contain a small amount of caustic soda and nitrite of soda, and such red lead, although otherwise pure, makes a very poor paint, because the caustic soda saponifies the linseed oil, and exposure to weather of a few months will turn the red lead white or pinkish white and make it very soluble in rain water. Rust is also rapidly produced under such red lead, and therefore in specifying red lead it is well for the engineer to insert a clause that an aqueous mixture of red lead shall show no reaction with phenolphthalein.



No. 12. LITHARGE—Photomicrograph ×300.

Within the last five years a great improvement has been made in the manufacture of red lead, and this

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[1] See Holly's "Analysis of Paint and Varnish," p. 221.

improved form has been known as Dutch Boy Red Lead, which is practically a chemically pure Pb_3O_4. Pure red lead was the one material which had never been sold either ground in oil or ready for use, owing to the fact that the large content of litharge combined with the fatty acid of the oil and the glycerine and formed a lead soap. It is well known that litharge cement, used for many purposes around a factory, is litharge and glycerine, which sets up hard within an hour and forms a vitreous product. It is also well known that when linseed oil is neutralized with caustic soda, and the resulting linoleate of soda soap filtered out, a ready mixed or semi-paste red lead can be made which will remain soft for many months, but the proprietary brand of red lead just referred to manufactured by the National Lead Company, is a pure red lead similar in composition to orange mineral, which remains soft and produces a paint that has many advantages over the old-fashioned red lead.

Many engineers and shipbuilders prefer to use dry red lead, and a proper specification for dry red lead should be one that will contain the minimum amount of litharge.

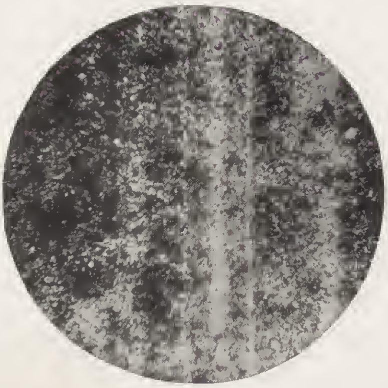
It cannot be denied that red lead is one of the best priming materials that we have, but under no circumstances should less than 28 lbs. of dry red lead be mixed with one gallon of linseed oil. Many of the bad effects and failures of red lead are not due to the lead itself, but to bad application and insufficient dry materials. As a matter of fact, the best results with red lead are obtained (in the author's experience) by using 33 lbs. and one gallon of linseed oil. To this oil may be added one half pint of any good Japan drier.

As a priming coat red lead possesses excellent preservative qualities, providing it be properly applied within a reasonable time. If red lead be used in the proportion of 17 lbs. to one gallon of linseed oil it forms a very poor coating on account of the separation of the pigment from the oil, particularly on a vertical surface. In a pamphlet published by a manufacturer a large number of precautions were given to the consumer for the preparation of red lead as a priming coat, the neglect of any one of which might produce failure for the paint. As a prominent engineer remarked, he did not care to specify a paint in which there were seventeen chances of its failure due to a possible fallibility of human nature. The use of a dry pigment mixed with oil and applied within one hour of its mixture is contrary to the progress of the present day, when paints finely ground by machinery are taking the place of all others. A dry pigment stirred by hand in a pail of oil carries with it a large number of air bubbles which become encysted and carry oxygen and other gases to the surface to be protected. The engineer should, therefore, not specify that a paint be made entirely of red lead and linseed oil and sent ready for use to the place of application when such specifications cannot be reasonably executed. On the other hand, where red lead is specified the engineer or paint manufacturer who can supply a material containing between 40 and 50 per cent red lead and 50 and 60 per cent inert base is delivering a far better article,

No. 13. French Orange Mineral — Photomicrograph ×250, not very uniform in grain.

which can be more easily applied than the undiluted red lead alone.

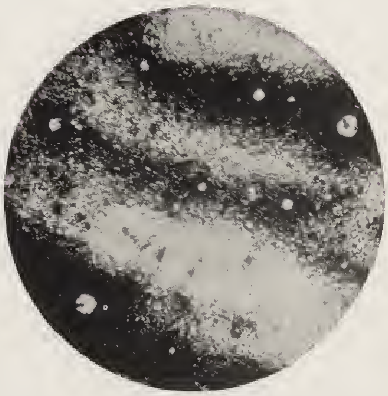
The author made a large number of experiments on red lead mixed with linseed oil containing a small percentage of drier, applying these mixtures to steel. The mixture was first applied the moment it was thinned, and then at short intervals, up to the moment the red lead began to combine with linseed oil so as to make it impossible to handle the brush. The results of the experiment showed that freshly applied red lead was not as good as it was if applied one hour after it was mixed. The paint with which these experiments were made contained 24 lbs. red lead to one gallon of paint, which is approximately equal to 33 lbs. dry red lead to one gallon of oil. The difficulty in handling paint of this kind is very great, owing to the excessive weight of the paint as carried by the brush. Structural iron painters all complain that muscular fatigue ensues where undiluted red lead is used, and when the inspector is not watching they will surreptitiously add an excessive quantity of oil, or volatile thinner, in order to lighten their labor, and for this reason red lead has frequently failed, when as a matter of fact it would have proved a perfect success had the original specifications been adhered to. On the other hand, there should be no need of using a protective paint involving such great difficulties when there are dozens of others



No. 14. Red Lead — Photomicrograph ×200 of paint film freshly applied, showing separation of the pigment from the oil.

that are as good, not only from the standpoint of protective influence but also on account of the ease of mechanical application.

It has been mentioned by many writers that one of the serious defects of red lead is the ease with which it is attacked by sulphur gases, but this objection does not hold good where it is properly and quickly coated over with a protective coat of the bituminous class. That red lead in its pure or concentrated state is not as good as a paint containing a solid diluent has been shown time and again where silica, lampblack, graphite, silicate of alumina, and such lighter pigments were mixed with it. Its extraordinarily high specific gravity is very much against its use as a paint, but if a mixture of one pound red lead and one pound wood black is taken the average specific gravity of the two is equal to that of zinc oxid. Its spreading and lasting power is increased, so that a mixture of this kind is equal to a mixture of any of the good prepared paints for structural steel. Two large exposure tests made by the author in 1899 and examined in 1905 showed that a mixture of 50 per cent red lead and 50 per cent graphite ground fine and mixed in a pure linseed oil containing 5 per cent of lead drier wore almost as well as a mixture of 75 per cent Fe_2O_3 (ferric oxid), 20 per cent silica, and 5 per cent calcium carbonate. The former paint, when the hand was rubbed over it,



No. 15. Red Lead — Photomicrograph ×150, applied one hour after mixing, showing separation and air bells encysted in film.

showed slightly more destruction of the oil, the graphite giving a stove polish effect on the hand. The latter paint also showed a very slight stain on the hand, but not quite as marked as the former. The metal underneath both was in a good state of preservation, three coats of paint having been applied. The exposure was made on a slanting roof in New York City.

Red lead has had the great advantage of having been the first protective paint ever used, for years no better paint being known. In this respect it is analogous to white lead. Much of the good reputation of white lead is due to the fact that for centuries there was no other white paint, consequently no comparison could be made. It must be borne in mind that all these experimental researches concerning red lead are based on very fine red lead, and no consideration is given to the detrimental reports concerning red lead due to the fact that it was improperly made and coarse.

A laboratory test of red lead always shows up remarkably well. A steel saucer painted with red lead in the laboratory will demonstrate that this pigment is superior to many others, but a field test of material made according to a laboratory formula and applied on several tons of steel will generally show the opposite, for the obvious reason that in the laboratory a small test is usually carefully applied and little exertion is necessary, either with the mixing of material or for its application. The temperature conditions of the laboratory being normal, the person who mixes the paint usually scrutinizes the result carefully. On the other hand, in the field or at the shop a brush is used which will do the greatest amount of covering with the least amount of exertion. The mixture may not be made by the best possible formula, and, if it is, more thinning material is generally added until it works freely. The vertical part of the surface will, on account of its position, be more difficult to cover, and the paint will sag or run from it; whereas, the flat plate or saucer-shaped cup used in the laboratory holds the material in place by virtue of its position.

Blue Lead

In the sublimation of Galena a peculiar sulphide of lead is produced, which has been known commercially as blue lead, on account of its blue-gray appearance. This product has been on the market for several years. The contention is that sulphur fumes do not affect it as they affect red lead. As a priming coat it has been well spoken of. Its composition is as follows:

Carbon	2.25	1.73
Lead Sulphate	52.92	49.79
Lead Sulphite	.36	1.44
Lead Sulphide	4.55	4.93
Lead Oxid	37.48	41.34
Zinc Oxid	2.45	1.00
	100.01	100.23

No truly representative analysis of this material can be given, owing to the variation in the amount of sulphate, sulphite, and sulphide. The material is not very fine; in fact, it contains an appreciable amount of grit, which, however, is removed in the second grinding.

The pigment is not permanent to light, but in all probability this change in its tone is due to a chemical rather than to a physical decomposition.

CHAPTER IV

THE RED PIGMENTS

THE red pigments used in the manufacture of mixed paints are principally the oxids of iron, the red oxids of lead, and the permanent vermilions. No space will be devoted to the sulphide of mercury (quicksilver vermilions), as the use of these materials has been superseded entirely by aniline or para-nitraniline vermilion. Likewise no attention will be paid to the sulphide of antimony reds, as they are obsolete in paint manufacturing.

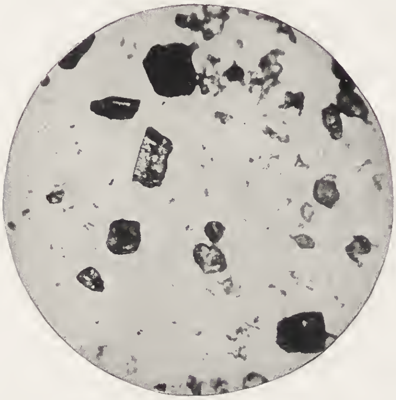
Among all the red pigments in the paint industry the oxids of iron take the lead as by far the most useful. Several years ago the author called attention to the fact that various forms of ferric oxid having the formula Fe_2O_3 could be used as rubber pigments. The sulphur used in the vulcanizing of rubber had no effect on the ferric oxid, no sulphide of iron being formed in the combination. On investigation it was found that some forms of ferric oxid are remarkably stable in composition, acting in many regards like a spinel. Exhaustive tests made with some of the ferric oxids used as paints for the protection of steel and iron show that they are far superior to red lead and to graphite as paint protectives, being midway between the two in specific gravity. A mixture of graphite and ferric oxid (containing 75 per cent Fe_2O_3 and 25 per cent silica) outlasted graphite by two years and red lead by three years. These tests were made on horizontal roofs, and eliminating the question of the cost of the paints, the ferric oxid stood the test and was the cheapest in the end. No argument can be adduced that ferric oxid is a carrier of oxygen, for it is a complete chemical compound, is not readily acted upon by dilute acids, not affected by alkalis nor by sulphur gases, and as a paint the author has not been able to demonstrate that it reacts on linseed oil.

All of these arguments refer, of course, to a ferric oxid of known purity and definite composition either as pure Fe_2O_3 or as Fe_2O_3 containing 25 per cent of silica. In the course of its manufacture from the waste products of wire mills, for instance, or direct from ferrous sulphate, the processes being analogous, there is a likelihood that a small percentage of free sulphuric acid may cling mechanically to the substance. A good sample boiled with water and tested with methyl orange will demonstrate this defect. It is wise, therefore, under all circumstances to add up to 5 per cent calcium carbonate in any or all of these ferric oxid paints. There is, however, another ferric oxid made from Persian ore. Over one hundred analyses of this ore in the laboratory of the author have shown that its composition will not vary more than 2 per cent either way, it being 75 per cent Fe_2O_3 and 25 per cent SiO_2.

VENETIAN REDS

Venetian reds have sometimes been described as burnt ochres, but this definition of the Venetian reds is incorrect. The generally accepted composition of the Venetian red is a combination of ferric oxid and calcium sulphate, in which the ferric oxid will run from 20 to 40 per cent, and the calcium sulphate from 60 to 80 per cent. When ferrous sulphate is heated with lime an interchange or reaction takes place, the sulphuric acid of the copperas going to the lime while an oxidation of the iron takes place. Another method known as the wet method is the direct reaction between ferrous sulphate and wet slacked lime.

Venetian red has been known as a paint pigment for upwards of a century, and while theory would indicate that it is by no means as desirable a pigment to use as other mixtures of ferric oxid, it must be apparent that in view of the fact that it has given general satisfaction it is by no means as undesirable a pigment as chemists indicate. The tendency, however, at the present time is for manufacturers to buy strong pure oxids and reduce them with other inert fillers, for the principal reason that a Venetian red carrying a high percentage of calcium sulphate and an unknown quantity of water or moisture tends to become hard in the package, whereas the mixtures of known composition remain soft for many years. Venetian reds are all of the familiar brick color shade, the color of bricks being caused by the same pigment as the one that gives the color to Venetian red.



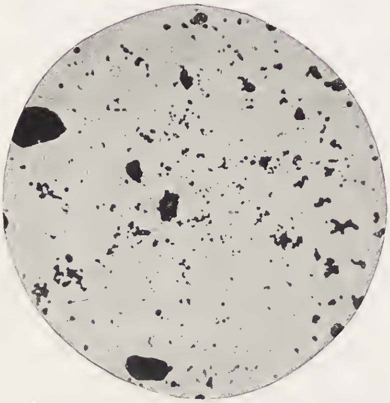
No. 16. English Venetian Red — Photomicrograph ×250, showing calcium sulphate crystals.

Indian Red

This is supposed to have been named by Benjamin West, a celebrated American artist who lived more than a century ago, and who as a boy used a few primary earth colors as pigments for paint. One of these was a natural hematite, and he observed that the Indians used this for painting their faces. The name is also supposed to have had its origin in the fact that "Persian Gulf Ore," which was found in the Orient, was exported to England under the name of "East Indian Red." This Persian Gulf Ore is likewise a hematite, and later on a similar ore was found in parts of England which, when mined, looked very much like coal, but when crushed and ground in water turned a deep blood-red. The old name for this mineral is still "blood-stone," and some very fine specimens of this mineral are still mined in England in conjunction with beautiful quartz crystals, so that we find in England a careful selection.

No. 17. American Venetian Red — Photomicrograph ×250, showing fine grains of calcium sulphate.

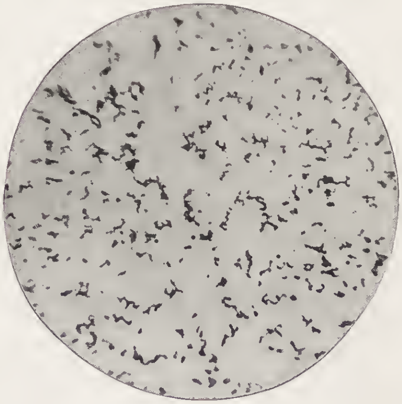
The native Indian red will run 90 per cent Fe_2O_3, the American 88 per cent, and the Persian 75 per cent, the balance in every case being silica. The Indian red of commerce, however, is an artificial product made like the base of the Venetian red by calcining copperas and selecting the product as to shade. There is no pigment, with possibly the exception of lithopone and artificial barium sulphate, which will approach Indian red in fineness of grain. The prices which a fine, pure Indian red or ferric oxid of any shade will command are most remarkable, many tons being sold every year in large quantities at as high a price as fifty cents per pound and used entirely for polishing gold, silver, and other metals. The well-known "watch-case rouge" is nothing but pure Indian red which has been ground, washed, and treated mechanically with so much care that three-quarters of its selling price is represented in the labor of manipulation. If, therefore, fine ferric oxid be mixed with linseed oil it can be easily seen from the nature of the physical characteristics of the pigment that a remarkably good result is obtained.



No. 18. American Hematite — Photomicrograph ×250, showing a few large grains.

Permanent Vermilion

It may be of interest to the chemist unacquainted with the manufacture of dry colors to know that English vermilion (sulphide of mercury), of which the prototypes are Chinese vermilion, American quicksilver vermilion, etc., was formerly used wherever a permanent red was desired; and particularly for railroad work was this vermilion the only red that could be used, for it did not fade. It has, however, the disadvantage of darkening in the light and eventually turning brown. The real sulphide of mercury is black, and red sulphide of mercury is a forced compound. The mineral cinnabar, which has the com-



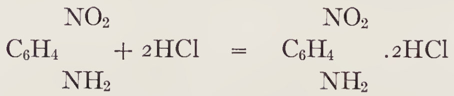
No. 19. Indian Red — Photomicrograph ×300, 98 per cent Fe_2O_3, very fine uniform grain.

position just described, is also red, but not very bright, and that found and made in Austria, known as Trieste vermilion, has always been regarded as the most permanent of these sulphide of mercury reds. Mixed paint manufacturers do not use it, and in fact paint manufacturers generally have discarded it, for the reason that the so-called para-nitraniline reds are better, cheaper, and more permanent.

In order that the chemist may understand the composition of the para-vermilions, a complete formula is given for their manufacture.

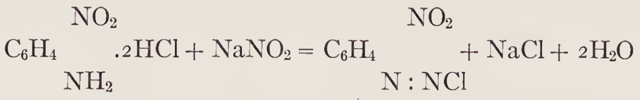
Reactions involved in Making Para-red

Part 1. (Solution of Para-nitraniline and Diazotizing.)



$$\underset{NH_2}{\overset{NO_2}{C_6H_4}} + 2HCl = \underset{NH_2}{\overset{NO_2}{C_6H_4}}.2HCl$$

(para-nitraniline) (para-nitraniline hydrochloride)



$$\underset{NH_2}{\overset{NO_2}{C_6H_4}}.2HCl + NaNO_2 = \underset{N:NCl}{\overset{NO_2}{C_6H_4}} + NaCl + 2H_2O$$

(benzene nitro-azochloride)

Part 2. (Beta-naphthol Solution.)

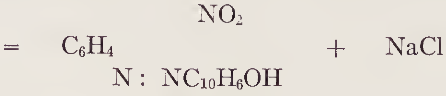
$$C_{10}H_7OH + NaOH = C_{10}H_7ONa + 2H_2O$$

(beta-naphthol) (sodium beta-naphtholate)

Part 3. (Mixing of No. 1 and No. 2 to Produce Color.)

$$\underset{N:\ NCl}{\overset{NO_2}{C_6H_4}} + C_{10}H_7ONa$$

(benzene nitro-azochloride) (sodium beta-naphtholate)



$$= \underset{N:\ NC_{10}H_6OH}{\overset{NO_2}{C_6H_4}} + NaCl$$

(Para Red)

PARA-NITRANILINE LAKE

NAPHTHOL SOLUTION

15 grams beta-naphthol or beta-naphthol R.; 30 grams caustic soda lye 22° Be.; 10–20 grams para-soap P. N. (In sufficient boiling water to dissolve thoroughly).

DIAZO SOLUTION

14 grams para-nitraniline dissolved in boiling water; 25 grams hydrochloric acid 20° Be.; 200 grams ice.

When the solution is cooled to 32° to 35° F., add very slowly, while stirring constantly, 34 grams nitrite of soda solution (29 gms. nitrite in 100 gms. cold water).

Allow to stand 15 to 20 minutes. Then add slowly 35 grams acetate of soda previously dissolved in cold water.

To the naphthol solution add the base you intend to use. 250 grams of blanc fixe give good results. For bluer shades use beta-naphthol R. For yellower shades use beta-naphthol.

When these colors have been precipitated on an orange mineral base they have been known to catch fire spontaneously in the drying room, and therefore great care should be exercised in their manipulation with lead bases.

There appears to be a difference of opinion among consumers as to whether these reds are really permanent or not. Careful investigation reveals the following: The para-vermilions are soluble in linseed oil, and therefore even when a pigment contains only 5 per cent tinctorial matter it is useful and effective as a red paint. White lead in any form mixed with a para-red destroys its color and turns it brown. A few years ago when this color first appeared on the market it frequently happened that it turned perfectly white when exposed to the air, but when it was rubbed with raw linseed oil it turned a brilliant red again, and a microscopic examination showed that the film had been entirely incrusted with very fine crystals of sodium nitrite and other salts that had not been completely washed out of the lake pigment, and so para-red obtained a bad reputation, not due to the color, but due to the ignorance of the manufacturer.

Para-red has penetrative powers in both directions; when painted, for instance, on a sheet of cloth for sign work it will penetrate through and stain the under side yellow. If white lead paint be lettered over it, it acts the same and turns white lead yellow or a yellowish brown.

Enormous quantities of this vermilion are made every year, and so strong is this color that average analyses of the paint used for agricultural implement purposes will show the pigment to be composed of 90 per cent barytes, 5 per cent para-red, and 5 per cent zinc oxid or zinc sulphide. Its presence in mixed paints is very easily detected by boiling with varnish solvents and noting the peculiar orange color of the filtrate.

Helio Fast Red

This is also known as Harrison Red, and is perhaps one of the most permanent pigments that we have of the vermilion type. It is made from nitro-paratoluidine, and in tinctorial strength is practically ten times stronger than a quicksilver vermilion. It dries, however, very badly, and when a sufficient percentage of strong drier such as a resinate of lead and manganese is added, the color tends to darken slightly on exposure. This color does not bleed, and it is apparently insoluble in drying oil; nor does it turn a white pigment into a brown, as is the case with the para-reds. When this pigment is mixed or reduced with a large quantity of whiting, barytes, or other white base, and exposed to the air it apparently fades, and on close examination this fading is found to be washing out of the pigment itself and the exposure of the base upon which it is made, so that the conclusion we must arrive at as regards the permanency of this remarkable color is that when used in sufficient strength it is permanent, but when diluted, reduced, or adulterated to too great an extent the base upon which it is made overpowers or masks the permanent pigment itself.

LITHOL RED

This is 2-naphthylamine-1-sulphonic-acid-diazo-beta naphthol, and is sold to color manufacturers in paste form as a semi-finished color.

In the manufacture of permanent vermilion the following is the method of procedure:

The paste color is mixed with the desired amount of base (blanc fixe, clay, barytes, whiting, etc.) and water until a thin, uniform suspension is obtained. Barium chloride to the extent of 10% of the paste color is then added and the whole steamed for about $\frac{1}{2}$ hour until the shade is fully developed. The color is then washed once or twice, pressed, and dried.

Lithol red has the advantage over para-nitranilines in that it does not bleed, and that it does not turn dark upon exposure. It is very largely used in the manufacture of permanent railway signal reds, and when not reduced or diluted with too much clay and barytes is permanent, but when it contains an excess of the so-called reënforcing pigments it washes out and fades.

CHAPTER V

The Brown Pigments

The principal brown pigments used in the manufacture of paint, excepting the aniline lakes, are the burnt siennas, the burnt umbers, burnt ochres, Prince's Metallic or Princess Mineral brown and Vandyke brown.

The burnt siennas, whether they are American or Italian, are a translucent form of ferric oxid and clay. In other words, when the hydrated oxid of iron and clay mineral are burnt ferric oxid is the result, and the clay remains unaltered, any water in combination, of course, being driven off. If the resulting color is translucent and is of the nature of a stain we call it a sienna, but if the resulting color is opaque and of the nature of a paint we call it an oxid.

The umbers are similar in composition to the siennas, with the exception that they all contain manganese and are of a much deeper brown and do not approach the red.

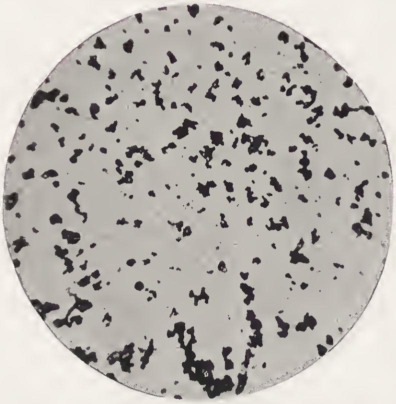
The Princess Mineral brown or Prince's Metallic oxids are calcined carbonates, silicates, and oxids only found in America, and are very largely used, particularly for the painting of wood.

Vandyke brown is a very deep brown, and is translucent when finely ground, containing more than 50 per cent of organic matter.

American Burnt Sienna

This is a permanent reddish brown pigment made by calcining raw sienna, raw sienna being a hydrated oxid of iron containing clay. When burnt the percentage of

Fe_2O_3, or ferric oxid, ranges from 25 to 60 per cent, depending upon the original ore. There is one grade found in the Pennsylvania section which assays as high as 80 per cent ferric oxid, and is known as double strength sienna. This is richer and deeper than the Italian sienna, and when reduced with ordinary clay and ground in oil makes a staining pigment equal to the Italian. From a raw-material standpoint the Italian siennas when tinted with 20 per cent of white show a bluish tint, whereas the American siennas show a brownish or yellowish tint, and only one who has had a great deal of experience in tinting out these siennas can tell empirically the difference between an American and a burnt sienna. The Italian and the American siennas normally contain some calcium salts, but occasionally some ores are found which are free from lime compounds. For paint purposes, however, these are no better than those that contain lime, for many grinders add from 5 to 10 per cent of whiting to umbers and siennas to prevent them from running or disintegrating when used as staining colors.



No. 20. American Burnt Sienna — Photomicrograph ×250, excellent quality, uniform grain.

Italian Burnt Sienna

Italian burnt sienna is made from raw sienna, the raw sienna being a hydrated oxid of iron containing clay, in which the iron predominates, the burnt sienna being of the same composition minus combined water. The hydrated oxid of iron is normally yellow, and when this is burnt the ferric oxid which is produced is reddish or reddish brown.

Italian burnt sienna differs from most American burnt siennas in that its ferric oxid content is generally greater. The Italian burnt siennas average from 60 per cent Fe_2O_3 to as high as 75 per cent. The American burnt sienna, known as double strength sienna, which is equal in iron content to the Italian, differs totally in shade, the American being of the order of an Havana brown, the Italian being of a maroon type.

Siennas in mixed paints are largely used for their tinting quality, the resulting shade being a yellowish maroon or salmon color of extreme permanence. After several years' exposure a mixture of white and burnt sienna will darken slightly, but will never fade.

Under the microscope a finely ground sienna shows little or no grain.

Burnt Umber

Burnt umber is a very useful pigment, and is found in the United States and also imported from Italy, Cyprus, and Turkey-in-Europe. All umbers normally contain over 5 per cent of manganese dioxid, while some of them contain as high as 20 per cent manganese. The Turkey umbers are generally richer in manganese than the American umbers.

A typical analysis of burnt Turkey umber would be as follows:

Calcium Carbonate	7%
Silica	34%
Manganese Dioxid	14%
Ferric Oxid	42%
Alumina	3%
	100%

A typical analysis of an American burnt umber would be:

Silica and Alumina (clay)	60%
Ferric Oxid	25%
Manganese Dioxid	8%
Calcium Carbonate	5%
Carbon and Carbonaceous matter	2%
	100%

These types would indicate that an American umber is not as strong and does not contain as much ferric oxid and manganese dioxid as a Turkey umber.

Burnt Ochre

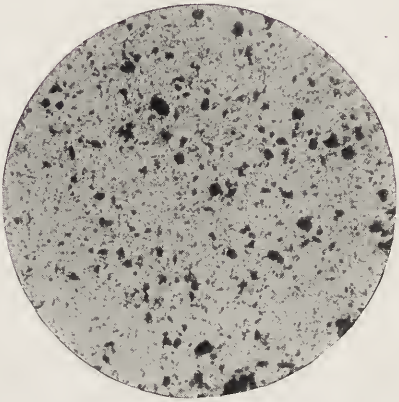
Burnt ochre is distinctively an American color, and differs in physical quality from burnt sienna in so far as the burnt ochre has hiding power and the sienna has translucent or staining power. Burnt ochre is more like a brown paint, and burnt sienna like a mahogany stain. Burnt ochre covers solidly; burnt sienna covers translucently.

Some of the American siennas which are not good enough for staining purposes are burnt and find their way to the market as structural steel paints and railroad paints of the brownish red order; as such they are remarkably good in their protective quality against corrosion.

No standard of composition can be given, as burnt ochre varies very much in the percentage of iron, some of the burnt ochres ranging as low as 30 per cent iron oxid and others as high as 70 per cent, the balance in both cases being clay.

Prince's Metallic or Princess Mineral Brown

This is one of the best known paints, and has had a successful career for more than fifty years. It is a very pleasing brown pigment, which has an enormous use all over the United States for painting wooden freight cars and for painting tin roofs. Where it is applied to a flat surface like a tin roof it has been used for many years in its dry state, and mixed with half raw and half boiled linseed oil in the field. It is at times fairly fine, and while it is an excellent preservative for steel it may be regarded as a better preservative coating for wood, as many of the wooden barns in the country in the States have lasted ten years when coated with two coats of this pigment. The analysis of the material varies very much.


No. 21. Prince's Metallic — Photomicrograph ×300.

Geologically, the ore is a carbonate, and lies between the upper silurian and lower devonian. It is a massive material of bluish gray color when mined, and resembles limestone, although it contains a very low percentage of lime. The process of mining is by shaft-work. The ore itself lies between two hard rocks and rarely ever exceeds three feet in width, and as a consequence the mining is an expensive operation. The ore is hauled to the kilns, where it is roasted, which drives off the carbon dioxid and converts it into a sesqui-oxid. The milling is the ordinary process used in grinding any of the iron oxids.

The material was originally manufactured by Robert Prince of New York, who became interested in a slate quarry located in Carbon County, Pennsylvania, from which locality the original material came.

A fair analysis of this material is as follows:

Oxid of Iron ($Fe_2 O_3$)	48.68%
Silica	33.37%
Alumina	12.08%
Lime	2.02%
Magnesia	1.25%
Loss on Ignition	2.34%
Undetermined	0.26%
	100.00%

As the material is not alkaline, the lime and magnesia are undoubtedly combined with the silica, so that the material other than oxid of iron is silicate of alumina, lime, and magnesia. Sometimes, the percentage of Fe_2O_3 will run below 40 and sometimes it will go as high as 50, but this really makes no difference in the paint, and in view of the fact that it is a natural product and may from time to time contain a little gang rock some leeway must be given as regards its composition.

VANDYKE BROWN

Vandyke brown is a native earth, and is identical with cassel brown. It is popularly supposed that Vandyke first used this pigment as a glazing color in place of bitumen, and as it is composed of clay, iron oxid, decomposed wood, and some bituminous products, it is fairly translucent and adapts itself for glazing purposes. Because of the bitumen which it contains, it dries very badly and very slowly, and has a tendency to crack or wrinkle if the under-coat is either too hard or too soft. Concerning its permanence, there can be no doubt that it darkens considerably on exposure, like all the bituminous compounds, and many painters use a permanent glaze composed of a mixture of ochre and black tinted with umber. Where the effect of age is to be simulated, there is no objection to its use.[1]

This pigment is used in mixed paints, principally on account of its deep shade and translucent appearance. It contains upwards of 60 per cent of organic matter. A typical analysis would be as follows:

Organic Matter	65%
Ferric Oxid	3%
Calcium Carbonate	5%
Potash and Ammonia Salts	2%
Moisture	25%
	100%

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[1] "Materials for Permanent Painting" by Maximilian Toch.

CHAPTER VI

THE YELLOW PIGMENTS

THE yellow pigments are the ochres, the raw siennas, chrome yellow, and the chromates.

The ochres are all rust-stained clay, and both the French and the American contain approximately 20 per cent of rust or ferric hydroxid and the balance clay.

The raw siennas differ from the ochres in that the amount of hydrated oxid of iron is often in excess of that of clay, and the nature of the pigment is such that when finely ground it is a stain and not a paint.

The chrome yellows are all lead chromate variously precipitated and of varying composition, depending upon the shade.

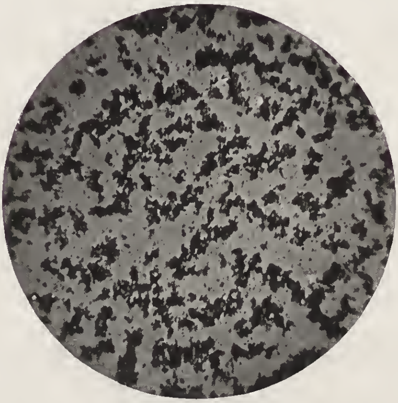
The other chromates, such as zinc chromate and barium chromate, have come into use in paints within the last ten years, owing to their alleged property of preventing rusting.

AMERICAN YELLOW OCHRE

There are large quantities of ochre found in the United States, but principally in Pennsylvania and in Georgia. There are, of course, a great many other deposits, but for the paint industry these are the principal sources. American ochre ranges in composition from 10 to 30 per cent of ferric hydroxid, the balance in either case being clay, and on this point it is well to note that ochre and sienna have the same composition, excepting that there is generally a reversal in the percentages of clay and oxid of iron. Some ochres found in America are finer than those imported from France, although French ochres as a general rule are decidedly more brilliant in color.

In the trade there are many other ochres, which are sold under the name of cream ochre, gray ochre, white ochre, and golden ochre, all of which are clays containing either carbonaceous matter or iron rust, for, after all, ochre is simply clay stained with rust.

Cream ochre contains as low as 5 per cent of iron rust or ferric hydroxid, the balance being silica and clay. It has very little hiding power, and is considered of very little value as a primer on wood, for which it is used to quite a large extent.



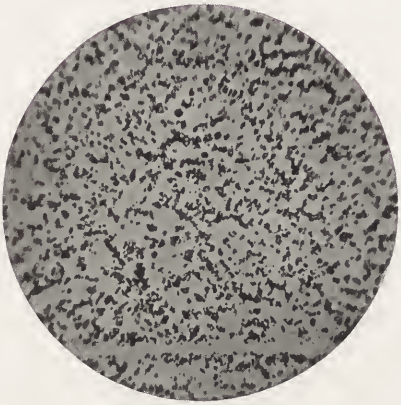
No. 22. Ordinary American Washed Ochre — Photomicrograph ×250, powdered and bolted; lower in iron than the French, but of uniform grain.

Gray ochre is silica, clay, and carbonaceous coloring matter, or is colored with a trace of ferrous hydroxid or greenish rust. It is used as a filler, or for a cheap paint.

White ochre is nothing more or less than clay, and has no value whatever as a paint material.

Golden ochre is either French ochre or American ochre which is brightened with some chrome yellow. There are various shades of golden ochre sold, depending upon the shade of chrome yellow with which it is mixed. Some of them are perfectly orange colored, and contain as high as 12 to 15 per cent of chemically pure orange chrome yellow.

Green ochre is similar in composition to gray ochre, excepting that it contains a larger percentage of ferrous hydroxid. It is principally found in Bohemia under the name of terre verte. It has little or no hiding power of itself, but is very largely used as a base for cheap lakes on account of its adsorbent quality for certain aniline colors.



No. 23. American Washed Ochre — Photomicrograph ×250, of the same composition as French ochre.

Yellow oxid is a synonym for raw sienna, and is practically the same thing. A typical analysis of yellow oxid will show hydrated oxid of iron 70 per cent and clay 30 per cent.

For the benefit of the chemist it must be stated that when analyses are not given and small percentages of lime and magnesia are found, it is understood that these are natural concomitants of ochrey earths.

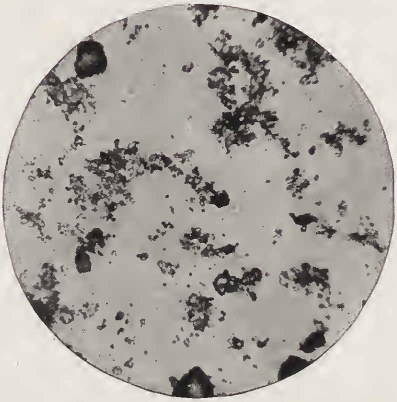
French Yellow Ochre

French yellow ochre has been used in America for many years, and is analogous in composition to American ochre; but as a general rule the French ochres are more brilliant in shade. Nearly all of the French ochres which are imported into the United States have a composition of about 20 per cent of hydrated oxid of iron and 80 per cent of clay, and one of the most popular brands has for years been known as J. F. L. S. These letters stand for "Jaune, Foncé, Lavé, Surfin," which mean, "Yellow, Dark, Washed, Superfine." These letters are varied according to the treatment that the ochre gets, but the J. F. L. S. is the most popular.

In color, the French ochres are more brilliant, as has been stated, but the American ochres are invariably finer; but this, of course, refers only to the American grades of equal price.

CHROME YELLOW

Chrome yellow is a lead chromate of medium shade, as precipitated from a solution of nitrate of lead and potassium bichromate. The lemon or lighter shades are made from solutions acidified with organic or inorganic acids. An organic acid such as citric acid, which forms a lead citrate, changes the shade, producing a greenish lemon, which may vary from a greenish lemon to a brilliant canary, particularly if sulphuric be added. If an alkaline solution of potassium bichromate be used an orange precipitate is produced, so that a great variety of shades of this pigment can be obtained.


No. 24. J. F. L. S. OCHRE — Photomicrograph ×250, showing crystalline structure.

All of the chrome yellows are perfectly permanent, provided they are thoroughly washed to free them from residual salts. Manufacturers are now abandoning the old mechanical method of stirring chrome yellow after it is precipitated, and are substituting air stirring, which avoids any possible tendency to produce lead sulphide, the air converting the sulphide into sulphite and sulphate.

Chrome yellows when thoroughly washed are permanent to light, but they cannot be recommended where sulphur vapor is generated, owing to the formation of lead sulphide, traces of which detract from the brilliancy of the color of the pigment.

The composition of chrome yellow is as follows:

LIGHT CHROME YELLOW

$PbSO_4 + PbCrO_4$

or,

$2PbCO_3 \cdot Pb(OH)_2 + PbCrO_4$

or,

$$PbCrO_4 + \left.\begin{array}{l}\text{Citrate}\\ \text{Tartrate}\\ \text{or Sulphate}\end{array}\right\}\text{of Lead}$$

MEDIUM CHROME YELLOW

$PbCrO_4$

ORANGE CHROME YELLOW

$PbO \cdot PbCrO_4 = Pb_2CrO_5$

CHROMATE OF ZINC

Chromate of zinc has only come into general use within the last ten years in mixed paints and paints generally, on account of its alleged rust preventing properties when used as a priming paint on steel.

Chromate of zinc is made as follows: Zinc oxid is boiled in a solution of potassium bichromate for several hours and filtered and dried with slight washing; or a hot neutral solution of zinc sulphate is precipitated with potassium chromate.

Chromate of zinc is soluble to a considerable extent in water, and therefore should not be used as a finishing coat, as rain will streak the surface. For example, a green paint made of chromate of zinc and blue shows yellow streaks when exposed to the weather.

This material is used to some extent by artistic painters, and as oil paintings are never subjected to the elements it is under those circumstances a perfectly permanent color.

For interior painting and flat wall paints, chromate of zinc, therefore, has an advantage, as much more brilliant tones are obtained and much more delicate shades are obtained than with the chromate of lead. It has very little hiding power or opacity, and in tinctorial strength is much weaker than the chromate of lead.

If contained in a mixed paint, when the pigment is thoroughly washed with benzine and freed from oil or medium, chromate of zinc can easily be recognized, because the pigment when shaken with hot water in a test tube is invariably colored yellow. This, however, must be further verified, as barium chromate reacts the same way.

CHAPTER VII

The Blue Pigments

The blue pigments usually used in the paint industry are artificial ultramarine blue, artificial cobalt blue, and Prussian blue. The types of Prussian blue vary very greatly with their manufacture, and are known under the names of Milori blue, Bronze blue, Chinese blue, Antwerp blue, Paris blue, etc.

Ultramarine and cobalt blues are permanent to light and alkali-proof. The Prussian blues are permanent to light, but not alkali-proof.

Ultramarine Blue[1]

Ultramarine blue, whether it is artificial or genuine, is chemically the same, with the one difference that the genuine ultramarine blue is the powdered mineral known as lapis lazuli, and ordinarily is the blue known under that name. Furthermore, the mineral itself is found at times in an impure state either admixed with slate or gang rock, or contaminated slightly with other minerals, and the genuine ultramarine blue may run, therefore, from a very deep blue to a very pale ashen blue; in fact, the lapis lazuli which lies adjacent to the gang rock is ground up and sold under the name of ultramarine ashes, which is nothing more nor less than a very weak variety of genuine ultramarine blue.

From the standpoint of exposure to light or drying quality, the artificial ultramarine blue is just as good

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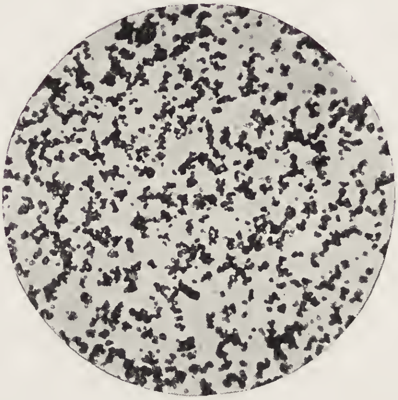
[1] "Materials for Permanent Painting," by Maximilian Toch.

as the genuine, and the only advantage that the genuine has over the artificial is that the genuine is not so quickly affected by acids as the artificial is.

It may be of interest to know that in 1814 Tessaert observed the accidental production in a soda oven at St. Gobain (France) of a blue substance which Vanquelin declared to be identical with lapis lazuli. In the following year the same observation was made by Huhlmann (at St. Gobain in a sulphate oven) and by Hermann in the soda works at Schoenebeck (Prussia).



No. 25. Ultramarine Blue — Photomicrograph ×300.

In 1824 La Société d'Encouragement pour Industrie offered a prize of 6000 francs for the production of artificial ultramarine blue, which, in 1828, was awarded to J. B. Guinet, a pharmacist of Toulouse, later of Lyons, who asserted that he first produced ultramarine in 1826. Vanquelin was one of the three "trustees," holding the secret contrary to the rule of the Société.

In December, 1828, Gmelin of Goettingen explained his process of making artificial ultramarine before the Acadamie des Sciences of Paris. He used as

No. 26. Ultramarine Blue, ground in oil, very uniform and fine — Photomicrograph ×250.

the basis a mixture of precipitated hydrate of alumina and silex, which was later on superseded by China clay (kaolin).

In 1829 Koettig produced ultramarine at the Royal Saxon porcelain factory at Meissen.

In 1834 Leverkus, at Wermelskirchen, and later at Leverkusen, on the Rhine, produced the pigment.

In 1837 Leykauf & Zeltner, at Nueremberg, introduced the manufacture of ultramarine into Germany.

Prices of ultramarine in 1830:

Natural	$50.25 per pound
Artificial	4.05 per pound

Ultramarine is composed of alumina, silica, soda, and sulphur, as follows:

Ultramarine (pure blue) containing a minimum of silica seems to be a more or less well-defined chemical body, i.e., a double silicate of sodium and aluminium with sulphur as a poly-sulphide of sodium, or as a thiosulphate.

Ultramarines	Poor in Silica	Rich in Silica
Alumina	29.00	23.70
Silica	38.50	40.80
Soda	22.50	19.30
Sulphur	8.20	13.60
Undecomposed	1.80	2.60
	100.00	100.00

R. Hoffman gives the following proportions:

	Alumina	Silica
Poor in silica	100	128
Rich in silica	100	170

In resistance to alum the different products rank as follows:

Lapis Lazuli	First
Artif. Ultramarine (rich in silica)	Second
Artif. Ultramarine (poor in silica)	Third

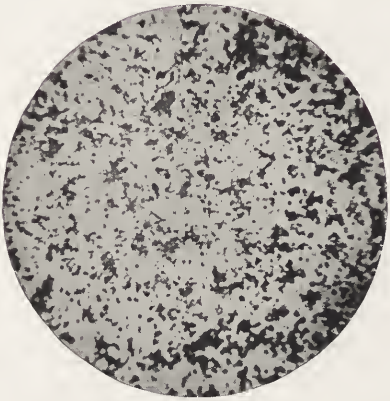
In 1859 Leykauf discovered the purple and red varieties of ultramarine, which were produced by the action of hydrochloric and nitric acids, and by heating ultramarine with calcium chloride, magnesium chloride, and various other chemicals. In this way there were produced a variety of shades, and by the addition of such substances as silver, selenium, and tellurium, even yellow, brown, purple, and green shades were produced.

All of these colored ultramarines are exceedingly permanent to light, but have little or no hiding power, and when used alone are perfectly permanent.

The ultramarine blue which is made by means of a potash salt instead of a soda salt has every analogy of color and shade to genuine cobalt blue, excepting that the genuine cobalt blue is not affected by acids as rapidly as the artificial.

Artificial Cobalt Blue

The cobalt blue of commerce is the same as ultramarine blue, the difference being in the shade. Ultramarine, when mixed with thirty parts of a white pigment, such as zinc oxid, produces a violet shade, whereas the cobalt blues when mixed in the same proportion produce a turquoise or sky-blue shade. Chemically, the composition of these ultramarines and cobalts will average about 50 per cent silica, 22 per cent alumina, 15 per cent sodium sulphide, in combination with 3 per cent water and 10 per cent sulphur. The addition of the slightest trace of acid to a paint containing ultramarine blue liberates H_2S, which always indicates the presence of ultramarine in a blue or bluish pigment. Under the microscope ultramarine blue has a distinct crystalline appearance. When these crystals are badly destroyed by fine grinding the color suffers very much, the characteristic brilliant blue of ultramarine becoming an exceedingly muddy shade. Its tinctorial power is very weak, but it is exceptionally permanent to light. In blue shades of mixed paints the percentage of ultramarine blue can be determined either by difference or by the percentage of sulphur present. If 10 per cent is accepted as the amount of sulphur in ultramarine blue, a fairly accurate quantitative determination can be arrived at. Where ultramarine blue is mixed with lithopone the zinc sulphide of the lithopone as well as the ultramarine evolve H_2S. When determining the ultramarine, the total H_2S evolved must be calculated as sulphur. The zinc must be precipitated as carbonate and weighed as oxid and calculated to sulphide. The sulphur in the ZnS must then be deducted from the total sulphur. From the difference the percentage of ultramarine blue in the original pigment may be calculated. As acetic acid liberates the H_2S from the ultramarine but does not attack the S in lithopone, this acid may be used and the percentage of sulphur in the ultramarine determined directly.



No. 27. Artificial Cobalt Blue (same as ultra blue) — Photomicrograph ×250, crystalline grain.

Ultramarine blue reacts with corroded white lead but not with zinc oxid. It does not react very quickly with sublimed lead or zinc lead, but for the making of pale blue shades, which should remain permanent in the package, zinc oxid is to be recommended in preference to any other white pigment. Ultramarine blue should not be mixed with any of the chrome yellows or chrome greens, because a darkening effect is sure to take place. Ultramarine blue behaves very badly with linseed oil containing an excessive amount of lead drier. For mixed paints of pale tints a resinate of manganese or oleate of manganese drier is to be recommended. Most of the Japan driers contain large quantities of lead, and a white Japan composed of rosin, manganese and linseed oil will make the most permanent mixture.

Prussian Blue

Synonym : Milori Blue, Bronze Blue, Antwerp Blue, Chinese Blue, Paris Blue, etc.

Almost every text-book on elementary chemistry gives a description of Prussian blue, which is a ferri-ferrocyanide of iron, and in a general way it can be produced for laboratory purposes by the simple mixture of ferrocyanide of potassium and a ferric salt of iron. Commercially, the well-known ferric iron reaction of analytical chemistry is reproduced on a large scale. Prussian blue, however, is made from a ferrous salt and is obtained by the mixture of ferrous sulphate (copperas) and ferrocyanide of soda or potash (yellow prussiate). This mixture produces a pale bluish white flocculent precipitate, and the chemist will easily understand how, with the addition of any oxidizing agent, such as bleaching powder, potassium chlorate, etc., the precipitate is converted from a bluish white into a dark-blue pigment.

There are a number of varieties of Prussian blue, all approximating this composition but made differently, being sold under the names of Steel blue, Milori blue, Bronze blue, Antwerp blue, Chinese blue, and Paris blue. Although each of these blues is chemically the same as Prussian blue, they have different physical characteristics. Prussian blue, for instance, is like a mixture of indigo and black in its dry state, and when tinted with one hundred times its own weight of zinc oxid the shade produced is a muddy violet. Chinese blue, when treated in the same manner, gives a purer blue which has no trace of violet in the shade. The Steel blue, when diluted one hundred times, gives a turquoise shade. And so for the manufacturer of pale blue shades the tones of these blues must be taken into consideration.

There is much discussion among paint manufacturers as to whether Prussian blue is a permanent pigment or not, and the author is frank to say that this matter can be decided as follows: Prussian blue, or any of its varieties may be considered permanent or fugitive, according to the manner in which it is made and according to the base with which it is mixed. If Prussian blue contains more than a trace of soluble salt (sodium sulphate), it has a decidedly yellowing action on the oil, and a light blue or light green made of such Prussian blue is supposed to be fugitive. On the other hand, a number of experiments made with thoroughly washed Prussian blue have demonstrated that it is a perfectly stable color and does not change its shade. As a tinting color for making pale blues in mixed paints Prussian blue has caused an enormous amount of trouble. A pale blue mixed paint that contains white lead in any proportion changes color in the package, a reduction process taking place which converts it from a ferric into a ferrous state, so that when a can of light blue mixed paint made with Prussian blue and white lead is opened it is a sickly green instead of a blue. If such a paint be applied to an exterior surface it is completely converted into its original blue shade as soon as it is dry. The zinc oxid paints have the same action, but to a very small degree, and a paint manufacturer who desires to make a pale blue by the use of Prussian or Chinese blue must avoid the use of white lead in his paint. The artificial cobalt blue mixed with zinc oxid is, however, more desirable.

Prussian blue is also used in small quantities for mixing with bone black to produce intensely black shades.

It is a simple matter to determine the presence of Prussian blue in any pigment by the addition of caustic soda to the dry extracted pigment, warming, filtering, and testing the filtrate with a drop of ferric chloride after acidifying. The Prussian blue made in laboratories will contain approximately 30 per cent of iron, so that if an analysis is made of a mixed paint tinted with Prussian blue and the percentage of iron is multiplied by three, a fairly correct estimate of the percentage of Prussian blue is obtained; and while the factor given cannot be absolutely correct, owing to the difference in the various blues made, it is so nearly correct that a synthesis made from such an analysis has invariably given the same shade.

CHAPTER VIII

THE GREEN PIGMENTS

THE greens used in the manufacture of paints are the so-called chrome greens, which are mixtures of chrome yellow and Prussian blue, the genuine chrome greens or chromium oxid, the aniline lakes, zinc green, and the verte antique or copper green.

CHROME GREEN

Chrome green is sold under various proprietary names, and must not be confounded with the oxid of chromium. Chrome green is essentially a mixture of Prussian blue with chrome yellow, but the chrome greens, unless chemically pure, are always mixtures of blue and yellow on a barytes or mixed base.

A green paint made entirely of Prussian blue, chrome yellow, and an inert base, such as silica or barytes, is very easily analyzed by ignoring the pigment and weighing the base, calculating the pigment by difference. This is, however, not a desirable method to recommend except in the hands of an expert who knows that the pigment or paint is made on an inert base. Inasmuch as there is a great variety of shades of chrome green, ranging from a yellowish green to a very dark olive, and as the dark shades may be composed of either a mixture of orange, chrome yellow, and Prussian blue, or a light chrome yellow and Prussian blue and black, it is not safe to multiply the percentage of iron by a factor to obtain the percentage of Prussian blue, because many shades of green are produced with the use of ochre. The iron factor would therefore be misleading. The lead chromate can be washed out with hot hydrochloric acid and will precipitate on cooling. The Prussian blue may be washed out with a caustic alkali solution, the iron being left behind, but it can be reprecipitated as Prussian blue with a ferric salt, the necessary amount of chrome yellow and Prussian blue originally used being thus recovered. This method is uncertain only when an olive-yellow is being analyzed.

Chrome green should never be mixed with white lead for the pale shades, as it changes color in the can in proportion to its content of Prussian blue. Zinc lead, zinc oxid, sublimed lead, or lithopone should therefore be used. If chrome green is not well washed the soluble salts are likely to affect the linseed oil. At the seashore the salt atmosphere invariably attacks chrome green and bleaches it, and where an absolutely permanent green is required chromium oxid should be used.

CHROMIUM OXID

Chemical Formula : Cr_2O_3

This green is one of the oldest greens in existence, having been used for very many years, but never having been used for mixed paints or by the paint manufacturer, excepting for artists' use, until within the past six years. While it is expensive compared to the chrome green as previously described, and while it is weaker in tinting power and lacks in brilliancy, it nevertheless is the only perfectly permanent green made. It mixes with every other pigment without decomposition and stands the light without fading or darkening. No alkali discolors it, and therefore in the modern flat wall paints where delicate greens are desired chromium oxid has come to play a very significant rôle. Many manufacturers get more for their fancy colors, such as greens, blues, and vermilions, and any man who makes a perfectly alkali-proof wall paint is entitled to a higher price if the goods are better than those of his competitor.

Chromium oxid frequently possesses coarse qualities. It is made as follows:[1]

Eight parts potassium dichromate and 3 parts of pure boric acid are ground with water to a stiff paste. The mixture is then heated to dull redness for about 4 hours in a reverberatory furnace. The melt is thrown into water and boiled, to decompose borates of chromium and potassium into boric acid and chromium oxid (hydrated). The latter is then washed, dried, and ground.

After it comes out of the dry room it has to be ground in a burr stone mill with water exactly like an oil color. This develops whatever brilliancy there is in the color and increases its hiding power, but unfortunately it also develops a "float" of a very much more brilliant green than the natural chromium oxid. This float is similar in color to the well-known Veronese green or hydrated oxid of chromium, but is not apparent in the quicker drying types of paints.

Chromium oxid is now largely used as a basic color in automobile painting, particularly in the painting of the hoods, and also for the manufacture of the best type of dark green engine enamels, because excessive heating, or alternate heating and cooling, does not affect it in shade as it does the chrome green made from yellow and blue.

There is every reason to believe that this pigment will be used in greater quantities than it has been because of its sterling qualities.

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[1] Chem. Ztg. 9, 851.

GREEN ANILINE LAKES

Flat wall paints, which are very largely used in America, are the cause of the manufacture of certain green aniline lakes which are not permanent to strong light but are permanent to alkali, and are therefore used to some extent for making very brilliant green house paints for interior decoration.

These lakes can be readily tested by mixing them with soapy water and lime, and if they remain unchanged for five minutes they may be regarded as permanent, because the majority of the aniline lakes which are not alkali-proof are immediately converted into a yellow or yellowish brown color when mixed with this reagent.

The aniline lakes have no hiding power, but have tinting strength, and are only used as tints. For making very brilliant greens that have hiding power the chromium oxid is used as a base and the aniline colors to obtain brilliancy.

ZINC GREEN

Zinc greens are generally mixtures of chromate of zinc and Prussian blue, and are extremely brilliant, permanent to light, but not permanent to alkali or to water, as the chromate of zinc remains slightly soluble under many conditions.

This particular type of green is also largely used for interior decorative purposes and for the manufacture of flat wall paints. It is much more expensive than the chromate of lead green. It is also used to some extent as a coach color. Where it is varnished over this color is not soluble.

VERTE ANTIQUE (COPPER GREEN)

The pigment for making verte antique or antique green for copper imitation is generally the bicarbonate of copper. It has little or no hiding power, but the corroded copper effect cannot be very well imitated with any other pigment. It is manufactured as follows:

A solution of blue vitriol is precipitated with sodium carbonate, yielding a basic copper carbonate, carbon dioxid being evolved in the course of the reaction.

$$2CuSO_4 + 2Na_2CO_3 + H_2O = CuCO_3 \cdot Cu(OH)_2 + 2Na_2SO_4 + CO_2$$

There are a number of other methods in use for making copper green which are more lengthy and troublesome to carry out.

The lack of hiding power of this color is one of its good qualities, because the under coat usually is a copper color, made by so mixing a para toner and Princess Metallic brown that the translucency of the bicarbonate of copper gives the effect of actually corroded copper. Frequently this color is stippled on, and sometimes it it flowed on. Where opacity or hiding power is wanted chromium oxid and bicarbonate of copper are mixed. This pigment is permanent to light, and is at present practically the only pigment made or used which contains copper.

CHAPTER IX

THE BLACK PIGMENTS

THE principal dry pigments used in making black paint are as follows:

Lampblack
Carbon Black
Graphite
Charcoal
Vine Black
Coal
Ivory Black
Drop Black
Black Toner
Benzol Black
Acetylene Black
Mineral Black

There are quite a large variety of bone blacks, beginning with ivory black and going down to the by-product of the sugar mills known as "Sugar House black." In composition all of the animal blacks are alike, in so far as they always contain carbon and calcium phosphate. The carbon varies between 15 and 23 per cent, the rest being phosphate of lime and moisture. Some of the best blacks used for mixed paints are made from the shin-bone and skull of the sheep, it having been found that these blacks are of the most intense color. Occasionally variable amounts of calcium carbonate are found in these blacks, depending largely upon the length of time the bone was burned. For making a very intense and good quality black which will not settle when mixed with varnish, carefully selected bones or burnt ivory chips are taken, and digested in hydrochloric acid, which removes all the lime salts and leaves the carbon as a flocculent residue. This carbon is probably the highest priced and most intense black used by paint makers, and is frequently sold under the name of black toner, because it sometimes is used for giving an intense tone to an otherwise pure black. In the material known as Black Color in Varnish, it is found that black toner serves its purpose best, and a black paint which is composed of black toner ground in linseed oil and reduced with a very high grade of coach varnish is worth from $4 to $6 per gallon.

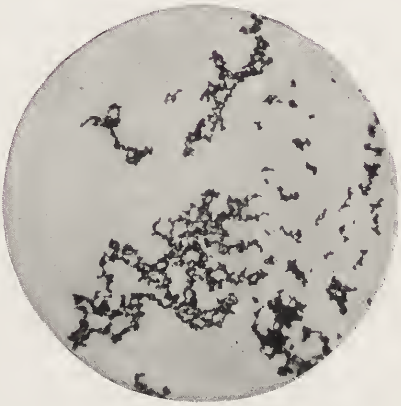
LAMPBLACK

Lampblack is the condensed smoke of a carbonaceous flame, and at present is made from a hydrocarbon oil of the type of dead oil, or it may be made from a number of distillates which on burning give a condensed black soot. Lampblack is still made from resinous woods, tar and pitch where the dead oil is not obtainable, and while many people are inclined to regard lampblack and carbon black as the same, they are not by any means the same from the paint manufacturer's standpoint, for lampblack is distinctly gray when compared with ivory black, bone black, or carbon black, and as a general rule lampblack makes a bluish gray when tinted out with white, one hundred parts to one, whereas bone black and ivory black as a rule make a brownish tint. This is an empirical method for differentiating them.

The specific gravity of lampblack is generally less than two, and one pound of a very pure lampblack without undue pressure will fill a package which is over 200 cubic inches in size, and very often over 230 cubic inches or one American gallon.

Lampblack is distinctly an American product, as is evidenced by the enormous amount of blacks of this type which are exported; a careful search of the imports fails to show any appreciable amount which comes into this country.[1]

Lampblack as it is made now is exceptionally pure, and contains more than 99 per cent of carbon. Occasionally, however, samples are found which contain a small percentage of unburned or condensed oil, which will retard the drying of lampblack to such an extent as to make it at times unfit for use. Prior to 1906 there were many cases where lampblack contained unsaponifiable grease, and the author devised a method for removing this with 62° naphtha, changing the slow drying lampblack into one which dried definitely; but since that time, due to improvements in the selection of lampblack and the greater care taken in its manufacture, it is very difficult to find a lampblack which contains less than 99.5 per cent carbon and which does not dry within a reasonable time. It must be taken into account that lampblack is always a slow drier. Whether this is due to the fact that it prevents the blue rays of light from entering the oil, or whether it is an inherent paralysis, has not been definitely decided, but one thing is positive, that where lampblack contains unburned or condensed oil the drying is in a large measure paralyzed.



No. 28. Lampblack — Photomicrograph ×300, very uniform.

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[1] A most excellent historical treatise on lamp and carbon blacks will be found in the original communications of the Eighth International Congress of Applied Chemistry, Volume 12, page 13, by Godfrey L. Cabot.

CARBON BLACK

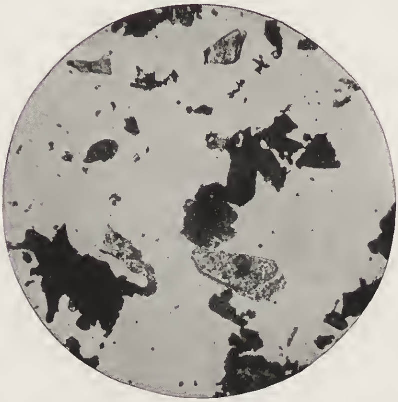
Carbon black is in all respects similar to lampblack, except that it is intensely black in color, and while it shows no crystalline structure under the microscope it condenses itself so hard on the places from which it is scraped that it is largely interspersed with flakes of black which to all appearance are crystalline and are very refractory in the mill. Its tinctorial power is very great, one pound being sufficient to tint one hundred pounds of white lead to a dark gray. Paint manufacturers have, however, abandoned its use as a tinctorial material for several reasons, the principal ones being that it is likely to produce a streaky color when used as a tint, owing to the presence of very small nodules that do not show up until it is applied as a paint (and these streaks cannot be brushed out). In the second place it shows a peculiar tendency to attach itself to minute air bubbles, so that when made into a mixed paint of a lighter tint and allowed to stand in the package for a considerable time, fairly large amounts of black rise to the top of the liquid. Only with the greatest difficulty can these be remixed with the rest of the pigment to produce a uniform tint.

No. 29. CARBON BLACK — Photomicrograph ×300, very uniform.

GRAPHITE

Synonym: Black Lead, Stove Polish. Specific Gravity: 1.19 to 2.5, depending upon the impurities contained in it

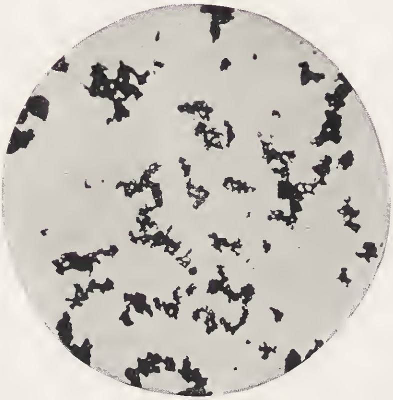
Graphite is found as a mineral almost all over the world. It is very largely used as a paint pigment, and it is remarkable that in its natural state it has all the defects of bulkiness which red lead has for weight. The purer a paint pigment is as to its content of carbon the poorer is the paint produced. If graphite be taken with a content of 80 or 90 per cent carbon and mixed with linseed oil, it forms a porous, fluffy film, and the particles of graphite coagulate in the linseed oil and produce a very unsatisfactory covering. If graphite be diluted with a heavier base its weakness then becomes its strength and a very good paint is formed. Many of the characteristic chemical and physical defects of red lead are largely reduced and frequently eliminated when it is mixed in proper proportion with graphite, a high grade of graphite when finely ground with linseed oil acting as a lubricant and sliding under the brush.



No. 30. NATURAL GRAPHITE — Photomicrograph ×250, containing about 40 per cent of silica, showing crystals of silica and graphite.

Pure graphite, as is well known, will cover from 1000 to 1600 square feet to the gallon. Such a paint film is so exceedingly thin that, while it looks good to the eye, in a short period decomposition more easily takes place beneath it than beneath many poorer paints. It is therefore essential to reduce graphite with a heavier base, and to this end it has been found that a mixture of silica and graphite produces very good results; but even this paint has the objection of having too much spreading power.

Misnomers have crept into the paint trade in regard to graphite paints, such names as green graphite, red graphite, brown graphite, etc., being in use, when in reality such graphites do not exist, excepting as far as graphite has been mixed with pigments of these colors.

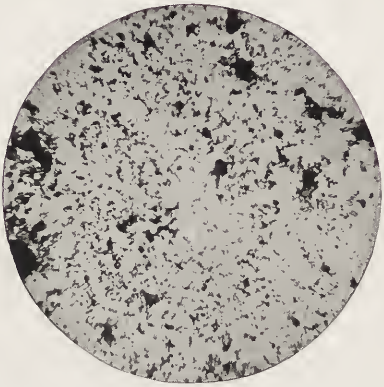


No. 31. Natural Graphite — 90 per cent carbon, very finely powdered.

A six-year test of a linseed oil paint made with a neutral ferric oxid, containing in its composition 75 per cent ferric oxid and 20 per cent silica mixed with graphite containing 85 per cent graphitic carbon, has proved itself to be as good a paint as can be desired for ordinary purposes. The pigment in a paint of this kind will withstand the chemical action of gases and fumes, but the oil vehicle is its weakest part.

Since the electro-chemical industry has been developed at Niagara Falls graphite has been made artificially and is sold under the name of "Acheson Graphite." This graphite is to be commended as a paint material on account of its uniformity and fineness of grain, but it should not be used alone as a pigment, for as such it possesses the physical defect of lightness just described. A graphite paint containing more than 60 per cent graphite does not serve its purpose very well unless 40 per cent of heavy pigment is added, such as a lead or a zinc compound. A rather unfortunate defect in the graphite paints containing a large amount of graphite is the smooth and satin-like condition of the paint film, which is poorly adapted for repainting. It has often been noted that a good slow-drying linseed oil paint will curl up when applied over certain graphite paints, because it does not adhere to the graphite film. On the other hand, if particular forms of calcium carbonate, silica, or ferric oxid are added to graphite a surface is presented which has a "tooth," to which succeeding films adhere very well.

The question of the coefficient of expansion in paints has not been thoroughly considered, and many a good paint will fail because it is too elastic. Engineers sometimes prefer a paint which when scraped with a knife blade will curl up like ribbon. Priming coats suffer very much when they are as elastic as this, but the paint chemist can overcome these defects by the proper admixture of inert fillers and hard drying oils.

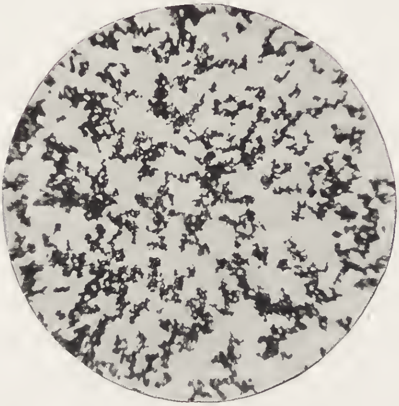


No. 32. Artificial Graphite (Acheson) — Photomicrograph ×250, containing 90 per cent of carbon.

Graphite is known as a very slow drier, but this is true only when too much graphite is used in the paint. There is no reason why a graphite paint should not be made to dry sufficiently hard for repainting within twenty-four hours.

CHARCOAL

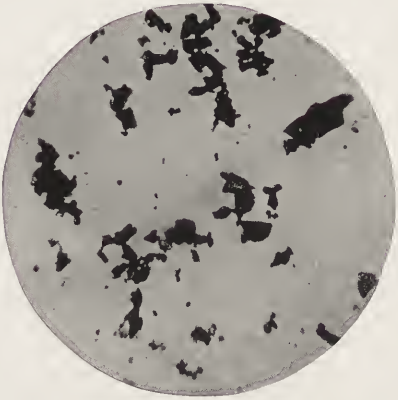
It is not generally known that charcoal from the willow, maple, and bass trees is largely used as a pigment for black paints. There are a number of black paints on the market which are composed of charcoal, lampblack, litharge, and linseed oil in varying proportions, and in the early history of these paints it was difficult to make them so thin that they would not turn semi-solid in the package. It was found that as a preservative coating on steel they did remarkably well. Investigations by the author have shown that this preservative action is incidental and is due entirely to the alkali contained in the charcoal. Some of the charcoal used is a by-product from paper mills and contains as high as 2 per cent of potassium carbonate. In fact, the carbonate is produced by the burning or calcining of wood, most charcoal being more or less alkaline. In the examination of paints of this character it was noticed that the spectroscope showed the potash lines, and thus it became a very simple matter to determine by means of the spectroscope whether a paint was a charcoal paint or not. The author has demonstrated on previous occasions that the oxidation of metal cannot take place in the presence of certain alkalies, and therefore these charcoal paints when freshly made are excellent preservatives for the metal. But, inasmuch as moisture is always present in these paints,



No. 33. ARTIFICIAL GRAPHITE (Acheson) — Photomicrograph ×250, uniform in grain.

having been added in the form of water or contained in the raw materials, saponification takes place more or less rapidly, so that the paints are sometimes unfit for use two months after they are made.

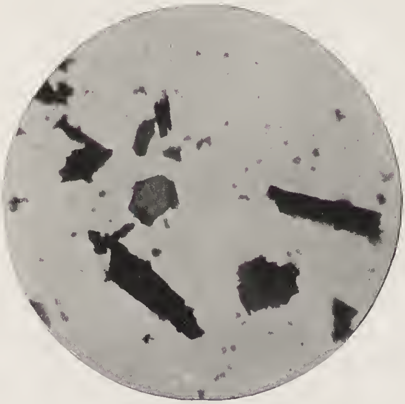
The charcoal above referred to, which is the by-product from the paper mills, while not so suitable for the manufacture of mixed paints, has, however, been very largely used in the manufacture of oilcloth and coated leather.



No. 34. Fine Charcoal — Photomicrograph ×600.

Vine Black

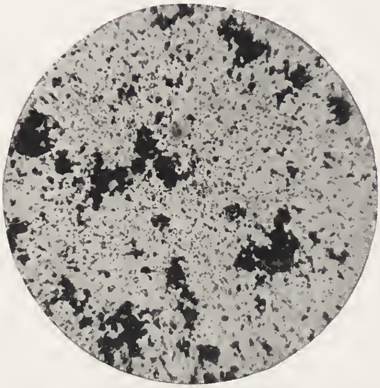
In all essentials this pigment is the same as the powdered charcoals for paint purposes, excepting that the grain is smaller and the black denser. It is made in Germany by charring the grapevine. If overcharred it is likely to become too alkaline. The same tests may be applied to this black which were used for all the charcoal and wood pulp blacks, the simplest and most effective test being to boil the black in water, filter, and add a few drops of phenolphthalein.



No. 35. Charcoal Black — Photomicrograph ×600, showing hexagonal structure of the wood.

COAL

Powdered anthracite and bituminous coal are likewise used in black paints, but the origin of their use is due to some extent to poorly written paint specifications. An engineer will at times prescribe a paint containing a certain percentage of ash, and in order to meet this requirement a paint manufacturer will have to add coal in order to conform with the requirements, but as sulphur compounds such as SO_2 and SO_3 always exist in coal a paint is produced which is exceedingly harmful to metal.



No. 36. VINE BLACK (German make) — Photomicrograph ×250, two sizes of grain.

IVORY BLACK

Ivory black is still used to some extent for very intense coach colors, and there is also a very fine species of carbon black on the market known as the "Extract of Ivory Black," which is made by digesting charred ivory chips in hydrochloric acid until nearly all of the calcium phosphate is dissolved. Such a black has intense staining power, and is by far the blackest material made. It is very expensive, colloidal in its nature, and used therefore for ready prepared color-in-varnish or high grade black enamels.

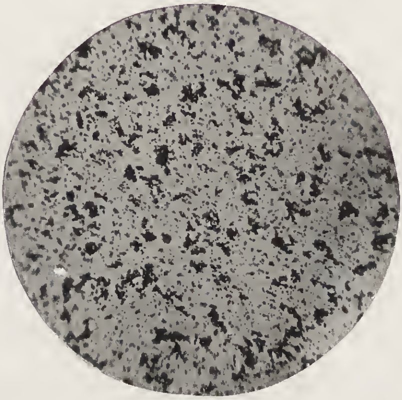
DROP BLACK

Drop black is generally made by calcining sheep bones, which are then impalpably ground in water, and when in paste form cast into small drops; hence its name, "Drop Black." These cone-shaped drops were largely used twenty-five years ago, and then were an indication of a good black, but at present the name "Drop Black" still clings to finely powdered bone black. So-called drop black is generally composed of from 10 to 20 per cent of carbon and from 80 to 90 per cent of calcium phosphate, and is sold entirely for its intensity of blackness.

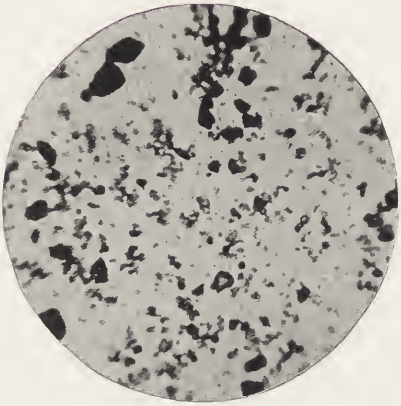
BLACK TONER

Black toners may be either the extract of ivory black, the extract of bone black, or certain forms of carbon black, or carbon black upon which nigrosine has been precipitated. Another method for making black toner is to precipitate red, yellow, and blue aniline upon the extract of ivory black, which produces an intensely black pigment that is flocculent and remains in suspension a long time.

The principal difficulties with these coal tar blacks, however, are: first, they are not really black in the sunlight; and second, they paralyze the drying quality of any varnish with which they may be mixed. There are a number of specially fine blacks that can be used for black toners, such as condensed carbon from benzol or acetylene. Benzol black is remarkably fine and intensely


No. 37. WOOD PULP BLACK — Photomicrograph ×500, very fine uniform grain.

black, and inasmuch as there may be an overproduction of benzol in the United States within the next few years it is very likely that benzol black will become a reasonable article of commerce.



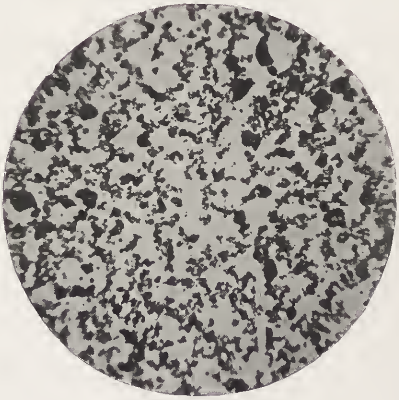
No. 38. Drop Black — Photomicrograph ×300, not very uniform.

Benzol Black

Benzol black is a carbon black which, however, is much better than the carbon black produced from natural gas. It is soft, contains no granular particles, and remains in suspension for many weeks in both oil and varnish. It is, however, a very poor drier, like most of these blacks, and therefore a mixture of litharge and red lead oil is recommended when they are to be used.

Acetylene Black

This black is not quite as common as it was some years ago. It has very desirable properties and can be used for tinting purposes without showing granules or streaks, as is often the case with carbon black made from gas. It is flocculent and somewhat colloidal in nature.



No. 39. Drop Black — Photomicrograph ×300, very finely powdered.

MINERAL BLACK

Mineral black is usually composed of heavy black slate, more or less finely ground, and as a paint pigment is inert. It is often toned with lighter (in specific gravity) carbons and lampblacks, but is not largely used on account of its destructive action on paint mills. Where iron paint mills are used these mineral blacks are found to be very expensive, because they will dull the sharpest mill in a few hours' run. As they possess very little tinctorial power it is more advantageous to use a 200-mesh silica, tinted with lampblack.

CHAPTER X

The Inert Fillers and Extenders

These materials, which at times have been called the "reënforcing pigments," have their value when used in moderate proportions, and yet it is not within the province of any paint chemist to say to what extent these materials can be classed as adulterants and to what extent they can be classed as inert fillers or reënforcing pigments. In every case where this question comes up common sense, judgment, and best practice provide the answer.

In the manufacture of mixed paints, with one exception which will be described later, every mixed paint must contain an inert filler or extender, or else the paint will not remain in a ready-to-use form, but will set hard and lose much of its value. In white paints 45 per cent of zinc, 45 per cent of lead, and 10 per cent of asbestine are regarded as a standard formula, and 60 per cent of these pigments are usually mixed with 40 per cent of oil to produce the proper kind of paint. There are many instances where the inert fillers may reach as high as 20 per cent, that is, to 40 per cent of zinc and 40 per cent of lead or other white pigments, 10 per cent of gypsum and 10 per cent of white mineral primer are added in order to give certain physical results; and yet there are any number of instances where more than half of the paint in question is composed of an inert filler, and the inert fillers under those circumstances cannot be regarded as adulterants. If we make a ready mixed paint of ochre we are taking a natural pigment which contains 80 per cent of clay, and no man can say that the clay naturally contained in ochre is an adulterant. In the manufacture of a flat wall paint in which lithopone is the principal pigment we have a pigment which contains 70 per cent of artificial barium sulphate, and yet no man can say that this artificial barium sulphate is an adulterant. In the Battleship Gray paint which the author devised for the United States Navy, it was found that the 45 per cent of zinc and 45 per cent of lead, with the addition of 10 per cent of black coloring matter, which was formerly used, gave very poor results, for such a paint was not salt-water-proof nor resistant to abrasion; but since the United States Navy has adopted the formula made by the author of 45 per cent of zinc oxid, 45 per cent of blanc fixe, and 10 per cent of graphite and lampblack, a far better paint is produced which costs the Navy very much less money than the old type of paint. It is therefore not within the province of any man to say that the addition of this 45 per cent of blanc fixe constitutes an adulterant. Judgment, common sense, and the particular case involved must therefore decide the difference between pigment and adulterant. A large number of other cases can be cited, but these are sufficient to illustrate the point.

The principal paint made which contains no extender and which remains in suspension is the well-known white enamel paint composed entirely of zinc, in which the medium is either a heavy bodied oil or a damar varnish. This paint needs no extender to keep it in suspension, on account of the very slight chemical action that takes place between the acids in the oil or varnish and the zinc itself.

In spite of all the good qualities of white lead it has been impossible up to now to manufacture a ready mixed paint composed entirely of white lead without the help of an extender like asbestine or a slight saponification or emulsification by the addition of about 1 per cent of water.

It is not so difficult to decide what constitutes an adulteration if we take the simple case of ready mixed white paint intended as a priming coat, which should have the maximum hiding power and physical qualities. If a paint like that were composed of 50 per cent white pigment and 50 per cent of barytes or whiting, it would not possess the physical qualities necessary for a good priming paint, and therefore the addition of this quantity of barytes would be strictly regarded as an adulterant.

The principal fillers used in the manufacture of paints are as follows:

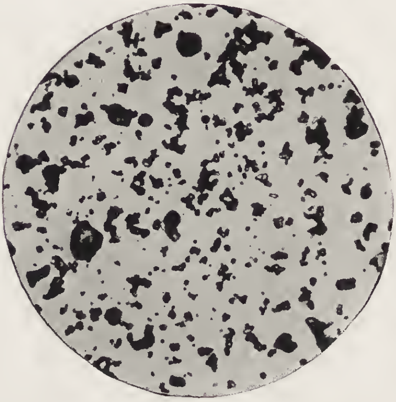
Barytes
Barium Sulphate, (*Artificial*)
Barium Carbonate
Silica
Infusorial Earth
Calcium Carbonate
Gypsum
Calcium Sulphate
Clay
Kaolin
Asbestine
White Mineral Primer
Whiting

BARYTES (BARIUM SULPHATE, NATURAL)

Formula, $BaSO_4$; Specific Gravity, 4.5

Barytes is a white mineral having the same chemical composition as precipitated barium sulphate. In the United States Geological Survey Reports for 1904, the following statement occurs: "The value of barytes as a white pigment is being recognized more and more each year, and although very little, if any, is used alone for this purpose, it is used in large quantities in combination with white lead, zinc white, or a combination of both of these white pigments. This addition is not considered an adulteration, as was the case a few years ago, for it is now appreciated that the addition of barytes makes a white pigment more permanent, less likely to be attacked by acids, and freer from discoloration than when white lead is used alone. It is also believed that barytes gives greater body to the paint and makes it more resistant to the influences of the weather. As is well known, pure white lead when remaining in the shade or in a dark place becomes discolored, turning yellowish, while mixtures of white lead and zinc white, or white lead and barytes, or white lead, zinc white, and barytes retain their color permanently even in dark places."

The amount of barytes that can be mixed with colored pigments without injuring them is remarkably large. There are hundreds of brands of para-red paints made and consumed every year by the agricultural implement trade which contain as high as 90 per cent of natural barytes. When it is taken into consideration that these extremely diluted para-reds cover well and serve their purpose most admirably, the expert should be very careful not to condemn barytes when used in large quantities, for this remarkable behavior is repeated with a large number of other pigments.



No. 40. Barytes, irregular, broken crystals—Photomicrograph ×300.

No paint chemist will dispute the fact that barytes adds wearing quality to paint, but inasmuch as white lead has set the standard for ease of working it is admitted that all the other pigments and fillers are not as unctuous as white lead. Therefore the house painter will notice that the so-called lead combination, which contains large quantities of barytes, does not work as freely under the brush as white lead; nevertheless, this objection does not hold good when the barytes is used in moderate quantities, that is, not in excess of one third of the total pigment of a paint. An experiment was made with a mixture of one third carbonate of lead, one third zinc oxid, and one third barytes on an exposed wall of a high building in New York City, in 1885.[1] Up to 1905 this surface was still in a moderately good state of preservation, and as a comparison a wall painted in 1900 with a pure Dutch process white lead showed that the Dutch process white lead had not stood as well in five years as the combination mixture had stood for twenty years. It is conceded that no paint is supposed to last twenty years, but as a matter of record it is interesting to note that the inert filler added so much to the life of the paint which contained it. In view of this fact, the paint manufacturer is justified in recommending to his customers the use of inert fillers in his paint on the ground of increased longevity.

One hundred pounds of barytes will yield two and three-quarters gallons of paint. Owing to its crystalline structure and specific gravity it is a more expensive pigment to use than many others when sold by volume, and a paint manufacturer who uses barytes in a mixed paint and thinks he is the financial gainer thereby is very much mistaken, owing to the small volume which barytes occupies in a mixed paint. It is also interesting to note from an experimental standpoint that if barytes be mixed with

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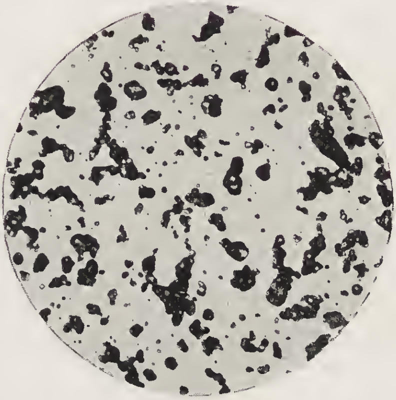
[1] This building was demolished in 1908.

linseed oil and turpentine in the proportion of two pounds to a gallon it will be found that, on allowing these two pounds to settle in a glass jar where it can be observed, it occupies only 4 per cent of the bulk. In spite of much that may be said in favor of barytes, it is not better than some of the forms of calcium carbonate and some of the forms of silica. As an inert extender silica has advantages over barytes; namely, that while it produces the same physical effects with equal wearing quality, its cost is lower and it produces a surface for repainting, having what is technically known as "tooth."



No. 41. Barytes, American—Photomicrograph ×300.

Barytes is made from the mineral barite, and the principal deposits in the United States which are worked at present are in Missouri, Tennessee, and Kentucky. There are also deposits in Virginia and in Georgia, and large amounts are also found west of the Mississippi, but freight plays a very important rôle in the shipping of barytes, and furthermore, only those mines nearest the surface can be worked at a profit. Barytes is not found in ledges or solid masses, but rather in isolated nodules. The pieces vary in size from an onion to a man's head, and vary in weight from one ounce to twenty or twenty-five pounds. There are, of course, larger isolated lumps found, but generally speaking this is the manner in which the material is mined. The mining of barite, as a general rule, is simply done in an open cut, and much of the barytes found in the United States is associated with a material called "chirt," which looks like barytes but can be very easily distinguished on account of its difference in weight. Chirt is a silicate of magnesia and alumina, and workmen very soon become adept in separating chirt from barite. Barite is usually contaminated with iron or with a sticky ferruginous clay, which can be separated by weathering or by washing. Some of the deposits in Virginia and Kentucky contain more than 1 per cent of lime and fluorine, which makes the ore undesirable for manufacturing purposes but is not supposed to render it valueless as a paint base. To free it from iron it is bleached by what is known as the sulphuric acid process, but as it is generally washed, lixiviated, and floated after this treatment it is very seldom contaminated with any degree of acid.

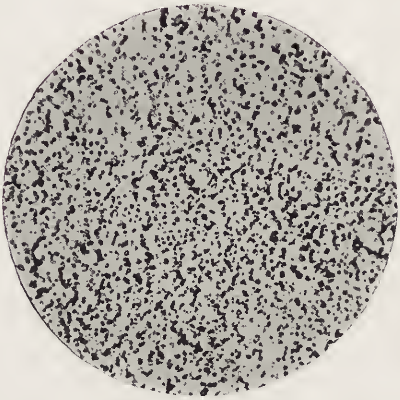
Barium Sulphate (Artificial)

Synonym: Blanc Fixe, Lake Base, Permanent White;
Specific Gravity, 4.1–4.2

When a solution of chloride of barium is mixed with a solution of sulphate of soda a heavy white precipitate is formed which is known as artificial barium sulphate. In all of its chemical qualities it is identical with the barytes of nature, but in its physical qualities it is totally different. Depending somewhat on the method of its manufacture, the grain is exceedingly fine.

Blanc Fixe has for years been used for the surface coating of paper, because when properly calendered it gives a very high polish and a permanent white surface. Originally it was a French product, the words "Blanc Fixe" meaning "permanent white." In the early days of the paper industry various compounds of bismuth were used for coating the paper. There are still visiting cards in existence which were surface-coated by means of bismuth carbonate and bismuth subnitrate. These cards were readily affected by sulphur gases, and when it was found that precipitated barium sulphate produced an equally high glaze and the surface retained its pristine whiteness the name "Blanc Fixe" was universally adopted for the new product.

In the paint industry it was recognized that precipitated barium sulphate was a valuable adjunct in the manufacture of paint, owing to the fineness of the grain and other physical characteristics of the material. It was found, however, that when it was dried and powdered it had lost its extreme fineness and did not mix readily with oil paints. In 1895 Henry M. Toch succeeded in making Blanc Fixe, which, when dry, was a soft, impalpable powder of great value as a base upon which to precipitate lakes, and, likewise, when used in mixed paints and enamels imparted to them, under proper conditions, a vitreous surface which improved their wearing quality. To this product the name of Lake Base was given. A great many paint and chemical concerns have succeeded since then in producing Lake Base of a soft fine texture, and it has become one of the established bases of the paint trade. Its intrinsic value, when properly made, is about half that of American zinc oxid, but a number of writers



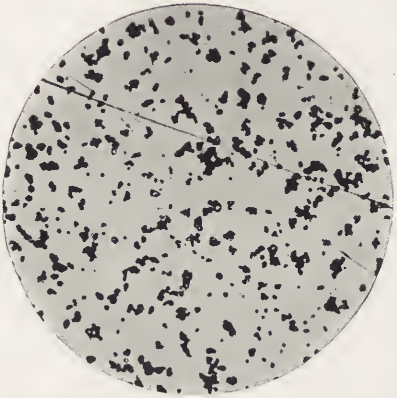
No. 42. Blanc Fixe — Photomicrograph ×300. Precipitated from cold, dilute barium chloride.

have erroneously stated that its body and covering capacity were equal to zinc oxid. Lake Base is successfully used up to 70 per cent in white pigments, and in colored pigments up to 95 per cent. It is amorphous under the microscope, and is used to a great extent to increase the spreading of weaker or coarser colors.

Since 1906 artificial barium sulphate or Blanc Fixe has been used by nearly every paint manufacturer in the United States, for its excellent qualities have been proved beyond a doubt. The value of this material as a reënforcing pigment or filler in the manufacture of paints has been thoroughly demonstrated by the elaborate experiments made by the United States Navy, another indication of how futile it is for any man to say without careful consideration what shall be regarded as an adulterant and what shall be regarded as a pure material. In 1910 the Bureau of Construction and Repair of the United States Navy had come to the conclusion that the Battleship Gray, which had been in use since the termination of the Spanish-American war — a period of about ten years — did not give good results. The formula for the Battleship Gray as it then existed was practically 45 per cent of white lead, 45 per cent of zinc oxid, and 10 per cent of lampblack. From the standpoint of purity this should be regarded as a very pure paint, and from all precedent it should be inferred that a paint of this type would be the best that could be made; but two things demonstrated themselves beyond peradventure. One was that such a paint was not hard enough to resist abrasion; furthermore, salt water in the form of spray or the water itself had a decidedly bad effect. When a paint of this type became wet it absorbed water, changed its color, and became very soft and spongy. The Navy officials most interested in this consulted the author, who devised a paint which then would probably have been condemned by painters in general. Previous experience, however, had taught that the addition of large quantities of artificial barium sulphate or Lake Base to a proper pigment improved the entire value of the paint, to say nothing of reducing its cost over 20 per cent. As a result the formula decided upon by the author was: 45 per cent of zinc oxid, 45 per cent of Blanc Fixe or Lake Base, and 10 per cent of graphite and lampblack. The proper oils and driers were then added. A three months' test was made on the machine repair ship "Panther," and when this ship came back from a cruise it was found that the paint was sufficiently hard so that the anchor chains rubbing against the paint did not abrade it, and that the salt water, wherever it had wet the paint, did not produce any effect whatever. For upward of a year the Navy experimented in a small way painting other ships, until in 1915 as much as several hundred thousand pounds of Blanc Fixe had been bought by the Navy for the manufacture of Battleship Gray. There may come a time when a new paint superior to the present one will be devised, but this much has been absolutely proved —that a mixture of 45 per cent of zinc and 45 per cent of Blanc Fixe for sea water purposes is far better than a similar mixture made of zinc and lead only.

At the time the Navy formula was originated Blanc Fixe was worth about 2 cents per pound, which made a considerable saving to the Navy. At the present writing, owing to the European war and the fact that only one concern is at present manufacturing Blanc Fixe in the United States from American materials, and that the demand is great and the supply small, the price has risen to over $85 per ton. If the price should rise as high as zinc oxid or lead itself, it is quite obvious that in view of the purity of a paint made of Blanc Fixe the question of adulteration could not enter. It will therefore be seen that this question of adulterated pigments is all relative, depending entirely upon the results obtained and upon the cost of the material.

As far as the influence of salt water on a paint made of Blanc Fixe is concerned, the writer had determined long ago that the action of sodium chloride (salt) in the air or in water is one of the causes of the chalking or decomposition of white lead. It must not be understood that the author is condemning white lead as a pigment. This is simply written to show that there are instances when other materials are better for a given purpose.



No. 43. Blanc Fixe — Photomicrograph ×300. Precipitated from hot, concentrated acid solution of barium chloride.

Dry Blanc Fixe is destined to become a very useful paint material. In 1905 there were probably not over 100 tons per year used. In 1915 the use had risen to over 3000 tons per year, because the textile manufacturers had also found that its use in materials like linoleum and table oilcloth not only saved in cost of manufacture over the higher priced pigments, but produced more flexible and lasting materials. The same can be said of the printing ink manufacturers, who today are as large consumers of dry Blanc Fixe as the paint manufacturers.

As regards the manufacture of Blanc Fixe, this has also changed within the last ten years. Formerly it was known that only a solution of barium chloride and a soluble sulphate or sulphuric acid were the raw materials used for making this product, but today there are other methods which produce equally good materials, and in some instances better results than the chloride method. For instance, barium sulphide solution is precipitated with sodium sulphate, yielding a by-product, sodium sulphide, which can be sold at a considerable profit. The Blanc Fixe so made is denser than that made from the chloride. Blanc Fixe is also made from the peroxid of barium and sulphuric acid, but must be neutralized and freed from peroxid of barium before it is suitable for paint purposes. For certain color purposes the material is made from concentrated hot solutions, which produces a crystalline Blanc Fixe valuable for very brilliant colors, particularly greens and reds. Another method used is dissolving barium carbonate in nitric acid and precipitating with sulphate of soda, which then produces a Blanc Fixe equal to the chloride product.

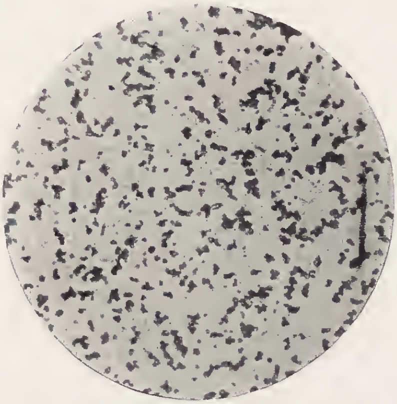
BARIUM CARBONATE

Formula, $BaCO_3$; Specific Gravity, 4.2; Synonym, Durex White

This material is practically new as a paint material, and has only come into use since flat wall paints have had such a tremendous success in the United States; and even at that, not very many manufacturers in the United States use it, although it probably is destined to become as useful an article as Blanc Fixe.

Barium carbonate, under the microscope, has a very peculiar structure. It is not made by mixing a solution of barium chloride and sodium carbonate, although that would be the normal way of making it, but it is made from barium sulphide and sodium carbonate in fairly concentrated solutions, so that the sodium sulphide becomes a valuable by-product, and therefore the barium carbonate can be successfully marketed at a reasonable price.

In hiding power it is between Blanc Fixe and zinc oxid, but when used in the proportion of 45 per cent barium carbonate and 45 per cent of zinc oxid or lithopone in a flat wall paint its physical quality makes it particularly valuable, because the resulting paint with the proper thinners produces a velvet finish unapproached by anything else.



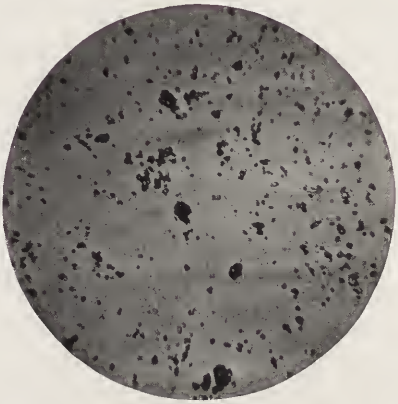
No. 44. Barium Carbonate — Photomicrograph ×300.

Barium carbonate such as is sold for paint manufacture must not be confounded with Witherite, the natural form of barium carbonate. This is not found in the United States, but is largely mined in England, Austria and Germany. Witherite has absolutely no paint qualifications, and is not even as good as barytes. In composition Witherite is identical with the artificial barium carbonate, but under the microscope powdered Witherite is a transparent crystalline material similar in appearance to table salt.

Silica

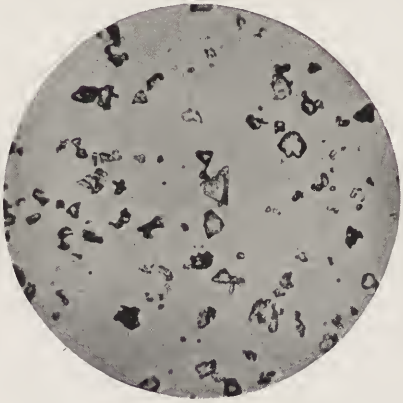
Formula, SiO_2; Synonym, Infusorial Earth, Silex

The introduction of silex in paint is due to the researches and investigations made by David E. Breninig, M.D., who in the early fifties had noted that when white lead was mixed with barytes it stood exposure better than pure white lead. Late in the fifties he came across some rock crystal quartz, and, on grinding and mixing it with white lead, found that it improved the paint. The preparation of silica, especially for the paint trade, became an established industry between 1865 and 1870.



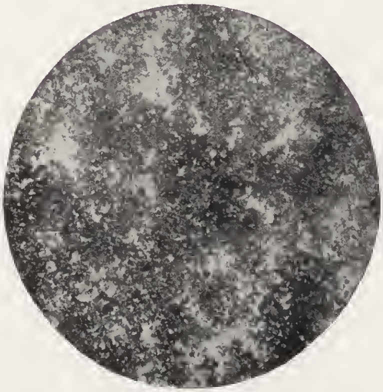
No. 45. Silica, or Silex—Photomicrograph ×250, very fine grain.

The earlier process for powdering quartz was the simple and economical method of dry grinding by the tumbling process. The quartz was simply crushed to a granulated state and then put into a tumbling barrel with pebbles, which was revolved until the silica was reduced to a comparatively impalpable powder. It was found, however, that this method was not satisfactory, because it did not produce uniform results, and the Silex Lead Company, which had been formed for the manufacture of silica or silex for the paint trade prior to 1870, adopted the process of heating the quartz to a visible red heat, plunging it into water, and crushing it after the sudden change of temperature had split the silica into



No. 46. Silica—Photomicrograph ×250, finely powdered and air floated, uniform angular grain.

a finer state of division. The silica was ground in tubs under water with stone bottoms and drag stones, and after it had been thoroughly comminuted it was washed, floated, dried, and then bolted to a given degree of fineness. There can be no question that the preparation of silica in this manner produced a material of great uniformity, the value of which in paint is unquestioned. In the early part of the seventies the first practical tests were made on the coast of Maine. It was found that pure white lead would not stand exposure at the seashore for more than a year. At the end of this time it resembled whitewash and presented a poor surface for repainting. A mixture was made at that time of one third silica, prepared by heating and washing, one third zinc oxid, and one third white lead. These materials were ground together in pure linseed oil and sufficient drier added. At the end of seven years this paint was still in good condition and presented an excellent surface for repainting.



No. 47. Silica—Photomicrograph ×250, very fine grain; this material has been ground in water.

Silica, like many of the inert materials, has the added physical advantage of presenting what is known as a "tooth," which fits it exceedingly well for repainting. Silica is inert as an extender or filler in paint, and does not combine with any other pigment or vehicle. The detection of silica in mixed paints is very easily accomplished by means of the microscope and Nicoll Prism, as the metallic pigments do not polarize. In chemical analysis we often find 1 per cent of silica in an otherwise pure paint. This 1 per cent of silica generally shows up in large arrow-head crystals scattered throughout the field of the microscopic vision, and is due to very small particles of silica which have been worn off from the grinding stones of the mill. The amount of silica which may be safely added to many colored mixed paints without detracting from their covering properties, and which will increase their wearing qualities, is less than one third of the total pigments used.

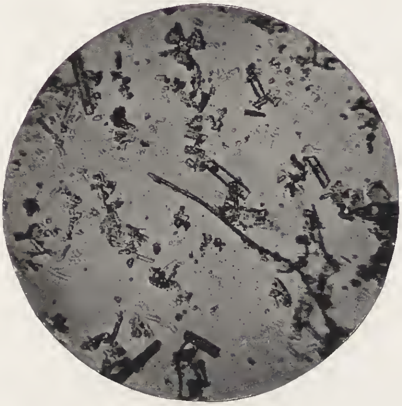
The composition of the various silicas on the market is quite uniform, and those that are made from clear colorless quartz, or faintly colored quartz, are practically free from iron. Silica made from rock quartz will assay 99.7 SiO_2.

Infusorial earth is almost pure silica and is largely composed of the skeletons of diatoms. It is exceedingly bulky, and is used by some paint manufacturers to prevent the settling or hardening of paint in cans, and owing to its light specific gravity it accomplishes this very well when added in even as small a quantity as 10 per cent.

The question comes up occasionally as to whether silica will hydrate when heated and thrown into water. This question must forever be settled by the fact that analyses of silica treated in such a manner show it to contain 99 per cent SiO_2. If any hydration took place it would be evident in the quantitative analysis. There can be no doubt that the silicas obtained on the market which are washed and treated are therefore pure SiO_2. The silicas made from infusorial earth contain a varying percentage of moisture, but the balance is almost pure silica.

INFUSORIAL EARTH; KIESELGUHR; FULLER'S EARTH

Infusorial Earth, Kieselguhr, and Fuller's Earth are forms of silica which are diatomaceous in nature. Diatoms are the remains of plant life — the silicious skeletons — the organic matter having been entirely decomposed, leaving these skeletons. The forms of these skeletons are wonderful, and a number of illustrations will show what they are like. Some are like beautiful chased jewels or filigree work; others are like the covers of boxes made of lace work; and still others are spear-shaped, but all of them have the quality more or less of absorbing dyes. They are not pure silica, for some of them are largely composed of silica and silicate of alumina or silicate of magnesia.



No. 48. INFUSORIAL EARTH — Photomicrograph ×250.

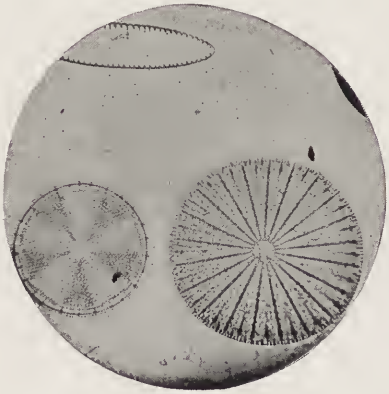
These materials are used both as bases for the lake colors used in making pigments, and for the purpose of preventing the settling of certain classes of mixed paint, particularly the first coats which are not so finely ground. In this respect these materials are frequently substituted for asbestine, because they are more or less free from moisture or water in combination. They can be readily identified under the microscope on account of their very peculiar and beautiful forms.

CLAY

Composition, Silicate of Alumina; Synonym, Kaolin, Fuller's Earth

Clay in small quantities is very largely used by paint manufacturers, first, to prevent settling or hardening of mixed paints, and secondly, to produce unctuousness or good brushing quality. Clay occurs naturally in many paints up to as high as 80 per cent, as for instance, ochre, which is 80 per cent of clay and 20 per cent of coloring matter. The siennas all contain clay up to as high as 60 per cent, and as clay is found naturally in the pigments referred to they cannot, of course, be regarded as adulterated, but when large quantities of clay are added to otherwise good paints the wearing quality is reduced, and therefore more than 10 or 15 per cent is not advisable. Clay always contains a large percentage of water, and the emulsification that ensues probably aids in the non-hardening qualities of paint. In paste paints of the cheaper variety, particularly barrel paints, clay becomes a necessity, for these

No. 49. DIATOMS — Photomicrograph ×500, found in whiting, clay, and infusorial earth.



No. 50. DIATOMS — Photomicrograph ×600, frequently found in whiting.

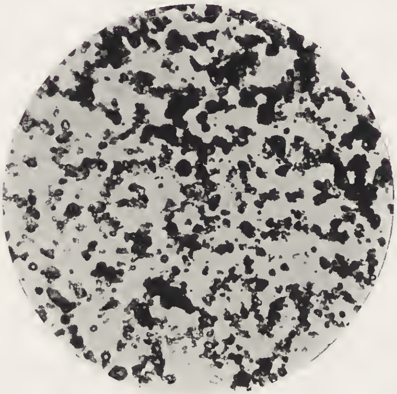
paints are sold at a very low price, and must remain soft indefinitely and easy to mix.

Kaolin is a type of clay which is used by the pottery trade; a typical analysis is as follows:[1]

SiO_2	46.27%
Al_2O_3	38.57%
Fe_2O_3	1.36%
CaO	0.34%
MgO	0.25%
K_2O	0.23%
Na_2O	0.37%
H_2O	13.61%
	101.00%

It has practically the same physical value as the ordinary clay, excepting that the pottery clay is usually whiter in color. Clay has no hiding power or opacity.

Kaolinite, $2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$, is the principal constituent of kaolin.



No. 51. Clay—Photomicrograph ×300.

Asbestine and Asbestos

Asbestine and asbestos are silicates of magnesia, the asbestine having a short fibre and the asbestos having a long fibre.

Asbestos fibre is used to a small extent in paint, but it is not as good as asbestine, because the fibre of asbestos is too long. However, considerable quantities of asbestos are used for the making of so-called "fire-proof" paints, and on this subject it is proper to say that there is no such

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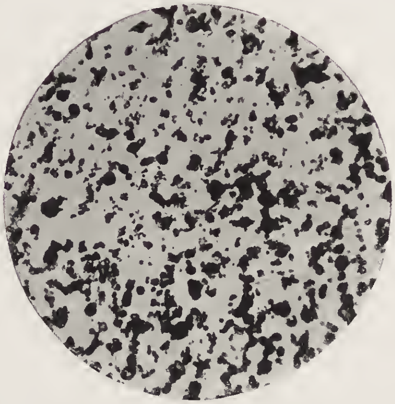
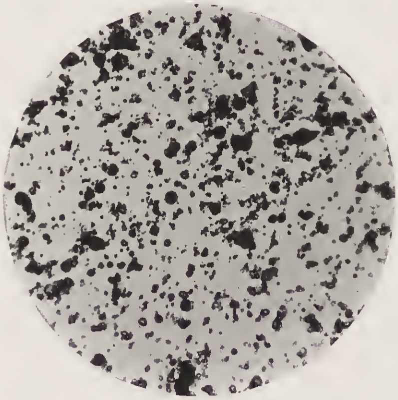
[1] Bull. 351 (U.S. Geol. Surv.), Clays of Arkansas, p. 21.

thing at the present time as "fire-proof" paint. It is perfectly possible to make a fire-resisting paint, but these paints usually are of the casein-whiting type. Casein, lime, phosphate of soda, and whiting, which when mixed with water produce fairly good kalsomine, resist fire for a little while. A typical experiment has always been to take a small shingle, paint half of it with a so-called "fire-proof" paint, and ignite the uncoated part; the fire dies out when it reaches the painted part. This can be done with a piece of wood from $\frac{1}{16}$ to $\frac{1}{4}$ inch in thickness, but no timber or board of any size can possibly be rendered fire-proof by paint application, for when such a piece of wood or timber is subjected to sufficient heat, distillation of the uncoated wood on the inside takes place, gas is generated, and the wood bursts into flame. The only successful method of treating wood to prevent it from burning is by impregnating with alum salts by means of a vacuum process; but this is not painting, because the crystallizing effects of the fire-proofing material destroy or peel

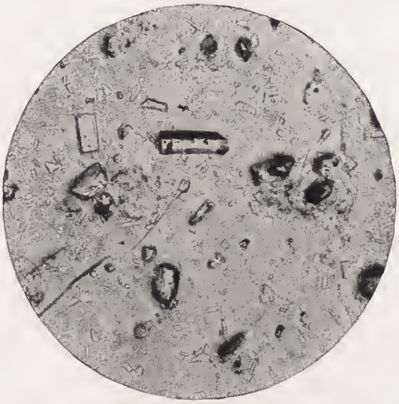


No. 52. China Clay—Photomicrograph ×300.



No. 53. Colloidal Clay—Photomicrograph ×300.

any subsequent paint or varnish, so that up to now there has been no fire-proof paint made which renders wood structures fireproof.



No. 54. Abestine — Photomicrograph ×300.

For the painting of shingles where sparks may possibly ignite them, oil paints containing boracic acid and powdered asbestos are used, as a paint of this type resists sparks.

Asbestos can be very readily identified under the microscope on account of its long fibre.

The average analysis of asbestine is:

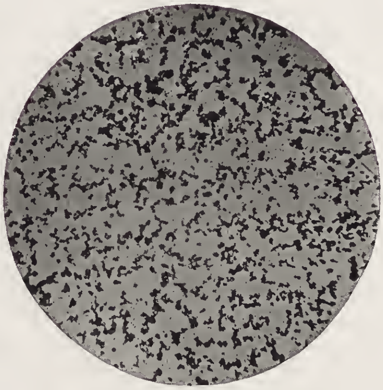
SiO_2	62%
MgO	31%
CaO	3%
Water of Crystallization	4%
	100%

Calcium Carbonate

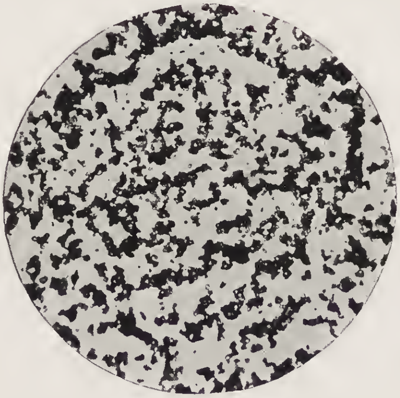
Formula, $CaCO_3$

Synonyms: Whiting, Paris White, Chalk, Marble Dust, Artificial Calcium Carbonate, Spanish White, and White Mineral Primer

Whiting and natural calcium carbonate are prepared from the natural chalk deposits of the cliffs in the south of England, and Paris White, Extra Gilder's White, and Spanish White are all different qualities of whiting, depending on the amount of levigation and fineness of grain. The mode of preparation is very simple. It consists in grinding the cliffstone in water, washing it, and allowing it to settle in large vats. The cream, or that which is nearest the surface, is dried over steam-pipes, bolted, and sold as Paris White. The next layers are sold under the name of Extra Gilder's White, and the bottom layer as Commercial White, of which putty is made. Whiting is a neutral calcium carbonate, and with the exception of the small percentage of water, which is very variable and depends upon how thoroughly it has been dried, it is remarkably pure and fine. The material at the bottom of the tubs known as Commercial Whiting is never used in the manufacture of mixed paint, because it is coarse, contains silica and iron, and in attempting to grind this grade the mills are ruined.

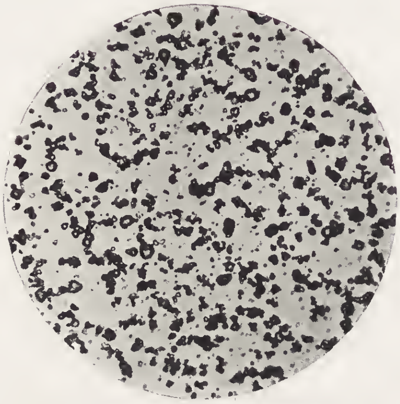


No. 55. Whiting — Photomicrograph ×300, very uniform grain.

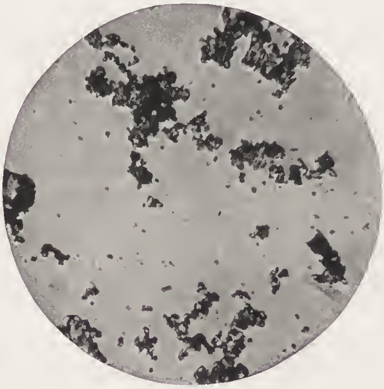


No. 56. Gilder's Whiting—Photomicrograph ×300.

There is a great difference of opinion as to the merits of whiting in paint, but it will be conceded by every manufacturer and paint chemist that the addition of calcium carbonate in some form or other is of great benefit to mixed paint. Some manufacturers put 5 per cent in all the paint they make, excepting that which is made according to specification, for the excellent reason that any acid which may either develop in the paint or be a part of the chemical composition of the paint is slowly neutralized. For paints intended for the protection of metal this practice is to be highly recommended. On the other hand, some writers, who, however, have had little or no practical experience, condemn calcium carbonate in any form because it lacks covering capacity or hiding power. If a paint were made of 100 per cent calcium carbonate this statement would hold true, but where other solid pigments are added the argument against whiting fails. No particular evidence need be brought to bear to prove the durability of whiting, for the reason that all putty is made of whiting and oil, and there are buildings and farmhouses in any number still existing where the putty, after being exposed to the elements anywhere from twenty-five to seventy-five years, is, if anything, better at the end of that period than one month after it was applied. Whiting has the added advantage of being bulky, and priming coats in

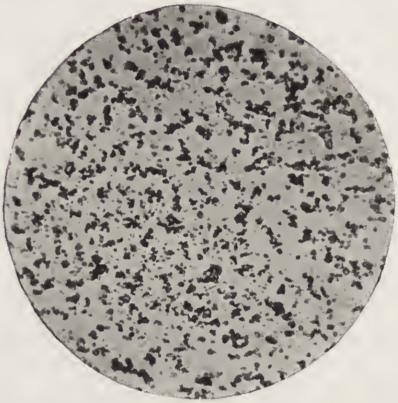


No. 57. Calcium Carbonate (artificial) —Photomicrograph ×300.



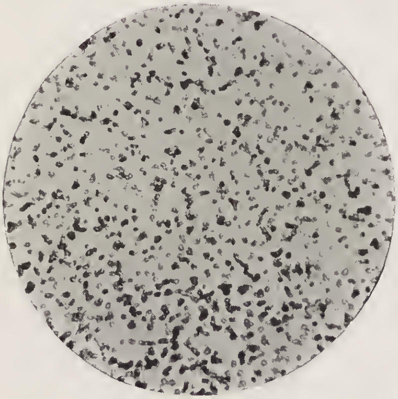
No. 58. Talc (Soapstone) — Photomicrograph ×250.

which it is used present a good surface for repainting. The amount that can be used as an assistant to mixed paint is very variable, depending largely on the pigments used or shade which is made. Where a paint is to be made for the interior of a building in which acid fumes are generated whiting should, of course, be omitted. But there are so many excellent fillers that the use of a single one is not always necessary. Whiting as it is made today is never alkaline, for in the drying process it is placed on steam-pipes and the temperature is so low that decomposition cannot take place.



No. 59. Basic Magnesium Carbonate — Photomicrograph ×300. Extremely light and fluffy.

The other forms of calcium carbonate which are in use are produced by grinding white marble very fine, and, generally speaking, these varieties are better for mixed paint purposes than the whiting made from chalk. In the first place, the ground marble or limestone contains little or no moisture; in the second place, they are ground exceedingly fine, and being angular or crystalline in shape they form a better surface, if anything,



No. 60. Alumina Hydrate, used as a base for printing ink colors— Photomicrograph ×300.

for repainting than whiting; and third, where an absolute chemical composition is wanted they produce more uniform chemical compounds. Whiting and white filler compounds bulk between 3¾ and 4¾ gallons per hundred pounds of dry unit.

There is another grade of calcium carbonate which occasionally appears on the market and is a by-product, principally from soap works. It has all the physical characteristics of a good article, but its chemical characteristics condemn it at once as a paint material on account of the free lime which it contains. It is worthless for the purpose of making putty and useless as a paint filler. When putty is made of it, it forms a lime soap and gelatinizes the contents of the packages.

White Mineral Primer

This is a white crystalline limestone which is found chiefly west of the Mississippi, and more largely used by western paint manufacturers than by eastern, for the freight is against its shipment to eastern points.

In physical structure it is similar to barytes, but of much lighter gravity and greater bulk. For instance, 100 pounds of white mineral primer will yield 4.6 gallons, while 100 pounds of barytes will yield 2¾ gallons. White mineral primer has very little opacity or hiding power, but it has the physical quality of "tooth," and when mixed with zinc or sublimed lead it is superior to any other form of whiting, with perhaps the exception of the artificial calcium carbonate. In many respects it is similar to finely powdered marble dust.

Marble Dust

Considerable marble dust is used in certain forms of paint, marble dust being chiefly composed of calcium and magnesium carbonate with 1 or 2 per cent of ferric oxid. It is a brilliant white, and when passed through a screen of 200 mesh is similar to white mineral primer. Its chief use is for carriage and coach paints and also as a primer for wood generally, because it prevents peeling on account of its structure, having the same properties of "tooth" which are ascribed to silica and white mineral primer.

Spanish White

Spanish White is similar in all respects to powdered chalk, Paris White, or whiting, and at the present time is a name only, for there is little or no whiting for paint purposes that is now imported from Spain, all of it being of the cliffstone variety from England.

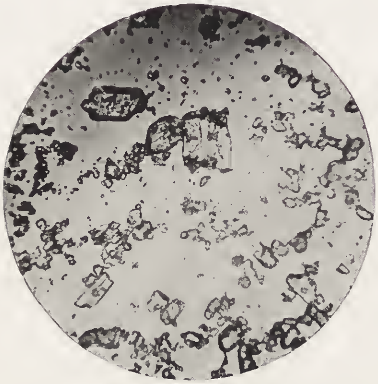
Artificial Calcium Carbonate

This material has already been referred to. It has very excellent properties, but usually has the one great defect, viz. the small percentage of free alkali both of lime and soda which it contains, and this produces "livering" of paints. Wherever it can be obtained in neutral form it is excellent when added in small quantities to many priming paints.

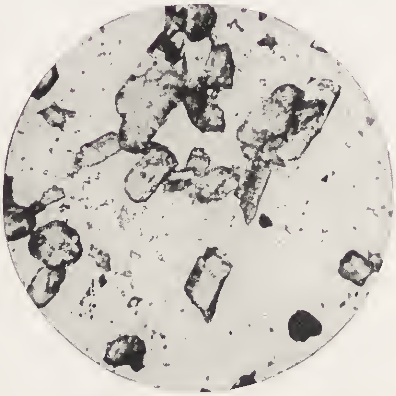
Gypsum

Formula, $CaSO_4 + 2H_2O$

As an inert pigment or filler gypsum is very largely used in the United States. It is found in twelve states and in very large quantities in Canada. Its specific gravity is 2.5 and its formula as cited above is $CaSO_4$ plus $2H_2O$. This formula represents the gypsum of commerce, as sold to the paint trade, so closely that the percentage of water in several samples averaged over 19, whereas the theoretical is 20.2.

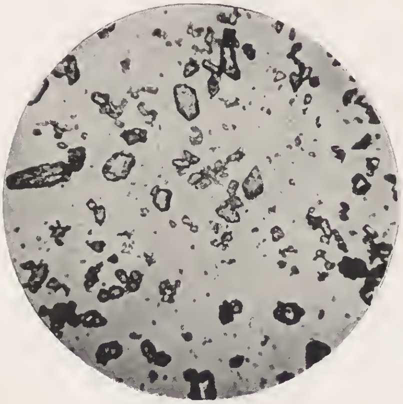


No. 61. American Gypsum — Photomicrograph ×250, fairly uniform and flat crystals.

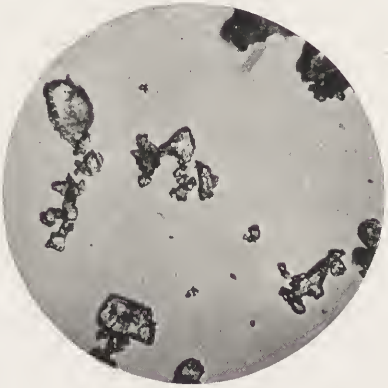


No. 62. American Gypsum — Photomicrograph ×300, transparent flat crystals.

There is a great difference of opinion as to the merits of gypsum as a paint filler, for it must be borne in mind that if it contains any free lime, or if it is not fully hydrated, the lime will act injuriously on the paint and

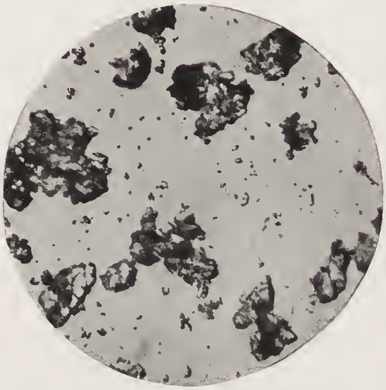


No. 63. American Terra Alba — Photomicrograph 250, very finely powdered.

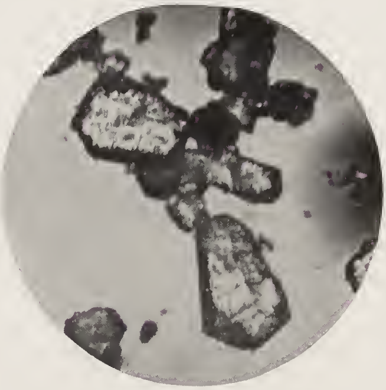


No. 64. Calcium Sulphate (Gypsum) — Photomicrograph ×250 (American).

thicken it unduly. The defect produced by its incomplete hydration will be to take up moisture from other



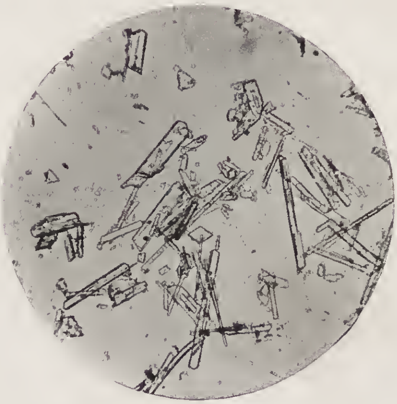
No. 65. FRENCH TERRA ALBA.— Photomicrograph ×250, composition $CaSO_4 + 2\ H_2O$, same as gypsum.



No. 66. TERRA ALBA (French Gypsum) — Photomicrograph ×600, showing crystalline structure of calcium sulphate.

materials in the paint so that a hardening or setting process goes slowly on.

No. 67. CALCIUM SULPHATE — Photomicrograph ×300. Ppted. from cold, moderately concentrated solutions.



No. 68. PRECIPITATED CALCIUM SULPHATE — Photomicrograph ×300. Note the long-fibred crystalline structure.

Some of the gypsum sold in the east is made from alabaster, this being a native, translucent calcium sulphate. The Pennsylvania Railroad in its freight car color permits the use of 70 per cent of gypsum, and as good results have been obtained by this company in the use of calcium sulphate as a filler the condemnation of this material is without much foundation. Due consideration must be given to the fact that thousands of tons of Venetian red are consumed by the paint industry every year, and that the composition of Venetian red will average from 15 to 40 per cent ferric oxid, the balance being entirely gypsum. It is nevertheless true that as one part of gypsum is soluble in five hundred parts of water, excessive rainfall will erode it in a paint, particularly where the binder is easily attacked.

Where calcium chloride is a by-product large quantities of calcium sulphate are artificially made, and many paint manufacturers prefer the artificial calcium sulphate to the natural. The photomicrograph shows this to have a long-fibred crystalline structure, and while it has no chemical properties which are different from the natural gypsum, its purity and physical structure make it valuable for many mixed paint purposes.

Composition of Various Samples of Gypsum

CALCIUM SULPHATE	WATER	PERCENTAGE OF GYPSUM	AUTHORITY
77.45	20.14	94.09	Conn. Exper. Station
77.79	21.39	97.59	Orton, Ohio Survey
78.44	20.76	99.18	David T. Day
77.46	20.46	99.20	G. E. Patrick
79.30	48.84	97.92	E. H. S. Bailey
64.63	18.75	98.14	E. H. S. Bailey
67.91	17.72	83.38	E. H. S. Bailey
71.70	18.68	85.63	E. H. S. Bailey
59.46	16.59	90.38	Okarche Cement Co.
69.92	18.85	76.05	E. H. S. Bailey
69.26	21.50	88.77	Paul Wilkinson
64.22	14.00	90.76	U. S. Geo. Survey
.....	.....	78.22	Wilbur G. Knight
.....	.....	88.80	Calif. Exper. Station
76.02	19.00	72.60	Calif. Exper. Station
77.76	20.28	95.02	G. P. Grimsley
.....	.....	98.04	G. P. Grimsley
76.44	20.02	94.84	Conn. Exper. Station
78.60	20.31	96.46	Conn. Exper. Station
.....	.....	98.91	G. P. Grimsley

CHAPTER XI

Mixed Paints

We have seen from the foregoing chapters the machinery necessary for the manufacture of mixed paints and the raw materials most generally used.

Of all the shades of mixed paints made, the white paints are the weakest and perish the most quickly, and the black paints, particularly those high in carbon and the ferric oxids, are those which last the longest. It is, for instance, impossible to state which of the white paints is the best, and individual opinions or single instances are not permissible for comparison. A test of white lead at the seashore will show that white lead is not as good as other white pigments, and at the same time, in a test in the interior of the country, or where climatic changes are not generally marked, white lead will show up wonderfully well. As an instance of this, it may be cited that the United States Light House Department ordered their white mixed paint to be composed of 75 per cent zinc oxid and 25 per cent white lead, for at the seashore this mixture is better than either pigment alone.

A series of experiments conducted by the author showed that white lead perishes through the action of carbon dioxid in rain water. As soon as a film of oil becomes vulnerable the white lead becomes soluble in the rain water, the so-called chalking being traceable to this cause. Zinc oxid is also attacked by carbon dioxid, but not nearly as quickly as white lead. Sublimed white lead is attacked still less than zinc oxid and zinc lead. The western zincs and leaded zincs, which vary in their proportion of lead sulphate, are slightly more permanent than zinc oxid, but the moment an inert filler such as barium sulphate, either precipitated or natural, silica or magnesium silicate, are added to the white lead and zinc oxid paints, their resistance to atmospheric influence is largely increased. Therefore these inert materials are an improvement to paint, and where no specification is to be followed they cannot be regarded as adulterants. The principal reason why these inert fillers are not added in greater quantities to white paints is due to the fact that the consuming public is not yet sufficiently educated to the use of such materials. Lithopone has proved itself an extremely valuable pigment, particularly for floor paints and for marine paints where shades other than white are demanded. In no sense can the 70 per cent of barium sulphate which is contained in lithopone be regarded as an adulterant, because it is a constituent of the paint itself.

The carbon and graphite paints have wonderful powers of resistance, provided they are properly diluted with a heavier pigment so that the film is thicker. The average graphite paint will cover one thousand square feet to the gallon, but the film produced is so thin that when it once starts to go, either through the abrasive influence of the solid contents of the atmosphere or the decomposing action of water, the surface is soon exposed; but when many successive coats are applied to produce a sufficient thickness far better results are obtained.

The ferric oxid paints strike a happy medium, for they cover from four to six hundred square feet to the gallon; but their color is limited to three shades — red, brown, and black. As priming and second coats they are, however, ideal, and as finishing coats where these shades are admissible they serve their purpose exceedingly well.

No single pigment is as good as a mixture of pigments, and the intelligent combination of the raw materials always produces the best results.

There is continued rivalry between the manufacturers of the lead pigments and the manufacturers of the zinc pigments, both of whom claim superiority for their particular pigments. If you read the advertisements in any of the weekly journals or in the paint magazines you will see after reading one advertisement that only white lead is the best pigment, and after reading another advertisement that only zinc oxid is the best pigment; but competent investigators who are more or less honest hesitate to say that zinc oxid is better than lead, or that white lead is better than any other pigment. As a matter of fact, it is a very difficult thing to decide; a just decision would be that they are all excellent. White lead, of course, stands supreme for hiding power. There is no pigment with the exception of lithopone that will show as much opacity as a single coat of white lead. On the other hand, there is no material that has such wonderful qualifications for enamel-making as zinc oxid, and, as a matter of fact, the only single pigment that can be used and is used for certain purposes is zinc oxid, all the others being unsuited for the manufacture of prepared paints on account of their gravity. It has been contended that white lead alone mixed with the proper oil and driers has stood for many years, and this is quite true; but zinc oxid alone, as a pigment at the seashore, does not give as good results as white lead, because zinc oxid dries too hard; and yet, from the large experiments made by the author, a mixture of the two is unquestionably better than any single pigment, although failures of mixtures are perhaps as frequent as failures of single pigments.

That mixed paints have become a necessity is evidenced by the fact that considerably more than one hundred million gallons have been made in the United States since 1907. The exact amount made at the present time is very difficult to determine, but it has been estimated as being over one hundred fifty million gallons. At the same time, the production of lead has increased, and the production of zinc pigments likewise. Likewise, the production of both the sublimed white lead and of the sublimed zinc and lead of the Ozark type are increasing, and have come to stay, so that the criticisms of the various pigments are more or less a question of commercial rivalry rather than an inherent defect in any of the pigments. They all serve an excellent purpose and all are exceedingly useful.

Many manufacturers of mixed paints guarantee that their paints will stand five years under ordinary conditions in the United States. This guaranty is probably excessive, for there are many details which on their face appear insignificant and are not taken into account by a manufacturer.

The priming of wood has much to do with the life of paint, and a paint that contains much oil or vehicle to which either pine oil or benzol has been added, so that penetration into the wood can be effected, will give much better results than very heavy paints containing only 40 per cent of vehicle and 60 per cent of solids. For the priming of wood this proportion should be reversed and the paint should contain at least 60 per cent of liquids and 40 per cent of solids, to which for raw new surfaces a penetrative solvent like benzol, toluol, or pine oil should be added.

On the other hand, the oxid of iron paints such as Princess Mineral or Prince's Metallic have been known to last twenty years on wooden barns in the country districts; this is undoubtedly due to the fact that a reduced oxid of iron of the Prince's Metallic type is not affected by gases, nor does it react on linoxyn. As cottages, villas, and private residences are never painted a dark brown or a deep red like any one of the ferric oxic combinations, it is therefore proper that this discussion relate entirely to the lead and zinc pigments which are most largely used for the purposes mentioned.

ANTI-FOULING AND SHIP'S BOTTOM PAINTS

Anti-fouling and ship's bottom paints are always sold ready for use, and there are two distinct types,— the copper paints and the mercury paints.

There is a continual difference of opinion among both consumers and manufacturers as to whether the anti-fouling type of paint should be one that does not dry and be of the exfoliating type, which means that it contains lard or tallow and that when the barnacle or seaweed attaches itself it drops off by its own weight, or whether the paint should be of the poisonous type, so that when the barnacle or submerged growth has absorbed a sufficient quantity of the poison it dies and drops off. This is a much mooted question, and there is much to be said on both sides. Naval Constructor Henry Williams of the United States Navy has probably done more work on this subject for the American Navy than anyone else, and his type of paint which contains the red oxid of mercury has undoubtedly given far better results than any other anti-fouling paint. The composition of the paint used by the United States Navy is as follows:

U. S. N. ANTI-FOULING PAINT

6½ gals.	Shellac Varn.	15 lbs.	Zinc Oxid
4 "	Den. Alc.	5 "	Blanc Fixe
2¼ "	Pine Tar	25 "	Indian Red
2¼ "	Turps.	10 "	Red Oxid Mercury
	Yield:	15 gals.	

The copper paints which are found on the market contain from 10 per cent copper scale (copper oxid — Cu_2O) to as high as 40 per cent. As a rule, this is added in a very fine powder to a mixture of linseed oil, pine tar, benzol or gas house liquor, and oxid of iron in some form, usually of the Prince's Metallic type, is added as a pigment for hiding power. This is a so-called red or brown copper paint. The green anti-fouling is generally a copper soap manufactured by saponifying either linseed oil, tallow or fish oil with caustic soda, and then adding sulphate of copper to this soap, which produces an oleate or linoleate of copper and sulphate of soda as a by-product. The sulphate of soda is washed out, the remaining water boiled off, and then pine tar and linseed oil added to the mixture together with chrome yellow and Prussian blue for hiding power. This yields a semi-drying or non-drying type of green anti-fouling, which in many instances has given excellent results, but which in some tropical waters does not show up as well as the oxid of copper paint. The copper paints do not show up as well as the mercury paints.

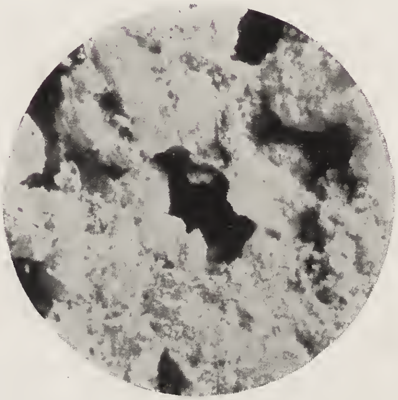
There is a third type which is not a paint, but which is really a soap that is applied hot. Oleate or linoleate of copper mixed with China wood oil when melted and applied to a thickness of about $\frac{1}{16}$ to $\frac{1}{8}$ of an inch has given very good results, and it is stated that this type of copper paint is a happy medium and possesses both the exfoliating and the poisonous qualities so much in demand.

Concrete or Portland Cement Paints

Portland cement is an alkaline rock-like substance, which after it has set liberates lime. The literature is replete with statements that Portland cement floors cannot be painted, and it was not until 1903 that the first successful experiments were made for the painting of Portland cement. Prior to that time all sorts of things were recommended, such as strong acids like sulphuric acid and acetic acid, but it was soon found that the application of acids of this type to Portland cement destroyed the Portland cement because it dissolved out the lime and left the sand and aggregate loosely bound.

Portland cement floors "dust" up under the abrasion of the heel, and until a successful method for painting them was found it was impossible to use them in an uncovered condition. In power houses where delicate electrical machinery was placed the contact points were ground out by the silicious matter floating in the air through abrasion of concrete under the feet. The accompanying photomicrographs show the appearance of a Portland cement floor highly magnified, and indicate in a general way the necessity for painting Portland cement. In warehouses, storerooms and offices generally, concrete floors had to be covered with linoleum or wood to prevent this continual dusting, which became obnoxious. The paints made of drying oils were readily saponified and gave unsightly effects, and it was not until the publication of a patent on this subject (U. S. Letters Patent No. 813,841) that the trade in general began to understand that a resin acid was necessary to combine the lime and not destroy it. Previous attempts had been made depending upon the destruction of the lime, but in this patent it was first shown that a chemical reaction took place and the lime instead of being destroyed was made to serve a useful purpose. A resinate of lime was formed when the coating applied had a sufficient acid number.

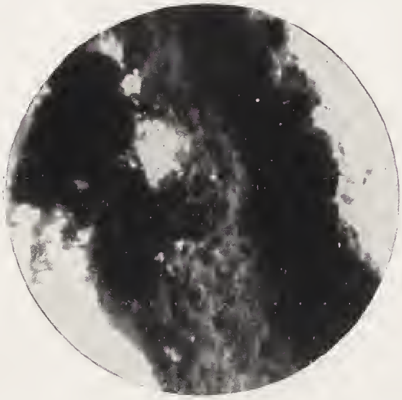
The amount of free lime in concrete is not very great, for in a 1:3 mixture, that is, a mixture containing one part of cement and three parts of sand, the top surface varies in composition from 0.87 to 1.6 per cent of free lime. A large number of analyses were made by the author, and it became obvious that an acid number of 5.0 is sufficient to more than neutralize the amount of lime present, and once neutralized dusting does not take place. It is well known that concrete of any kind and of any mixture is rapidly disintegrated by paraffin or machinery oils and reduced in time. If, however, the cement filler or neutralizing liquid is composed of China wood oil and a hard resin like copal, the resulting calcium resinate becomes insoluble in oil, so that oil dripping on a floor of this kind does not disintegrate the Portland cement. Oil collecting on an unpainted concrete floor will cause the floor to become as soft as cheese in time, and then there is no remedy for it excepting to take up the floor and put down a new one. There is no record that China wood oil and copal had ever been used on Portland



No. 69. Photomicrograph of Portland cement floor composed of 2 parts sand and 1 part cement. This floor is porous and will disintegrate rapidly unless properly treated with a cement floor paint.

cement floors prior to the application in question, and that this patent was new and useful is demonstrated by the fact that there are practically at this writing over forty Portland cement paints on the market, all of them based on the same theory.

In 1910 it was suggested that zinc sulphate be used to overcome the pernicious action of the free lime in Portland cement, and for a time this material had quite a vogue, but it has turned out that no man could tell how much zinc sulphate to use, for no man knew definitely the amount of free lime in any large area of Portland cement, and therefore either too much or too little was used. If too little was used there was still some free lime left; if too much was used sulphate of zinc crystallized out, and when the wall or floor became wet, either through rain or through washing, the film of paint peeled off.



No. 70. Highly magnified view of a fine crack in Portland cement construction — an example of incipient disintegration.

Practically all the paints for Portland cement that are on the market contain either China wood oil or a copal resin or both. Those composed of both of these materials have given the best satisfaction. Where ten years ago there was only one of these paints on the market today there are a large number, and it is estimated that more than a million gallons per year at this writing are used for the surface protection of Portland cement.

PAINT CONTAINING PORTLAND CEMENT

There is only one paint in existence thus far that contains a material equal to Portland cement, which is a tricalcium silicate and dicalcium aluminate, and which on setting liberates lime. This paint is known as "Tockolith," and it has been and still is very largely used among engineers for the protection of steel against corrosion.

The author cannot go into this subject any more deeply because this discovery is his and he is interested in the manufacture of this material, and furthermore, this book is not the place to exploit a proprietary article; but inasmuch as this paint has been regarded by many engineers as at least a step toward the solution of the question of the protection of iron and steel, it is fitting that this brief mention of the material should be made.

DAMP-RESISTING PAINTS

Paints of this character are comparatively new, the first one having been manufactured by the author's firm and put on the market in 1892. It was made for the purpose of coating brine pipes and pieces of machinery which were continually under water. The original paints of this character were produced by melting a good grade of asphaltum and adding a sufficient quantity of gutta-percha together with a suitable solvent and a small percentage of pigment. These paints served their purpose very well and were used very largely, but no matter how carefully compounded the gutta-percha separated from the asphalt base if the paints were allowed to stand for any length of time.

Further experiments showed that cement mortar would adhere most firmly to such a paint. The paint could be applied even to a new brick wall, lathing and furring being omitted. It took such a long time, however, to introduce a paint of this character to the building public that the author's firm never thought it worth while to patent the application.

Damp-resisting waterproof paints are now an adopted fixture in the paint industry, and while bitumen forms the base of paints of this character, treated China wood oil, and treated linseed oil in which glycerine is replaced with a suitable metallic base, should be added when making these paints. They are used widely and in various ways, having served their purpose so well that engineers are beginning to adopt such paints as priming coats for metallic structures wherever cement or cement mortar is to be applied, so that oxidation by electrolytic action may be prevented.

ENAMEL PAINTS

Enamel paints in former years were pigments ground in varnish, which dried with a high gloss. Some people objected to this high gloss, and where a good grade of varnish was used the film was rubbed with pumice stone and water until it produced an egg-shell finish. This then led to semi-gloss enamel paints, and finally we have the misnomer of having perfectly flat enamel paints today, for the very word "enamel" indicates gloss.

For decorative use the principal enamel paints are white, but it must be said at the outset of the chapter that this subject cannot be thoroughly treated in this book. It has become so vast that it would take a book of this size alone to do the subject justice. There are vast quantities of enamel paints made which are colored, but these are principally used for machinery of all kinds, for automobiles and for the so-called enamelling of various utensils, such as tool handles and the like. There are also vast quantities of black enamels made for technical purposes, and these are used for the manufacture of oilcloth, patent leather and mechanical appliances. Those for oilcloth and patent leather are true oil enamels; those for mechanical appliances are principally made on an asphalt base. This chapter will treat of the subject of enamel paints for decorative purposes, which are principally white and mainly based on zinc oxid ground in a varnish or varnish oil.

Prior to the mixed paint era white enamel was made by taking zinc oxid ground in either poppy oil or a bleached linseed oil, and thinning it with damar varnish as it was needed, and the painter did this himself. But as ready for use enamels were demanded improvements were made on this type of material. Today the three types of white enamels are:

First. The zinc oxid types ground in damar varnish.

Second. The lithopone types ground in China wood oil and rosin varnishes.

Third. The zinc oxid types ground in stand oil only.[1]

The damar type first mentioned is simple to make, but produces an enamel which does not flow out, which sets very quickly and which sometimes settles hard in the package and sometimes does not, depending entirely upon the gum damar used for the purpose. There are a great many varieties of gum damar whose acid figure ranges from 8. to 26., but the acid of gum damar is very weak as compared to the acid of the majority of copals, and

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[1] Stand oil has been described on page 176 in the chapter on Linseed Oil.

does not readily unite with a base like zinc; therefore a damar type enamel remains in suspension for several years. For enamel purposes damar varnish is usually cut cold, that is to say, six pounds are dissolved in a gallon of solvent in an ordinary vessel at room temperature; the resulting varnish is always cloudy, due to occluded water in the damar. To remove the latter the cold-cut damar is placed in a steam-jacketed kettle and heated to about 220° with steam under pressure. Steam at atmospheric pressure has a temperature of 212° F., so that at least ten pounds pressure is necessary in a steam-jacketed kettle to drive off the moisture contained in damar; but when this is done the damar darkens unless the operation is carried out in an aluminum or silver-plated kettle. Such solvents like cymene, toluol and xylol are added up to 5 per cent to damar varnish to overcome the cloudiness with fairly good results, but the action is not immediate, and the damar must be tanked for a considerable time.

The second type, or lithopone and China wood oil-rosin varnishes, are very good for household use, but not so good for painting furniture, unless the varnish is made by an expert varnish maker with a minimum amount of rosin and the maximum amount of China wood oil, otherwise varnish of this type becomes hygroscopic in damp weather or sticky in hot weather. White pigments other than lithopone are not recommended for enamels of this type because of the high acid figure of the varnish.

The third type, in which stand oil or linseed oil and zinc oxid are used alone, is the popular type of today, but has the disadvantage of drying slowly, yet this type of enamel will last for many years, and stands exposure even in the American climate for about eighteen months. It is made as follows:

Ten pounds of zinc oxid are ground in ordinary raw linseed oil, and this paste after having been finely ground two or three times is mixed with one gallon of stand oil, and then a gallon or less of turpentine or a mixture of turpentine and turpentine substitute is added. When made in this manner it takes 110° F. of heat four or five hours to dry it so that it is free from tack.

Another method is to grind ten pounds of zinc oxid in japan drier, which may be a drier made of resinate of manganese and lead, and then add ten pounds of this paste to one gallon of stand oil. This will air-dry in five hours, and while it gives good results for interior purposes it is not recommended for exterior use.

A third method of making these enamels is to grind the zinc oxid together with the stand oil in a roller mill, and then reduce with the necessary quantity of diluent and drier and strain very carefully.

All enamels made along these lines have a tendency to turn yellow in the dark. Some, in fact, turn exceedingly yellow — almost the color of beeswax — depending upon the amount of chlorophyll or green coloring matter in the original linseed oil, and no method has yet been devised whereby this can be prevented. Many experiments have been made by the author tending toward improving this with partially good results, such as, for instance, the addition of an oxidizing material like hypochlorite of lime to the enamel.

From the foregoing it is clearly evident that enamel paints may be nothing more or less than pigments ground in boiled linseed oil without the addition of any resin or gum, and the effect produced is that of high gloss and flexibility.

FLAT WALL PAINTS

Flat wall paints have come into existence in the United States, and it is estimated that hundreds of thousands of gallons are now made yearly, and that they give excellent results. Most flat wall paints contain lithopone as a pigment, the photogenic quality of which does not play a great rôle in interior painting. Many of the flat wall paints contain as high as 20 per cent of water in the form of an emulsion, as is the case where the water is admissible in mixed paints; for in England the flat wall paints which are sold under a different name, either in paste form or ready for use, are all white paints containing a small percentage of linseed oil, and are the reverse practically of the American type of paints. They are called washable in England when they are washed from the bottom up, for when they are washed from the top down and the water streaks the wall there is danger of dissolving some of the paint and producing a bad effect; whereas the American types of wall paints, even those that contain 20 per cent of water, withstand the action of washing either from the top down or from the bottom up. There are, of course, many types which contain no water, the principal vehicle for this type of paint being a semi-fossil damar mixed with linseed oil or more generally a rosin-China wood oil varnish containing over 50 per cent of solvent.

Many of the failures of the flat wall paints which peel and disintegrate are due to the sizing on which they are painted. Glue, shellac or cheap varnish sizings are generally worthless on plastered walls, while an oily resin acid type of filler gives results which are permanent.

Floor Paints

Wooden floors are painted as a rule with a varnish paint which dries hard over night and produces a wear-resisting waterproof surface. In composition, paints for wooden floors are analogous to paints for concrete floors, and are composed of a minimum amount of oil which dries by oxidation and a maximum amount of hard resin varnish. The rosin varnishes, particularly those of the China wood oil type, do not wear as well as the hard resin varnishes.

The pigments used in floor paints do not play a great rôle. Numerous experiments made show, for instance, that zinc oxid is not a useful pigment for the reason that the acid number of a floor paint varnish is sufficiently high to combine with the zinc and form an unstable paint — one which thickens up in the container and becomes unfit for use in a few months. Therefore lithopone is found very useful, and the inert pigments are preferred also for this reason.

Shingle Stain and Shingle Paint

Shingle stain is not to be confounded with shingle paint. A stain for shingles is translucent; a paint for shingles is opaque, and the difference between the two is quite marked. One shows the grain of the wood, and the other gives a painted effect and does not show the grain. There is hardly any difference between shingle paint and the average ordinary mixed paint, with the exception that some manufacturers add asbestine in order to give it some fire-resisting quality. On this point it is well to mention that shingles that are painted, particularly with a paint that has a fire-resisting quality, are superior to those coated with shingle stain, even though they may not look as artistic, because sparks flying from a chimney on a roof that has been stained and has thoroughly dried out are very likely to ignite the roof.

Shingle stain is generally made from the very brilliant pigments and crude creosote. These pigments are as a rule ground in linseed oil, and two pounds are generally added to a gallon of creosote. Ordinary creosote oil is used for this purpose, probably because it has some wood preservative quality. Other manufacturers use ordinary kerosene and take two pounds of the strongest colors in oil that they can get. Still other manufacturers use crude carbolic acid or crude cresol and kerosene, but in spite of all these treatments shingles rot just the same. It is the soft pastel effect which a shingle stain gives that commends it so highly; but the same pastel effect is produced with shingle paint after the lapse of a year or two, provided a good paint is properly reduced with about 50 per cent of volatile solvent.

On new work shingles are generally dipped. A bundle is taken and dipped into a barrel and allowed to soak so that the wood will absorb all that it can. On old work, of course, it must be applied with a brush.

Asbestine is frequently added in the proportion of one pound to the gallon of shingle stain containing heavy colors to prevent them from settling. One of the most difficult shingle stains or shingle paints to produce is a permanent red. For this purpose the oxids of iron (Fe_2O_3) are used, but wherever oxid of iron is exposed to the sunlight in the presence of linseed oil or other organic oils it probably changes to a ferroso-ferric condition, becomes considerably darker and is converted into a brown. This is less noticeable in a shingle stain than it is in a shingle paint, because the shingle stain is largely composed of a volatile solvent, and the small amount of binder has relatively a lesser action than the binder in the shingle paint. It has been suggested, and there is probably some value to the suggestion, that potassium dichromate to the extent of one ounce to the gallon should be ground in crystalline form with the paint in order to prevent any reduction. Hypochlorite of lime has also been suggested, and of the two the hypochlorite would be the better as long as it would last, because it would not wash out and be likely to stain the building. Dichromate would be very likely if it ran over the gutters or leaders to produce a bad stain.

CHAPTER XII

LINSEED OIL

THIS oil is still the principal oil used in the manufacture of paints, and within the last ten years very extensive work has been done on the constants and specifications for linseed oils generally, as will be noted from the reports of the American Society for Testing Materials and several other reports quoted by the author.

The raw linseed oil produced in the United States comes principally from the northwest. The foreign oils come from Calcutta, the Baltic, and the Argentine regions. There is considerable difference between these oils, the Baltic being perhaps the best and very highly prized by varnish makers.

The constants of linseed oil show very wide variations; for instance, its specific gravity will run from 0.931 to 0.935. Its iodine value will vary from 160 to 195 or more, while the saponification value will run between 190 and 196. The greatest differences are found in North American linseed oil, the figures being sometimes so perplexing that it is difficult to reconcile them with the standards of Baltic oil. These discrepancies are easily traceable to the natural impurities found in American linseed oil, as, for instance, oils from weeds growing in the flax fields. American linseed oil is likewise inclined to show the presence of water to a greater extent than foreign oils, but this, however, is a question of age. If raw linseed oil is allowed to settle until it becomes perfectly clear and shows no sediment or turbidity at 0° C., it cannot be said to contain water. The question here naturally arises as to the use of the term "pure." Calcutta and the Baltic seed are freer from foreign seeds than the American product, and although the amount of foreign seeds which appear as weeds in the field is very small, their presence alters the chemical and physical characteristics of the American oil. Taking Baltic as a standard, it could be reasonably argued that American linseed oil is adulterated, yet no man would have a moral or legal right to condemn American linseed oil because it differed from the Baltic. On the other hand both climate and soil have a well-known influence on vegetation; even the percentage of oil derived from a given seed cannot be said to be constant. It is also stated that virgin soil produces better seed than a replanted field and this statement appears reasonable.

To how great an extent the natural or negligible admixture of the oil from foreign seeds to linseed oil affects the wearing quality of the oil, it is impossible to say, but it must be admitted that an oil containing up to 3 or 4 per cent of the oil of foreign seeds or weeds will not act as well in the kettle for varnish or boiling purposes as a purer oil. Taking these facts into consideration, a chemist must beware of giving an opinion as to the quality of linseed oil, and where there is no evidence either chemical or otherwise that the oil has been intentionally diluted with other materials no adverse opinion should be forthcoming. If the examination of linseed oil shows an appreciable percentage of paraffin oil, it can be positively inferred that no weed growth had anything to do with this adulterant and the mixture must be regarded as intentional or accidental.

Raw linseed oil is extracted from the seed by the old-fashioned method of grinding the seed, heating it, placing it between plates and then pressing it until the remaining cake contains the least possible quantity of oil. The newer method is a continuous process by which the seed is ground and forced in screw fashion through a tube, the oil oozing slowly through an opening in the bottom of the tube and the cake falling out at the end in flakes. When the seed is fed in this manner without heating, a better quality of oil results. The third method consists in crushing the seed and extracting the oil by means of naphtha. The resulting liquid is evaporated, the naphtha recovered and the oil sold for painting purposes. It appeared, however, that this process, while very profitable for the manufacturer, was not profitable for the consumer, and although it made a very fair paint oil, it was found that for the purpose of coating leather, oilcloth, and window shades, the oil had the unfortunate faculty of soaking through the fabric, and when a piece of goods was rolled up too soon and allowed to stand for the greater part of the year it was almost impossible at the end of that time to unroll the goods, the whole having become a solid mass. Investigation showed that some of the proteids in soluble form were extracted by the naphtha. This was called "new process oil," and it was generally understood that cake made from new process oil was not as good cattle feed as cake made in the old-fashioned way, probably on account of the removal of part of the proteids.

If linseed oil were uniform, both as to source and nature of seed, a chemical formula could be established for it, but because it is not uniform the acids cannot be given in quantitative relation. Linseed oil should give no test for nitrogen; if it does, the proteids in the seeds have been attacked. Probably 95 per cent of all the linseed oil made is sold in the raw state, and, strange to say, probably 95 per cent or over of all the linseed oil used is consumed in any other but the raw state. It must not be inferred that all paint manufacturers manipulate or treat their linseed oil by heat and other methods of oxidation, for, while many of them claim to do so, not one that the author is acquainted with could afford to handle and manipulate linseed oil. At the same time, raw linseed oil cannot be used for the purpose of making paints unless a drier be added, and from the very moment that the drier, either in the nature of a siccative oil, resin, or Japan, is mixed with the oil, the chemical constants of the oil are altered. The change is an irreversible reaction. As an example, it may be cited that if 90 per cent of linseed oil be mixed with 10 per cent of volatile constituents and Japan driers, the chemist cannot separate the three substances and produce three vials containing raw linseed oil in the state in which it was used, and the drier in an unaltered condition. The volatile solvent, if it be benzine, is the only one of the three that can be recovered in any approach to its original condition.

The literature on raw linseed oil is very incomplete, and more attention should be paid by chemical experts and writers to the subject of identification of linseed oil as it really exists in the paint.

In the chapter on the "Analysis of Oils" it will be seen that when the iodine number of an oil is 180 the same oil when extracted from mixed paint may show 110 and still be absolutely pure, for the reason that the metallic salts which have been added to the oil in the form of Japan or other siccatives have in a measure saturated some of the bonds of the linseed oil, so that less iodine or bromine is absorbed.

Linseed oil dries by oxidation, and this oxidation is hastened by the addition of bases or salts of lead and manganese. There is no doubt that some of these act catalytically, and there is likewise no question that some of these driers continue to act long after the oil is physically dry. In drying, raw linseed oil is supposed to absorb as much as 18 per cent of oxygen, but in actual practice where solid linseed oil is used as an article of commerce it seldom absorbs more than 10 per cent of its original weight. The addition of a drier has much to do with the life of a paint, there being no two driers that act exactly alike. If it is the intention of the paint manufacturer to make a paint that will last the longest, he must study the chemical and physical characteristics of the drier which he uses. Red lead (Pb_3O_4) added to linseed oil at a temperature up to 500° F., will make a very hard drying film which in time becomes exceedingly brittle. This can be very easily demonstrated if the red lead oil be coated on cloth and its effect closely watched. On the other hand, the addition of litharge to linseed oil produces the opposite effect, and an exceedingly elastic film is produced. The various manganese salts all act differently and are frequently used to excess. Manganese starts the drying operation, the lead salts continue it, and the manganese again hastens the end. Borate of manganese is, perhaps, the least objectionable of all manganese salts, but the black oxid or peroxid is most largely used, and if not used in excess is an exceedingly valuable assistant in the drying of linseed oil.

These driers are usually prepared by adding the oxids of lead and manganese to melted rosin. After a resinate of lead and manganese is produced, a small quantity of linseed oil is added and the mixture then cooled either with turpentine or benzine or both. There are hundreds of varieties of the so-called Japan driers, the best ones containing the minimum amount of rosin and a certain percentage of the dust of Kauri gum. The oil driers are made in a similar way, excepting that no rosin is used, and these driers do the least harm. Lime is very frequently used in addition to oil, sometimes in conjunction with rosin and sometimes alone, in order to produce a drying effect. The so-called lime oil will dry with a hard and brittle film. The salts of lead and manganese are not as good for mixed paint purposes as they are for technical purposes. The chloride of manganese when added to linseed oil reacts upon it, and in the presence of any moisture in the oil will liberate traces of hydrochloric acid. Sulphate of manganese and lead acetate will act similarly, and wherever there is a trace of liberated acid in paints their rapid and uniform drying is interfered with. Zinc sulphate and lead sulphate are also excellent driers. It is considered good practice to add a small amount of calcium carbonate wherever these driers are used in order to neutralize the acidity, and when this is done no ill effect can be observed. Probably the most flexible drier is Prussian blue, which is soluble in linseed oil at 500° F., and produces such a flexible film that the patent leather industry is based upon it.

Some twenty-three years ago the author manufactured a new drier which is an improvement on Prussian blue. Briefly described, this drier is made out of a by-product Prussian blue which is treated with an alkali in the presence of calcium oxid and water. A brown powder is the result, which has no uniformity of color but has given excellent results as a drier. This brown has been erroneously called "Japanners Prussian Brown," or Japanese brown. It is soluble in linseed oil at 500° F., and produces a film which is neither too hard nor too soft, but remarkably elastic and admirably adapted for making certain paints and varnishes. It cannot, however, be said to replace any of the good linseed oil driers for mixed paints, where too flexible a paint is not desirable, particularly on steel work or exterior work, as blisters are likely to result from the difference in expansion. However, as a base for the manufacture of enamel varnishes and oils this drier has proved itself admirably adapted.

Linseed oil is a glyceride of several fatty acids, and Lewkowitsch has proved that water will replace the glyceride radical and hydrolize the oil. (See "New Paint Conditions Existing in the New York Subway" by Maximilian Toch, Journal of the Society of Chemical Industry, No. 10, Vol. XXIV.)

The action between a fat and a caustic alkali in boiling solution, by which a soap is formed and glycerin set free, is too well known to need further discussion. The fatty acids which are combined with the soda can be liberated by the addition of almost any mineral acid to the soap. This saponification can be produced by the action of water alone on raw linseed oil. Where a paint contains lime or lead this hydrolysis probably is hastened.

We have here an excellent explanation of the so-called porous qualities, or non-waterproof qualities, of linseed oil as a paint, which is further brought out by the fact that when linseed oil is treated with Prussian blue or Japanners Prussian brown it cannot be hydrolized by means of water, for the acid radical has formed a complete compound with the iron in both of these driers, and the prolonged heating has volatilized the glycerin. Consequently, when a paint is made by the treatment of linseed oil at a temperature of over 500° F., with a neutral and soluble base like the ferri-ferro cyanide of iron, the resulting film is not linseed oil nor a linoleate of any base with free glycerin, but a complex compound composed of the various linseed oil acids united with iron. This gives us the basis of waterproof paints. This is evident from the quality of patent leather, which is not only much more flexible than any paint made in the ordinary way, but is likewise waterproof.

The following are the probable formulas for linseed oil in its various stages:

$$\mathrm{C_3H_5} \left\{ \begin{array}{l} \mathrm{C_{16}H_{26}O_2} \\ \mathrm{C_{16}H_{28}O_2} \\ \mathrm{C_{18}H_{32}O_2} \end{array} \right\} \text{Raw linseed oil.}$$

$$\begin{array}{l} \mathrm{Pb} \\ \mathrm{C_3H_5} \\ \mathrm{Mn} \end{array} \left\{ \begin{array}{l} \mathrm{C_{16}H_{26}O_2 + O_n} \\ \mathrm{C_{16}H_{28}O_2 + O_n} \\ \mathrm{C_{18}H_{32}O_2 + O_n} \end{array} \right\} \text{Japan and linseed oil.}$$

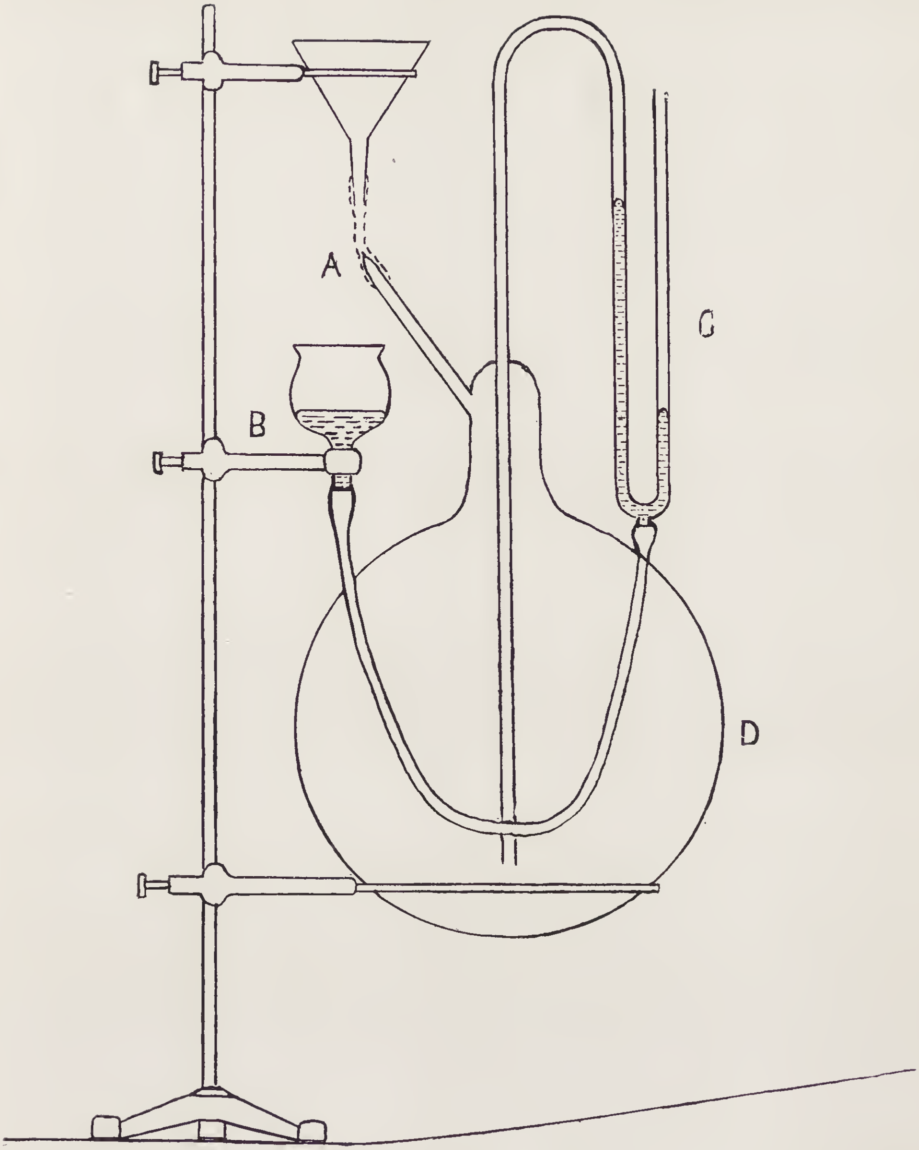
$$\begin{array}{l} \mathrm{Mn} \\ \mathrm{Pb} \end{array} \left\{ \begin{array}{l} \mathrm{C_{16}H_{26}O_2 + O_n} \\ \mathrm{C_{16}H_{28}O_2 + O_n} \\ \mathrm{C_{18}H_{32}O_2 + O_n} \end{array} \right\} \text{Boiled or varnish oil.}$$

$$\mathrm{Fe} \left\{ \begin{array}{l} \mathrm{C_{16}H_{26}O_2 + O_n} \\ \mathrm{C_{16}H_{28}O_2 + O_n} \\ \mathrm{C_{18}H_{32}O_2 + O_n} \end{array} \right\} \text{Waterproof oil.}$$

There are questions in regard to the physical and chemical characteristics of linseed oil on which there has been considerable discussion and naturally a difference of opinion. The first is whether linseed oil dries in a porous film, and the second is whether linseed oil while drying goes through a breathing process during which it absorbs oxygen and gives off carbonic acid and water. With reference to the porosity of the dry film of linseed oil, the following extract is made from the Journal of the Society of Chemical Industry (May 31, 1905, "New Paint Conditions Existing in the New York Subway" by Maximilian Toch).

"In a paper before the American Chemical Society on March 20, 1903, I gave it as my opinion that a dried film of linseed oil is not porous, excepting for the air bubbles which may be bedded in it, but that any dried film of linseed oil subjected to moisture forms with it a semi-solid solution, and the moisture is carried through the oil to the surface of the metal. We then have two materials which beyond a doubt have sufficient inherent defects to produce oxidation under the proper conditions, and granted that the percentage of carbon dioxid in the air of the tunnel is not beyond the normal, the fact that carbon dioxid together with moisture would cause this progressive oxidation is sufficient warrant for the discontinuance of paints that are not moisture and gas proof. Dr. Lewkowitsch demonstrated in his Canton lectures that the fats and fatty oils hydrolized with water alone, and linseed oil is hydrolized to a remarkable degree in eight hours when subjected to steam. It can, therefore, be inferred that water will act on linseed oil without the presence of an alkali, and that calcium added to water simply hastens the hydrolysis by acting as a catalyser. This, then, bears out my previous assertion that a film of linseed oil (linoxyn) and water combine to form a semi-solid solution similar in every respect to soap, and inasmuch as we have lime, lead, iron and similar bases present in many paints, it is almost beyond question that these materials aid in the saponification of oil and water."

If a drop of linseed oil is spread on a glass slide and one half of it covered with a cover glass, it will be readily seen under the microscope that the dried film is as solid as the glass itself, that there are no pores nor any semblance to a reticulated structure visible in the oil, and the author therefore makes the statement with



No. 45. D is a glass flask of about 2 litres capacity. Through the tube A 3.4 grams of refined linseed oil, which had been heated to 400 degrees F. for one hour, were introduced and well distributed over the inner surface of the flask. Dry oxygen free from CO_2 was blown through the flask, by means of tubes A and C, until the flask contained pure oxygen. The tube A was then sealed, as shown in sketch, mercury brought up into the manometer by elevating B to the position shown. The flask was then filled with oxygen at atmospheric pressure and effectually sealed. As drying proceeded and oxygen was absorbed, the diminished pressure was read off on the manometer. When this became constant the funnel which was connected to A by a rubber tube was filled with filtered Barium Hydrate solution, and the point at A broken, allowing this to run into the flask without admission of air. In a few minutes Barium Carbonate was formed, showing conclusively that some CO_2 had been generated by the oil.

absolute certainty that linseed oil dries with a homogeneous film in all respects similar to a sheet of gelatin or glue.

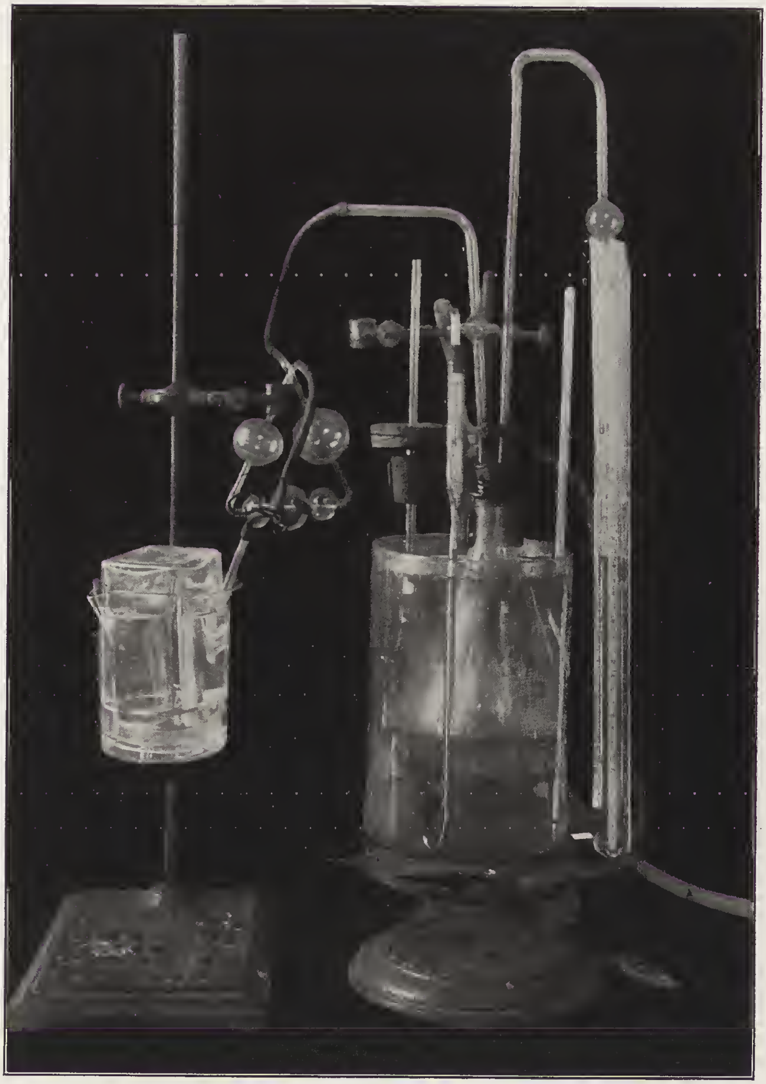
The question as to whether linseed oil goes through a breathing process, absorbing oxygen and liberating carbon dioxid and water, is one of great importance and one which the author has worked out very carefully with positive results. In the illustration a piece of filter paper two inches in diameter was dipped in linseed oil of known purity and suspended in a flask in air absolutely free from CO_2 and water. Investigators have always complained of the inability to obtain tight joints in an experiment of this kind, and in order to be certain that there was no leakage all joints were covered with mercury after having been first shellacked. The manometer gave a curve which indicated the drying, a thermostat being a part of this instrument, so that absolutely uniform conditions were obtained. At the end of thirty days the drying curve was obtained, and when the baryta water was led into the bottom of the flask there was hardly a trace of turbidity to be noted. This experiment was repeated many times, always with the same result, and the amount of water or moisture obtained could not be weighed. It was therefore reasonable to conclude that the linseed oil gave off neither CO_2 nor water, but had absorbed oxygen.

The author, however, concluded that this experiment was entirely too delicate, inasmuch as only one gram of linseed oil was absorbed by the paper. Therefore, an apparatus was devised as shown in the illustration, without joints and so absolutely air-tight that the question of leakage could not arise. The flask was filled with linseed oil and then emptied by replacing the oil by air free from water and CO_2, the inside and bottom of the flask being left heavily coated with linseed oil which had been previously heated to 400° F., for one hour. The manometer tube formed a part of this apparatus, and when the oil had dried completely (which was manifest by its wrinkled and bleached appearance and likewise by the manometer indication) a rubber tube was attached to the point E, a funnel inserted, and a filtered solution of barium hydrate was allowed to run in as soon as the tip E was broken. After ninety seconds the solution of barium hydrate turned milky, showing conclusively that CO_2 had been generated in the drying of linseed oil.

The next experiments were made quantitatively, and while the amount of moisture could not be accurately measured, the amount of carbon dioxid was in no case higher than $\frac{8}{10}$ of 1 per cent, whereas the absorption of oxygen was 19 per cent. It must therefore be admitted that linseed oil does give off CO_2, but the quantity is relatively so small that it is a question whether it should be taken into account at all.

It is now a known fact that carbon dioxid acts as a rust-producer on iron or steel, and if linseed oil gave off any appreciable quantities of CO_2 and water they would act as rust-producers in themselves rather than protectors; and while it may be possible that some linseed oils give off more of these two substances than others, the amount under normal conditions cannot be very great, as these experiments show.

Refined or bleached linseed oil is used to a very great extent for the manufacture of white paints. The methods employed for bleaching linseed oil have not undergone very much change until lately. The coloring matter in linseed oil is largely chlorophyll, the bleaching of linseed oil depending not on the extraction of this chlorophyll but on its change into xantophyll, which is yellow.



No. 46. DETERMINATION OF CO_2 AND H_2O IN DRYING OF LINSEED OIL — A piece of filter paper was immersed in pure linseed oil, and, after the absorbed oil was weighed, the filter paper was suspended in the Erlenmeyer flask, on the bottom of which was a solution of Barium Hydrate (free from CO_2) to absorb the CO_2 formed by the drying of the oil. The flask was immersed in a water-thermostat, the water of which was stirred by a revolving mechanical stirrer. A thermo-regulator, by means of which the gas-flame under the thermostat was automatically regulated, was placed under the flask. By opening the glass-cock, oxygen was admitted from time to time to the Erlenmeyer flask, and the absorption of oxygen was read on the mercury-manometer. The readings were always made at the same temperature. The oxygen, before entering the Erlenmeyer flask, was passed through the KOH bulb, where it was washed free from CO_2. This experiment was conducted in triplicate with great care, the joints being all sealed with shellac and placed under mercury. No CO_2 or H_2O beyond a trace could be determined, owing to the small quantity of linseed oil which the filter paper contained.

Sometimes linseed oil will have a reddish cast instead of the usual greenish cast. This color is attributed to another form of organic matter known as erythrophyll. These three tints, the green, yellow, and red, are analogous to the tints in autumn leaves.

All methods for extracting chlorophyll from linseed oil have proved extremely difficult and expensive. The accepted method, therefore, has consisted in the treatment of linseed oil with an acid in order to convert the green coloring matter into the yellow. This is probably the reason why no linseed oil exists which is water white, although the author has made several samples which are almost colorless, but when compared in a four-ounce vial with chemically pure glycerin it can readily be noted how far from colorless the so-called bleached linseed oil is. The method employed for bleaching linseed oil consists in the addition of sulphuric acid and the blowing of air into the oil at the same time. The oil becomes cloudy and develops small black clots. When this cloudiness is allowed to settle out, or the oil is filtered through a filter press, it is very much paler in color, and is then known as refined or bleached linseed oil.

Sunlight has a similar effect, the oil produced by bleaching with light and age being superior in quality to the sulphuric acid oil. In the sulphuric acid treatment the oil, the water, and "foots," together with an appreciable amount of emulsified oil, settle to the bottom of the tank. These are drawn off, and are of some value for making cheap barn paints by mixing with lime and the oxids of iron. In another method, which produces a still better bleached oil, chromic acid is used. If a solution of this acid, which is blood red, be added to linseed oil, and the mixture agitated, a very much paler and more brilliant oil is obtained, but it is rather expensive to produce. The treatment by means of an electric current in the presence of moisture is likewise used to some extent, but it appears that this method is far more suited to other oils. Great secrecy is maintained among those who have a knowledge on this subject. Peroxid of hydrogen has likewise been recommended, but from the standpoint of cost the sulphuric acid method is still the one that is used to the greatest extent.

The new methods which are favorably spoken of, and which the author has found to be inexpensive and efficient, involve the use of the peroxids of calcium, magnesium, and zinc. These peroxids are made into paste with water, one pound being sufficient for 200 gallons of linseed oil. This amount of oil is placed in an open kettle or vat, together with the peroxid, and thoroughly agitated. During agitation a strong solution of sulphuric acid is added, which liberates nascent oxygen. If the oil be allowed to settle, or is filtered, and is then heated to drive off any traces of moisture, a very brilliant pale oil is obtained.

It has always been understood that linseed oil contained albuminous matter which coagulated at a temperature of 400° F., or over, and produced a flocculent mass. When an oil answered this reaction it was said to "break" at the low temperature and was useless for making varnish oil and other high grades of linseed oil. G. W. Thompson found that this break was not due to the presence of albuminous and nitrogenous matter, but that it was caused by the separation of several phosphates. This explanation has generally been accepted as correct. If an oil, therefore, is allowed to age, the phosphates settle out and the oil does not break. Cold-pressed linseed oil, if it breaks at all, does not break at as low a temperature as hot-pressed oil. Bleached linseed oil does not wear as well as the oil that has been clarified by standing.

The demand for brilliant white paints or brilliant enamels is responsible for the manufacture of the so-called water-white oils. From a large variety of tests made by the author it was fully demonstrated that white paints composed of mixtures of pigments such as sublimed lead, zinc oxid, and white lead all showed absolutely the same whiteness within two weeks after they were exposed to the light, irrespective of the kind of raw linseed oil used. One of the five tests was made with a paint prepared with a linseed oil that had not been aged for more than two months, but within the time mentioned it was just as white as the rest.

Linseed oil paints are supposed to deteriorate after a few years and lose their value, owing to the decomposition of linseed oil. This statement is questionable, and while there is no doubt that the ready-mixed paint thickens and changes slightly in its chemical and physical characteristics, the change is exceedingly small in a container which is hermetically sealed. There is no doubt in regard to the reaction which takes place between the oil and white lead, zinc oxid, and a number of the unstable compounds in a mixed paint. While these reactions are very slow, they are at the same time very definite. If the value of a paint were reduced to a curve it would probably be found that the curve would be represented by the arc of a large circle approaching a straight line. As far as paste paints are concerned, particularly white lead, all painters prize white lead more highly when it is old than when it is fresh.

Typical Analysis of Bleached, Refined Linseed Oil

Specific Gravity	.932–.934
Iodine Value (Hanus)	Above 180
Saponification Value	190–194
Acid Value	3–5

STANDARD SPECIFICATIONS, AMERICAN SOCIETY FOR TESTING MATERIALS, 1914, p. 335

Purity of Raw Linseed Oil from North American Seed

Properties and Tests

1. Raw linseed oil from North American seed shall conform to the following requirements:

	Max.	Min.
Sp. gr. $\frac{15.5^\circ}{15.5^\circ}$ C	0.936	0.932
" or $\frac{25^\circ}{25^\circ}$ C	0.931	0.927
Acid Number	6.00	
Saponification Number	195.	189.
Unsaponifiable — per cent	1.50	
Refractive Index at 25° C	1.4805	1.4790
Iodine No. (Hanus)		178.

A linseed oil may however be pure if the iodine number is 165 and it may be just as pure if the iodine number is 195. The latter number was prevalent in the crop of 1913.

STANDARD SPECIFICATIONS FOR BOILED LINSEED OIL FROM NORTH AMERICAN SEED[1]

Properties and Tests

1. Boiled linseed oil from North American seed shall conform to the following requirements:

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[1] American Society for Testing Materials, 1915, p. 420.

	Max.	Min.
Specific Gravity $\frac{15.5^\circ}{15.5^\circ}$ C	0.945	0.937
Acid Number	8.	.....
Saponification Number	195.	189.
Unsaponifiable Matter, per cent	1.5	
Refractive Index at 25° C	1.484	1.479
Iodine Number (Hanus)		178.
Ash, per cent	0.7	0.2
Manganese, per cent	...	0.03
Calcium, per cent	0.3	
Lead, per cent		0.1

NAVY DEPARTMENT SPECIFICATIONS

BOILED LINSEED OIL

Composition

1. Boiled linseed oil shall be absolutely pure boiled oil of high grade, made wholly by heating pure linseed oil to over 350° F. with oxids of lead and manganese for a sufficient length of time to secure proper combination of the constituents and be properly clarified by settling or other suitable treatment. Evidence of the presence of any matter not resulting solely from the combination of the linseed oil with the oxids of lead and manganese will be considered grounds for rejection.

Chemical Constants

2. The oil shall upon examination show:

Unsaponifiable matter	Not more than 1.5 per cent.
Lead oxid (PbO)	Not less than 0.20 per cent.
Manganese oxid (MnO)	Not less than 0.04 per cent.
Iodine No. (Hanus)	Not less than 178.
Specific gravity at 60° F	Not less than 0.938.

The oil shall give no appreciable loss at 212° F. in a current of hydrogen.

Physical Characteristic

3. When flowed on glass and held in a vertical position, the oil shall dry practically free from tackiness in 12 hours at a temperature of 70° F.

Basis of Purchase

4. To be purchased by the commercial gallon; to be inspected by weight, and the number of gallons to be determined at the rate of 7½ pounds of oil to the gallon.

Quantity, How Determined

5. The quantity of oil delivered in 5-gallon shipping cans will be determined by taking the gross weight of 10 per cent of the total number of cans, selected at random, from which the average gross weight of the delivery will be determined. A sufficient number of these cans will be emptied to determine the average tare, and the net weight of the oil will be taken from the figures thus obtained.

STAND OIL

Stand oil is a very heavy, viscous form of linseed oil which has great use in the arts for the manufacture of both air drying and baking enamels. It is supposed that it originated in Holland, but there is a difference of opinion on this for the reason that the table oilcloth manufacturers in Scotland made a similar oil under the name of "marble oil" long before the Dutch made any enamel paints.

The method of making marble oil, which is a form of stand oil, is simply to heat a linseed oil which has no "break"[1] to 550° F., and to keep it at that temperature or slightly over until it becomes very heavy and viscous. Its specific gravity changes from .930 to .980, at which point a small quantity placed on a piece of glass and allowed to cool piles or stands up in a little mound and runs very slowly. With the oil still at 550° F., a small quantity of litharge is added; this is known as adding the drier on the downward cool, which simply

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[1] An oil from which no black flocculent particles separate at 500° F. is technically known as an oil which has no "break" or does not "break."

means that the oil takes up the drier not as the heat is increasing but as the heat is decreasing. The amount of litharge added is necessarily very small, because if more than one tenth of 1 per cent be added the oil becomes considerably darkened, while the object in making an enamel oil or marble oil is to retain its color. Oil made solely with litharge as a drier dries very tacky and must be baked to at least 110° F. for several hours before it will dry entirely. For this reason many add a small percentage of borate of manganese with the litharge, or chloride and sulphate of manganese, as a drier.

Of all the driers for making stand oil for enamel paints cobalt is the best, for a very small quantity is necessary to perform the function of drying and no bad results are obtained. Where manganese driers are used and continued oxidation takes place a white enamel paint may turn entirely pink, due to the formation of a manganese salt of that color. Where lead is used slow and sticky drying may result, but where lead and manganese are used together in dark colored enamels excellent results are obtained and any change in color value is not noticed.

Some stand oils are made also by partial oxidation or blowing and partial heating. These, however, are short, and when placed between the thumb and forefinger and rubbed rapidly do not form a long thread but a short thread. Experience has taught that a short oil is short lived and a long oil is long lived. There is obviously a good reason for this, as the short oil has been highly oxidized and continues to oxidize after it is dry. Yet for interior enamel purposes a short enamel oil will last many years.

One of the best features of enamel oil or stand oil is that brush marks even with a poor brush are eliminated and flow together. Zinc oxid is the principal pigment used in the manufacture of all of these enamel paints.

Japanner's Prussian Brown Oil

This is a stand oil or marble oil identical in all respects with that described under the heading "Stand Oil," excepting that it is dark in color and therefore only used for making dark colored enamels such as patent leather, machinery enamels and waterproof coatings which must have a high glaze.

The method used for making this oil depends very largely upon the good quality of the linseed oil, and the oil must have no tendency to "break" whatever. It must be heated to 550°, at which temperature three ounces dry or six ounces in oil of Japanner's Prussian Brown are added slowly until the oil which at first is muddy becomes clear and of the color and consistency of dark honey.

As the present tendency is to varnish or enamel automobile parts and bake them at fairly high temperatures this oil has become of great value, particularly when mixed with a fossil resin varnish, and as there are but very few automobiles which are painted white the dark color of this particular oil is no objection.

For the manufacture of an enamel paint for painting engines which are continually at a temperature of between 170° and 212° F. on account of being water jacketed, it has been found that the dark enamels used for this purpose when made with the Japanner's Brown oil containing at least 25 per cent of a high grade fossil resin varnish give results that are astonishing. Enamel paints on an engine, composed of the materials just described, will at the end of a year be practically as good as the day that they were applied.

Typical Analysis of Heavy Bodied Blown Oil

Specific Gravity	.988–.993
Saponification Value	195–210
Iodine Value	100–140
Acid Value	4–6

Typical Analysis of Enamel Oil

Specific Gravity	.9678
Iodine Value	174.5
Saponification Value	195.0
Acid Value	7.3

CHAPTER XIII

CHINESE WOOD OIL

CHINESE wood oil (China wood oil), or, as it is sometimes known, Japanese wood oil or Tung oil, is very largely used in the United States, but there appears to be very much secrecy with reference to its manipulation.

It is a peculiar fact that the majority of writers on this oil are inclined to condemn it, for the principal reason that when China wood oil, as it is commonly called, is brushed out on a sheet of glass it dries in about 12 hours to an opaque film which presents a rough appearance and does not adhere very well to the glass. It is perfectly true that this is a characteristic of China wood oil, and it is likewise true that it has no elasticity and that its waxlike appearance after drying condemns it very thoroughly, but it only goes to prove the difference between theory and practice, for, whereas China wood oil in its raw state is totally unfit for use and spoils any good paint to which it may be added, when properly treated it is one of the most remarkable paint assistants which we have, and those who have studied the subject carefully have made very successful paints.

It might be proper to cite as a parallel case that it would be manifestly unfair to condemn meat as an article of diet for the reason that it is tough, difficult to masticate, insipid in its taste, and hard to digest. On the other hand, the excellent flavor and nutritious qualities of meat which has been properly cooked and seasoned totally disproves the first statement. It is evidently very unfair to compare raw meat with properly cooked meat.

In the winter time, at ordinary freezing temperature, China wood oil looks like a mixture of tallow and sand and has a similar consistency. The head of the cask is removed, the oil cut out in slices and put into a kettle for treatment.

It is pretty well agreed that at 450° F. China wood oil gelatinizes, and if allowed to cool becomes insoluble. But experts in the manipulation of China wood oil add metallic salts or resinates at this temperature and a small percentage of untreated linseed oil, and before it is sufficiently cool small quantities of naphtha and benzol. The resulting liquid is a clear varnish-like oil which dries with a hard elastic film, much more slowly than the original China wood oil. In this condition it possesses most remarkable qualities.

By the use of China wood oil paints are made which dry in damp atmospheres. The advantage which the Chinese and Japanese have had over the Europeans on this subject has been recognized for a long time. It is now known to have been due to their knowledge of the proper manipulation of China wood oil. For the making of marine paints and waterproof paints China wood oil is indispensable.

In the United States preference is given to two brands of China wood oil; one is called the Hankow and the other the Canton, the Hankow being the better of the two. The Canton oil is darker, and it is very likely that it is expressed from the seed by a hot process, whereas the Hankow oil is expressed by the cold process.

The chemical constants of China wood oil are about the same as those of linseed oil, its specific gravity being slightly higher in the third decimal, its iodine value rather lower, and its saponification number almost the same. The oil has, however, a characteristic odor which cannot be easily destroyed, and a paint manufacturer who is once familiar with this odor can never be deceived. At the same time, where a small quantity of China wood oil is used for the purpose of making a particular kind of calcium oleate, it loses its characteristic odor. The calcium oleate so obtained is eventually split up by atmospheric moisture, and is therefore valuable for making a cement paint which has been patented.[1]

China wood oil is largely used in the making of enamel paints. Such paints give perfect satisfaction, last longer, and wear better than many of the resin varnish enamels. This work does not treat of enamel paints, although these paints could be classed as mixed paints, because they are a mixture of varnish or oil and pigment. As the ratio of the ingredients is totally different from that of oil-mixed paints, the subject of the use of China wood oil in these enamels has no place in this chapter. Where a manufacturer is at liberty to use any material, China wood oil can in no sense be regarded as an adulterant. It is more expensive than linseed oil and only on one or two occasions has the price of linseed oil approximated that of China wood oil, but even if the two in their raw state

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[1] The constants of a sample of China wood oil were compared with those of linseed oil in 1906, and it is of interest to know that the same sample was reanalyzed by the author in 1915, with the following results.

1906		*1915*
0.935	Sp. gr.	= 0.953 at 60° F.
	Acid Value	= 8.1
190.	Sapon. Val.	= 194.7
165.	Iodine Val.	= 146.6

The oil was kept in a glass-stoppered bottle. It had become very thick, viscous and clear.

were exactly the same in price, China wood oil would be very much dearer eventually on account of the high cost of manipulation. All factory experience indicates that the manipulation of China wood oil increases its cost 20 per cent if based on a cost price of 50 cents per gallon, whereas by the same manipulation the price of linseed oil would be increased only 5 per cent.

Tung oil is probably the glyceride of two acids—elæomargaric and oleic, while linseed oil is probably the glyceride of three acids. China wood oil has two peculiar qualities which make it very valuable for the manufacture of floor paints. The first is, its resistance to moisture, and the second, its extreme hardness so that it does not show scratch marks. For the manufacture of floor paints for railway and steamship use, these two qualities are essential. On the ferry-boats floating in the rivers of the United States it is customary to wash the floors several times a day. A linseed oil paint soon becomes spongy and is destroyed by this treatment. A floor paint composed of a large amount of China wood oil and a small amount of resin does not show a heel mark very readily, which is a decided advantage.

The Japanese are, however, more adept in the manipulation of China wood oil than any other nation. The author has three samples of varnish oil, one of which has almost the consistency and appearance of chemically pure glycerin. It has a faint yellowish tinge, and while it is no better in its physical characteristics than the nominally treated China wood oil, it indicates that without destroying any of its good qualities the Japanese can prepare this oil for lacquer and enamel purposes until it is practically water white.

It is a known fact that there has been great secrecy among the paint and varnish makers on the question of

China wood oil, and those who have used it successfully have forged ahead of their competitors. Its moderate use in a waterproof paint or damp-proof paint is of great benefit. Its use as a mixing varnish or combining medium in mixed paints is likewise of great value.

In its constants it is analogous to linseed oil, and it always has a most characteristic odor by which it can be invariably distinguished. It is, however, frequently subjected to adulteration with cheaper oils, and one of the first samples the author ever received was shipped from China in a 5-gallon kerosene tin which contained a considerable quantity of kerosene, either accidentally or intentionally. The oil from Canton, according to the experience of the author, is by no means as good as the oil from Hankow, the Hankow oils being paler in color and responding more clearly to the accepted chemical constants. One of the best tests for the determination of the purity of China wood oil is to heat it very slowly in boiling water for an hour; then transfer the test to a naked flame and heat it for twenty minutes to 450° F. Some care must be exercised not to flash the oil nor to char it. It is then allowed to cool, a good method being to place it in cold water for half an hour, after which time the oil must assume the appearance of an almost solid gelatin. The admixture of any adulterant, particularly cottonseed oil, prevents the coagulation or semi-solidification of China wood oil.

In order to manipulate China wood oil for paint it must be treated with an organic acid salt of lead and manganese which is sold for the purpose. A number of paint manufacturers have treated China wood oil with great success in the following manner: 10 gallons of China wood oil are slowly heated in a copper kettle to 350° F., and 10 pounds of this organic salt are added. When entirely dissolved, which takes but a very short time, 5 gallons of refined linseed oil are slowly stirred in and the whole heated to 400° F. and kept at that temperature for half an hour. The kettle is now withdrawn from the fire, and 2½ gallons of either turpentine or benzine, or a mixture of both, are added. This oil, known as China base oil, is then used in varying proportions in mixed paints for smoke stacks, floor paints, and varnishes, according to the experience or knowledge of the manufacturer.

The chemical detection of China wood oil is still somewhat empirical when it is contained in paints or varnishes. Some years ago the author made the statement that China wood oil could always be identified to a greater or lesser degree on account of its "heathen" odor. Anyone familiar with China wood oil or while cooking it can identify it at once. This may be empirical, but it is just as positive as the odor of fish oil when heated, and as the chemist has to depend to quite some extent upon his sense of taste and smell, the sense of smell when heating a varnish under examination is a fair guide when oils which have a specific odor are contained.

Formerly very little attention was paid to the acid figure of China wood oil, but today this acid figure plays a very prominent rôle. It is definitely known now that the high acid number of China wood oil prevents it from being used for making enamel varnishes where zinc or lead is used, for the reason that these pigments act as bases and thicken the resulting enamel paint. It is therefore either necessary to neutralize the acids or to use a pigment which is not attacked, like lithopone.

The polymerization of China wood oil is not understood. According to the patent of Beringer the addition of a sulphur compound prevents the polymerization. The author has made experiments using barium sulphide and finds that 1 per cent of barium sulphide prevents polymerization, but the addition of any one of these materials, including sulphur or selenium compounds, paralyzes the drying quality of China wood oil.

China wood oil plays a very important rôle in the manufacture of flat wall paints and neutralizing fillers and varnishes for the painting of Portland cement. From the analyses of various types of China wood oil that have come to the laboratory of the author it was noted that its acid number is considerably higher than that of linseed oil, and therefore care must be taken in the selection of the pigments with which China wood oil is ground, or else livering will ensue. As for instance, in the making of an enamel paint in which zinc oxid is used, the enamel paint may keep in suspension or be preserved as a ready mixed paint for several weeks, but at the end of a week it will gradually grow thicker until finally it becomes too thick for use. This is due entirely to the fact that the free organic acid of the China wood oil combines with the zinc or other base and forms a compound. In order to overcome this a fair knowledge of the chemistry of the pigments is necessary, and neutralization of the China wood oil must first take place before it is heated or converted into a varnish oil.

In a previous chapter which was written nearly ten years ago the author made the statement that raw China wood oil is not used to any great extent; in fact, it has always been regarded that raw China wood oil is decidedly unfit for use and spoils any paint to which it may be added, but since the flat wall paints and the Portland cement paints have come into use the addition of a small percentage of raw China wood oil has been found beneficial not only for producing flat surfaces but for producing a surface upon which a subsequent coat of paint will adhere better than it would to a surface which contained no raw China wood oil.

China wood oil has particularly good qualities for coating Portland cement surfaces, but this invention is fully covered by patent[1].

In the manufacture of baking enamels most excellent results have been obtained where China wood oil is prepared with soya bean oil at a temperature of 520° F. with or without the presence of resins or rosin. Rosin, of course, is not recommended in any high grade baking or stoving varnish, because it will distill and produce either a flat surface or one which will alligator, but the fossil or semi-fossil resins when added to a mixture of these two oils produce baking varnishes which are particularly good for the hoods of automobiles or the radiators, which are alternately hot and cold.

A Method for the Detection of Adulteration of China Wood Oils.[2]

"About July 15, 1912, there appeared a paper published by the New York Produce Exchange, which spoke of the Bacon method for the detection of at least 5 per cent adulteration of China wood oils. The paper set forth that the suspected oils were to be placed in a bath of between 280° and 285° C. for 8½ or 9 minutes. To detect

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[1] U. S. Letters Patent No. 813,841.

[2] This paper was presented by Louis S. Potsdamer before the Eighth International Congress of Applied Chemistry, 1912, Section Ve, "Paints, Drying Oils and Varnishes," of which the author was the President. This paper was written under the direction of the author and emanated from the research laboratory of Toch Brothers.

adulteration after polymerization the oils were to be cut with a knife, the pure offering little or no resistance to cutting and showing a clean cut surface; while the adulterated under similar treatment displayed a ragged cut, or else it could not be cut at all.

This was given a fair trial in the research laboratory of Toch Brothers' paint factory, with little success, until I decided to note the temperature of polymerization of the various samples, adulterated and pure. I had several samples of the pure oil, and these I made up into stock solutions as follows:

Pure,
5% Adulteration with Soya Bean Oil
10% " " " " "
7% " " Paraffin Oil
10% " " " "

(Soya bean and paraffin oils were chosen as representative of vegetable and mineral oils respectively.)

The apparatus used was such that a bath of oil (pure soya bean oil) was placed in a nickel pot of about 8 inches diameter. In this were suspended two test tubes, arranged to act as an air bath. The samples were placed in tubes of slightly smaller bore, and in turn in the air bath. Thermometers were suspended in these tubes so that the mercury bulbs extended below the middle of the oil under examination.

The bath was first heated to a temperature between 510° and 525° F., and the sample tubes, filled so that the oil surface did not extend above the surface of the bath, then placed in position. They were allowed to remain in this position until polymerization just set in, stirring once in a while with the thermometers.

At the point of polymerization the temperature was noted and the tubes withdrawn from the bath. Referring to the tables one can see that adulterations as low as 5 per cent cause a very perceptible drop in the temperature of polymerization.

I made only three sets of oils, but from these I obtained results on which I base my method for the detection of adulteration. I found that the first two oils under examination had an average polymerization temperature of 553° and the third (a mixture of two supposedly pure oils received at Toch Brothers' factory for testing) a somewhat lower temperature.

Disregarding such a small discrepancy, 15° F., we notice that the adulteration caused a decided drop in the polymerization temperature, and as soya bean oil is handiest to the oriental, we may expect adulteration with this.

By the method herein described, an adulteration of 5 per cent could be detected. To settle this finally I offer this suggestion: that the American Society for Testing Materials now working on the standardization of soya bean and China wood oils add the above to their tests and so obtain a standard temperature of polymerization in the manner described, and all oils meeting such a temperature (or those within a small range) call pure. It would then be a very simple matter to detect adulteration.

Supplementing the polymerization test the specific gravities of the oils were determined under standard conditions (60° F.). It was noticed that the higher the percentage of adulteration the lower the specific gravity, and further, when the adulteration was mineral oil the specific gravity was lowered at least four times as much as with a similar percentage of vegetable oil.

POLYMERIZATION TEMPERATURES

Sample	Set 1	Aver.	Set 2	Aver.	Set 3	Aver.
Pure	551	553	552	553	538	537
	554		554		535	
5% Soya Bean Oil adulteration	522	519	520	517	505	503
	516		514		500	
10% Soya Bean Oil adulteration	502	500	476	475	498	499
	498		474		500	
5% Paraffin Oil adulteration	516	516	518	517	494	497
	513		516		500	
10% Paraffin Oil adulteration	513	514	489	491	488	490
	515		492		492	

	Sp. Gr. at 60° F.		
Sample	Set 1	Set 2	Set 3
Pure	0.9423	0.9416	0.9409
5% Soya Bean Oil Adulteration	0.9417	0.9407	0.9391
10% “ “ “ “	0.9410	0.9401	0.9381
5% Paraffin Oil “	0.9348	0.9350	0.9326
10% “ “ “	0.9330	0.9323	0.9310

Iodine values were also made in the samples, with the following results:

Sample	Set 1	Set 2	Set 3
Pure	160.4	158.8	150.5
5% Soya Bean Oil Adulteration	158.0	155.4	147.8
10% “ “ “ “	156.2	151.9	141.6
5% Paraffin Oil “	155.2	150.8	140.5
10% “ “ “	143.9	143.4	136.8

The impurities make quite an appreciable lowering in the iodine values.”

STANDARD SPECIFICATIONS FOR PURITY OF RAW CHINESE WOOD OIL[1]

Properties and Tests

1. Raw Chinese wood oil shall conform to the following requirements

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[1] Amer. Soc. Test. Materials 1915, 423.

	Max.	Min.
Specific Gravity $\frac{15.5^\circ}{15.5^\circ}$ C	0.943	0.939
Acid Number	6	
Saponification Number	195	190
Unsaponifiable, per cent	0.75	
Refractive Index at 25° C	1.520	1.515
Iodine Number (Hübl 18 hrs.)		165
Heating Test (Browne's Method), minutes	12	
Iodine Jelly Test, minutes	4	

CHAPTER XIV

SOYA BEAN OIL[1]

FROM 1890 to 1909 the price of linseed oil fluctuated between 30 cents and 50 cents per gallon. On a few occasions the prices were higher, but a fair average for the 19 years was 40 cents per gallon, although in 1896 it went as low as 25 cents. Toward the end of 1909 it rose from 60 cents to 68 cents within two months, and in September, 1910, it reached $1.01 per gallon. After that it fluctuated between that price and 75 cents. Owing to the high price of linseed oil in 1910 many painting operations were deferred awaiting a lower price, or inferior material was used in place of linseed oil.

The value of menhaden fish oil had already been recognized, and while it is admitted that fish oil replaces linseed oil for many purposes, it is by no means a true substitute. The principal use, however, for fish oil to-day is in the manufacture of linoleum, printing inks, and certain paints which are exposed either to the hot sun or on hot surfaces.

In 1909 soya bean oil as a paint oil was practically unknown. Since that time many investigators have published more or less conflicting articles concerning soya bean oil, in which even the physical and chemical constants of soya bean oil varied to some extent. Owing to the fact that discordant results were continually obtained, it is only within the past few years that it has

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[1] Journal of Society of Chemical Industry, June 29, 1912, No. 12, Vol. XXXI, by Maximilian Toch.

been possible to state with some degree of certainty whether soya bean oil is a substitute for linseed oil, an adjunct to it, or neither. The reason for this uncertainty and discrepancy is apparent when it is stated that the author himself has experimented with 33 different varieties of soya beans, while in the records of the Department of Agriculture at Washington no less than 280 varieties of soya beans are listed.

From time immemorial the soya bean has been grown in China and Japan, where it has served as one of the staple articles of food and as the basis for a number of food preparations. In Europe and the United States, however, the value and uses of the bean have been but little appreciated until very recently (1908), when, on account of the scarcity in the cotton seed supply of the world, soap and glycerin manufacturers began to turn their attention to its possibilities. In Manchuria, where by far the major portion of soya beans are grown, practically the entire crop is available for export. The following figures taken from the Consular Reports will serve to show the extent of the soya bean industry during recent years:

	1909 Tons.	1910 Tons.	1911 Tons.
Total shipments of beans from Far East	1,470,870	1,200,000	1,500,000
Imported into Europe	400,000	500,000	340,000

As the above statistics indicate, China and Japan retain for domestic consumption practically two-thirds of the available supply of beans. The sugar plantations in Southern China and the rice fields of Japan annually consume enormous quantities of soya beans and bean cake as fertilizer, while the extracted oil is used as food by the natives.

In connection with the use of soya beans and soya bean oil for edible purposes, it may be mentioned that there has been recently established at Les Valées, France, a thoroughly up-to-date factory for the production of a wide assortment of food products from soya beans. Among the more important of these may be mentioned: milk, cheese, casein, oil, jellies, flour, bread, biscuits, cakes and sauces. According to Dr. G. Brooke, Port Health Officer of Singapore, the soya bean, more nearly than any other known animal or vegetable food, contains all the essential and properly proportioned ingredients of a perfect diet.

All soya beans are leguminous plants, which do not tend to deplete the soil of nitrogen, for the typical soya bean plant is self-nitrifying and grows in almost any soil that contains a reasonable amount of potash. In addition to this, the soya bean enriches even very poor ground when used as a ground manure. This is done by planting the seed promiscuously, allowing it to grow to a height of about 6 inches, and then turning it in. In this way both nitrogen and potash are given to the soil for future use in an available form. The average height of the soya bean plant is about 36 inches. The pods resemble those of our sweet pea. They are about $2\frac{1}{2}$ inches in length and are covered with a hairy growth. Generally there are two or three beans in each pod. After the oil is extracted from the bean the cake appears to be very valuable as a cattle food, while the leaves and stalks, if collected and set in a dry place, make excellent silage. We thus have practically the entire plant available for use, with the exception of the roots.

The average composition of the soya bean varies within fairly narrow limits among the different varieties of soya beans. In the following table are listed the analyses of a few of the varieties of soya beans:[1]

Variety	Water	Protein	Fat	Nitrogen free extract	Fibre	Ash
	%	%	%	%	%	%
Austin	8.67	36.59	20.55	24.41	4.00	5.78
Ito San	7.42	34.66	19.19	27.61	5.15	5.97
Kingston	7.25	36.24	18.96	26.28	4.79	6.28
Mammoth	7.49	32.99	21.03	29.36	4.12	5.01
Guelph	7.43	33.96	22.72	25.47	4.57	5.85
Med. Yellow	8.00	35.54	19.78	26.30	4.53	5.85
Samarow	7.43	37.82	20.23	23.65	5.05	5.82

When the author obtained discordant results from the soya bean oil then on the market, the first impression was that the oil might have been adulterated, but this did not prove to be the case. The oil was, in all cases, pure soya bean oil, but from a seed which was not particularly adapted for making a paint oil. Through the U. S. Department of Agriculture many varieties of seeds were received, and through the various seed dealers in the United States quantities of seeds of all kinds were purchased. The method of extraction followed was to grind the seeds very finely in a mill and digest with gasoline in the cold. The solvent was then evaporated and the oil recovered. Without going into any lengthy details, the percentage of oil extracted averaged 18 per cent, and although soya beans range in color from a cream white to a jet black it must be noted here that all the oils extracted from the various seeds were paler than finely pressed linseed oil, and none of them showed the

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[1] U. S. Dept. of Agric. Bulletin of the Bureau of Plant Industry.

chlorophyll extract as markedly as fresh flaxseed. On obtaining the various samples of oil it became evident why the discordant results were obtained, for some of them dried within a reasonable time and some did not.

It has been stated that soya bean oil is not as pale as raw linseed oil and belongs to the semi-drying class of oils. I must correct this statement; soya bean oils made from cold pressed seeds such as Haberlandt, Austin, Habaro, Ebony, Meyer, and Ito San give excellent results. They have a specific gravity as high as 0.926, with a yield ranging from 16 to 19 per cent. Furthermore, a drier made from red lead or litharge is unsuited for soya bean oil, but a tungate drier, which is a mixture of a fused and a precipitated lead and manganese salt of China wood oil and rosin, acts on soya bean oil exactly the same as a lead and manganese drier acts on linseed oil. In other words, a fairly hard, resistant and perfectly dry film is obtained within 24 hours by the addition of from 5 to 7 per cent of this drier.

Tungate Drier

Soya bean oil, and when I mention this name hereafter, I refer only to that suitable for paint purposes, is the nearest oil we have to linseed, and under the proper impetus of the Department of Agriculture much of our waste and unproductive land between Maryland and Georgia, and from the Coast to the Mississippi, will yield productive and profitable crops. The only drawback to the planting of soya bean is the fact that it needs much water. In 1911 many of the experimental plantings failed on account of the drought which was prevalent in the United States, but in low marsh land this plant ought to yield a profitable crop. It is doubtful whether the soya bean would grow profitably in the extreme South. In Cuba the cow-pea, which is analogous to the soya bean, will sometimes grow to a height of 20 feet, and form a thick mat around the base or abutment of a railroad bridge, and that within a few months. This would indicate that a soil would have to be selected where the bean would not grow to a height greater than 5 feet, otherwise the stalks would be too thick and it would be difficult to harvest it. Farmers' Bulletin No. 372 of the Department of Agriculture makes the statement that 20 lbs. of seeds are required to the acre, and that the production is from 25 to 40 bushels, each bushel weighing 40 lbs. If this is a fact, and since little or no fertilizer is needed, and when fertilizer is needed a preliminary crop can be grown and turned in to form its own fertilizer, the American farmer should be encouraged to try this crop. Furthermore, in Kentucky two crops during the summer can be grown, for some of the soya beans that have been tried there have ripened early, and the second crop has ripened late, two different selections of seed having been used. The statement has been made that soya bean could not be harvested properly in this country on account of the high cost of labor as compared with that of Manchuria and Japan, but this is evidently erroneous, in view of the fact that enormous quantities of beans are grown in Minnesota for food purposes and harvested by machinery. Even in Manchuria the beans are allowed to dry and then thrashed out by means of horse power. At any rate, if we have any difficulties now with the harvesting of a new kind of crop, it is safe to assume that with the American inventive genius in harvesting machinery, appliances will be invented which will overcome this, for the soya business has no greater harvesting difficulties than the edible bean.

Soya bean oil appears to consist of from 94 to 95 per cent of glycerol esters.[1] Of these 15 per cent are saturated acids such as palmitic acid, and 80 per cent are liquid unsaturated fatty acids containing 70 per cent oleic acid, 24 per cent linolic acid, and 6 per cent linolenic acid. The iodine number of soya bean oil has been given as ranging from 121 to 124, but the Manchurian cold pressed oil will average as high as 133.

It may be of interest to show a comparative table here between the physical and chemical constants[2] of soya bean oil of known origin like Manchurian cold pressed oil as compared with linseed oil.

SOYA BEAN OIL

Name	Color of seed	Color of oil	Sp. gr. 15° C	Acid value	Iodine value
Meyer	Brown	extremely pale	0.9264	0.44	127.0
Peking	Black		0.9279	0.14	135.4
Haberlandt	Straw-yellow		0.9234	0.00	129.8
Farnham	Straw-yellow		0.9234	0.65	131.8
Taha	Black, olive saddle	pale amber somewhat deeper than above	0.9248	0.16	127.0
Mammoth	Straw-yellow		0.9222	0.47	118.2
——	Brown		0.9248	0.17	129.3
Edward	Straw-yellow	med. amber	0.9257	1.14	124.6
Shanghai	Black	same depth as previous, olive tone	0.9241	0.63	127.8
Refined linseed oil			0.933	1.0	180.1

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[1] H. Matthias and H. Dahle — Arch. Pharm., 1911, 294, 424–435.

[2] Results obtained in the research laboratory of Toch Brothers.

The specific gravity determinations were made with the pyknometer. The iodine values were obtained in accordance with Hubl's method. The iodine values indicated are somewhat lower than those of cold pressed Manchurian bean oil. This is no doubt to be ascribed to the circumstance that the solvent with which the oil was extracted was driven off by evaporation in open vessels on the water bath, so that the oil became slightly oxidized.

Soya bean oil which is suitable for paint purposes has two characteristics which enable the chemist to determine whether this oil is suitable or not. In the first place, soya bean oil when heated up to 500° F. for a few minutes will bleach and remain bleached. Some samples which the author has examined have turned almost water white. Linseed oil has this characteristic, but not to the same degree. Cold pressed soya bean oil made from the samples indicated in the previous table, when heated to 500° F., and blown with dry air for from 5 to 7 hours, thickens exactly the same as linseed oil, and attains a gravity of 0.960 or over. This is the surest indication that the soya bean oil which will thicken under these conditions and remain pale is suitable for paint purposes. This thickened oil has excellent qualities and advantages for making what we call in this country "baking japans," and what are known in England as "stoving varnishes."

A sample of standard cold pressed Manchurian bean oil was heated to 500° F., and blown vigorously for 7 hours after cooling to 300° F. The following results were obtained:

	Sp. gr. 60° F.	Acid value	Iodine value (Wijs.)
Original oil......	0.929	2.6	133.6
Blown oil........	0.963	1.9	105.3

It is interesting to note that the acid value was reduced by blowing. The blown oil dried in 3½ days, whereas the original sample required from 5 to 6 days.

It appears that the varnish made from a suitable soya bean oil bakes very hard and retains an abnormal flexibility. As regards the wearing quality of pure soya bean oil compared with pure linseed oil for paint, the author has had somewhat less than three years' experience, and can only say that it is not quite as good as that of linseed oil. A 2-year exposure on a 100-foot fence gave slightly better results for the linseed oil as to hardness and less gloss for the soya bean oil, but a mixture of half soya bean and half linseed oil showed approximately the same results, while a varnish made of 25 per cent of China wood oil with 75 per cent soya bean oil gave equally hard results as linseed oil. It is too soon to prognosticate the value of soya bean oil for exterior painting, but for interior painting soya bean oil is the equal in every respect of linseed oil, and particularly when treated with a tungate drier.

Cobalt drier will, under many circumstances, dry even those soya bean oils which are not suited for paint purposes, but for the present cobalt drier is rather too expensive. It has been stated that from 1 to 1½ per cent cobalt drier will dry soya bean oil and fish oil. This is practically true, but 2½ per cent is really needed to get the proper drying within 24 hours. Cobalt Tox Tungate[1] is probably the ideal drier for soya bean and fish oils. This drier, when present in soya bean oil to the extent of from 5 to 7 per cent, will dry the latter within 12 hours.

It is, of course, possible to determine and differentiate a mixture of raw soya bean oil and raw linseed oil, for the iodine values and specific gravities are good indications, but when 25 per cent of soya bean oil is added to a mixed paint neither the author nor anyone in his laboratory can, in all instances, detect its presence.

Blown and thickened soya bean oil is already used by a number of the linoleum and table oilcloth manufacturers, and for printing ink purposes it presents some advantages. For the manufacture of enamel paints heavy bodied soya bean oil produces most beautiful results, and as perhaps 95 per cent of all enamel paints are used for interior decorative or protective purposes in this country its use should be encouraged.

It is not within the province of the writer to forecast the future of any paint oil, but there is no doubt that if a campaign of education be urged among the farmers, particularly in those states where soil has been regarded as unproductive, and the proper selected seeds of soya beans are planted, no scarcity in the flaxseed crop will ever again be a menace to the paint and varnish industries. At the time of writing linseed oil is quoted at 75 cents per gallon and soya bean oil at 55 cents per gallon. As soon as thousands of acres shall have been planted

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[1] So called because it was first prepared by the author. It is a cobaltic salt of China wood oil. Unless the cobalt is trivalent, it will not act as a drier.

with soya beans, the proper machinery installed, and the sale for the cake and the silage arranged, soya bean oil will sell at from 25 to 35 cents per gallon, and after the ground has been productive of soya beans for some time it will be fit for the growing of even the most difficult crops.

CHAPTER XV

FISH OIL

WE are all prone to call all oils of a fishy nature "fish oils," and the author desires to differentiate between the real fish oils and the pseudo fish oils, for there are several marine animal oils which have fishy characteristics but which are not strictly fish oils, and which do not serve as good a purpose as those which are strictly extracted from fishes. Some of the fish oils—like cod liver oil— even if they were cheap enough, are not totally adapted for paint use. The animal oils which have always been regarded as fish oils, but which the author calls pseudo fish oils, and that are in the market and easily purchased at a reasonable price, are whale oil, porpoise oil and seal oil. All of these oils are by no means drying oils, and even if they are admixed with drying oils like tung oil and boiled linseed oil, and an additional amount of drier added, they are peculiarly hygroscopic, and after three months, although these oils may be apparently dry, they become sticky when the humidity rises above 80.

The following figures represent some constants of fish oils, the specific gravity and the iodine number being given in each case. The iodine number is a characteristic indication of the value of a fish oil for paint purposes.

Fish Oil Constants

	Specific Gravity 20° C	Iodine No. Hübl, 4 hours
No. 1 crude whale oil	0.9195	136.1
No. 1 filtered whale oil	0.9168	125.0
No. 2 filtered whale oil	0.9187	142.9
Cod oil	0.9196	147.3
Porpoise body oil	0.9233	132.3
Seal oil — water white	0.9227	143.0
Menhaden Oil		
Extra bleached winter	0.9237	150.4
Bleached — refined	0.9273	161.2
Regular	0.9249	165.7
Dark brown	0.9250	154.5

The specific gravities were determined with the aid of the Westphal balance.

The iodine numbers were determined according to the standard method of Hübl.

The fish oil used for paint purposes is the variety obtained from the Menhaden fish, and the winter bleached is the variety to be recommended. When refined by the simple process of filtering through infusorial earth and charcoal its color is that of refined linseed oil, with little or no fishy odor; in fact, in the purchasing of fish oil for paint purposes it is well to beware of a fish oil that has the so-called characteristic "fishy" odor. In its chemical properties it is so similar to linseed oil that it is difficult to differentiate between them. It must be observed that oils in mixed paints are not presented to the chemist or practical man in their raw or natural state, but they have been boiled with driers and ground with pigments so that their characteristics are entirely altered. The old-time painter when he condemned a mixed paint would smell it, taste it, rub it between his thumb and forefinger, smell it again, look wise, and say despairingly, "fish oil." As a matter of fact, the adulteration of paints was seldom, if ever, caused by the addition of fish oil, for the reason that the price of a good fish oil always approximated that of a raw linseed oil, and there were so many other cheaper paraffin oils to be had that the occurrence of fish oil in a mixed paint was relatively rare. The specific gravities of fish oils freshly made and containing no admixture of other species, but representing the pressing of only one species, are as a general rule below .927. Its iodine number is so close to that of linseed oil that in its raw state, excepting for its characteristic odor and the Maumene test, it is rather difficult to differentiate these oils with certainty. The author is inclined to believe that this characteristic odor is due to phosphorous decomposition compounds. If a linseed oil be heated to 500° F., mixed with Japanners Prussian brown or Prussian blue, it develops acrolein, which is identical in odor with that from the fish oil. When Menhaden oil is treated with 8 ounces of litharge to the gallon and kept at a temperature of 400° to 500° F., for ten hours, it thickens perceptibly and can be reduced proportionately with naphtha, but the amount of loss by this treatment with litharge makes it very expensive in the end.

The results obtained from the proper grades of fish oil warrant the use of fish oil in the hands of an intelligent manufacturer, and if used up to 75 per cent produces excellent results for exterior purposes. For interior purposes fish oil does not seem to be desirable, for it gives off noxious gases for a long time. When fish oil is mixed with linseed oil even up to 75 per cent it gives excellent and lasting results and does not show any hygroscopic properties, but when used in the raw state, particularly in conjunction with pigments which in themselves are not catalytic driers, the results are not satisfactory.

For some years some of the enamel leather and printing ink manufacturers have adopted the use of fish oil as a medium to replace linseed oil with excellent results, and the enamel leather which is produced, while not so high in gloss as that made entirely of linseed oil, is much more flexible and possesses an unctuousness which prevents it from cracking. But fish oil for leather purposes shows a peculiar defect, and a campaign of education will be necessary if ever this material is to be used for the manufacture of shoes or auto tops, for fish oil, particularly when it originally has a high acid number, seems to effloresce and give an undesirable bloom to enamel leather, which, however, can be removed from the surface by the ordinary application of either benzine or a mixture of benzine and turpentine. At the same time, enamel leather is very largely used for carriage and automobile tops, and for shoes, and wherever it is used for these purposes these products are continually polished.

Menhaden oil is the only oil, with the possible exception of China wood oil, which can be used for making smoke-stack paints that will withstand the action of excessive heat and light. When treated as described, its intrinsic value is far beyond that of linseed oil, and a smoke-stack paint made in this manner sells for one-third more than a linseed oil paint. It is impossible, however, to treat Menhaden oil for this purpose, except at an excessive cost, because the acrolein developed nauseates the workmen, the loss in evaporation is very large, and the treatment with litharge is such that the oil must be thinned before it has an opportunity to compound or semi-solidify. In its raw state, after treatment with animal charcoal and infusorial earth, it is used to some extent with a heavy boiled linseed oil for making waterproof roof paints, for painting canvas, freight cars, ship decks, etc. When mixed with linseed oil up to about 25 per cent it is extremely difficult to determine the amount present by means of its chemical constants or characteristics.

The following are the constants of the Menhaden oil which is generally used in the United States for making heat-resisting paints:

CONSTANTS OF FISH OIL

Specific Gravity	0.931
Saponification	190.
Iodine Value	150-165

There is a great demand for baking japans which shall be flexible and at the same time be so thoroughly baked that they adhere to the surface most tenaciously and form an excellent enamel, and for this purpose we know that the reasonable use of fish oil improves baking japans very much indeed.

We are also aware that along the seacoast, where paint disintegrates very rapidly on account of the sea air, a fairly liberal use of properly treated fish oil serves a useful purpose.

When red lead is mixed 33 lbs. to a gallon of linseed oil it thickens up after a very short time and becomes unfit for use. A properly neutralized fish oil prevents the hardening or setting of the red lead in the package, and a paste of this material can be transported a great distance and will last many months in a fresh and soft condition.

In the tests made by the author on fish oils and linseed oil without the admixture of driers, it was found that the Menhaden fish oil and the linseed oil dried approximately the same, but the seal oil and whale oil were still sticky after two weeks. This may be an unfair test, for these other oils can be manipulated with the proper driers and they will serve a fairly good purpose, but inasmuch as Menhaden fish oil appears to be satisfactory for this test even without a drier its superiority over the animal oils is apparent.

Menhaden oil should, of course, be used with a drier, and for that purpose the best results are obtained by means of a tungate drier. A tungate drier is one in which tung oil or China wood oil is boiled with a lead and manganese oxid, and when the solution is complete this is then mixed with a properly made resinate of lead and manganese. Such a drier becomes soluble in the oil at temperatures over 100° C., and hardens the resulting paint very thoroughly. For fabrics, however, fish oil must be heated to a temperature of over 200° C., and if air is injected at such a temperature the glycerides are expelled and thick oil is produced which, in conjunction with the drier just named, is equally good for printing inks. It is advisable, however, to add at least 25 per cent of either a heavy bodied linseed oil or a raw linseed oil which does not "break" before the manipulation just referred to is begun.

For stacks, boiler fronts, etc., the treatment of fish oil up to 220° C., with litharge makes a heat-resisting medium that is far superior to anything excepting China wood oil, and for both heat-resisting and exposure to the elements fish oil is superior to China wood oil.

The following is taken from the U. S. Navy Department specifications for fish oil for paint purposes:

Quality

1. To be strictly pure winter-strained, bleached, air-blown Menhaden fish oil, free from adulteration of any kind.

Chemical Constants

2. The oil shall show upon examination:

	Maximum	Minimum
Specific gravity..............	0.935	0.930
Iodine number (Hanus).......	165	145
Acid number.................	6	——

Physical Characteristics

3. The oil when poured on a glass plate and allowed to drain and dry in a vertical position, guarded from dust and exposure to weather, shall be practically free from tack in less than 75 hours at a temperature of 70° F. When chilled, the oil shall flow at temperatures as low as 32° F.

CHAPTER XVI

MISCELLANEOUS OILS

HERRING OIL[1]

WITHIN recent years the subject of fish oils has received considerable attention, first from the leather and soap manufacturers and subsequently from the paint chemist. Hitherto fish oil played the rôle of a rather unimportant by-product in the course of fertilizer or "scrap" production, for which there seems to have been always a large demand.

As the peculiar properties and industrial possibilities of fish oils became more thoroughly appreciated in the light of investigations carried out by progressive manufacturers, the fish oil industry received a new lease of life and grew until it rivalled in importance the fertilizer industry to which it had previously been tributary.

Of the numerous varieties of fish oils which have at one time or another appeared upon the market, Menhaden oil alone seems to have established itself on a firm basis in the manufacture of special kinds of heat-resisting paints. Its application, therefore, is no longer an experiment; it is an established fact.

Latterly, attention has been more particularly directed toward seal, whale, cod, porpoise, and herring oils, with

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[1] By A. Lusskin, 8th Int. Congress of Applied Chemistry; written in the research laboratory of Toch Brothers under the direction of the author.

a view to investigating their utilizability in the industries. Of these, seal, cod and porpoise body oils have proved to be in many ways as good as Menhaden oil, but are beyond the reach of the paint manufacturer on account of considerations of price.

Whale oil, which is now obtainable in the form of a clear, pale material, comparatively free from objectionable odors, has not as yet been successfully manipulated to give very good drying results.

In the treatment of fish oils, several considerations must be constantly kept in mind in order to obtain the best results:

1. The oil must be free from high melting point glycerides or fatty acids; or, to use the technical term, the oil must be "winter-pressed." Most fish oils contain a large amount of saturated glycerides of the nature of palmitin which separate from the oils on standing for any length of time at a low temperature. When these have been removed from the oil, the resulting product is found to be much more amenable to successful treatment than it otherwise is. It would seem that these high melting point fats tend to retard or to prevent the drying of fish oils, giving films which remain greasy for a very long time.

2. Very frequently, oils are received which have a high content of free fatty acids. In the case of one sample of herring oil, this was as high as 41.9. Under such circumstances, it is perfectly evident that the drying of the oil would be very largely inhibited. In addition, such an oil, used as a paint vehicle, in conjunction with pigments like red lead, white lead, and zinc oxid will, in a very short space of time, "liver" up and form the lead and zinc soaps of the fatty acids. This was very largely responsible for the poor results obtained with the

fish oils which were first introduced on the market. The free fatty acids are formed when the oil, extracted from the fish by boiling in water, is subjected to the action of the decomposition products from the bodies of the fish for a longer time than is absolutely necessary to break open the oil-containing cells.

3. Finally it must be remembered that driers, which serve very well for vegetable drying oils, will not, in general, function properly, when utilized for fish oils. The tungate driers, and particularly the cobalt tungates, can generally be depended upon in the case of oils which do not yield to the action of the ordinary linseed oil driers, provided however, the two conditions named above have been satisfied.

The writer recently had his attention called to several grades of herring oil, which, at first glance, appeared desirable from the paint manufacturer's standpoint. Accordingly an investigation was started to test its adaptability for paint purposes, and to compare its behavior with that of Menhaden oil.

Herring oil occurs in the bodies of Clupeus C. and V. (Japanese herring varieties) and Clupeus harengus (European or North Sea herring).

The method of extracting the oil from herring is the one universally used in the fish oil industry, viz., extraction in boiling water.

Two representative samples of herring oil, furnished by two of the leading oil concerns in the States, were experimented with in conjunction with Menhaden and other fish oils. The following analytical constants were obtained:

No.	Color	Odor	Sp. Gr. 15° C	Acid Value	Iodine Value
#1 Herring Oil	Very Pale	Good	0.9240	2.4	137.9
#2 Herring Oil	Dark Brown	Bad	0.9210	41.9	136.1
Blown Oil #2	Deep Red	Almost None	0.9654	25.7	89.94
Winter-Pressed Refined } #2	Extremely Pale	Fair	0.920	39.4	136.1
* * * * * * * * * *					
#1 Crude Whale Oil	Very Pale	Good	0.9230	0.6	136.1
#1 Filt. Whale Oil	Very Pale	Good	0.9203	2.3	125.0
#2 Filt. Whale Oil	Pale Amber	Very good	0.9222	14.5	142.9
Porpoise Body Oil	Very Pale	Very good	0.9268	2.8	132.3
Menhaden Oils					
Ext. Bleached Winter Oil	Very Pale	Fair	0.9272	0.5	150.4
Bleached-Refined	Pale Amber	Not bad	0.9308	5.7	161.2
Regular	Deep Red	Bad	0.9284	8.4	165.7

* The part of the table below the asterisk (with exception of the acid values), is from a paper on Fish Oils delivered by M. Toch before the Amer. Chem. Soc., Dec. 1911, and published in the Journal of Industrial and Engineering Chemistry.

Crude herring oil, even though very dark in color, yields a very clear, pale product when treated with Fuller's earth for a short time at about 250° F., and then for some time longer, at the temperature of boiling water. In addition the odor is considerably improved.

In the case of the crude herring oil listed above, the sample was kept for several hours at about 60° F. to permit high-melting fats to separate out. The portion which remained liquid corresponded to a winter-pressed oil. Since the acid and iodine numbers were practically unchanged it seems that the solid fats contained saturated and unsaturated compounds in about the same proportions as the crude oil.

Another sample of the oil was heated to 320° F. and blown with air for about 8 hours. The effects produced on the constants are shown above. The oil was very heavy and viscous but had the deep red color which fish oils so readily assume. It must be noted also that the "fish" odor was very faint. The reduction in acid value would seem to indicate that the oil contained fatty acids which were volatile at the temperature of blowing.

Attempts to dry the samples of herring oil did not prove successful, even when very powerful driers were used. This cannot, however, be interpreted to mean that herring oils are, in general, not capable of drying.

Porpoise body oil and Menhaden oil, under similar conditions, dried satisfactorily.

The blown herring oil could very well be used for the production of smoke-stack paints and for paints intended to resist the "chalking" action of salt air. Herring oil is at present used to a certain extent in leather manufacture together with some of the other fish oils like Menhaden and whale oil. In regard to herring oil, as with many of the other materials which are being introduced from time to time, the final word cannot be spoken until many more specimens have been examined and given a fair test.

CORN OIL

Corn oil is made in very large quantities in the United States, and is of considerable value as a paint material. It is seldom so much cheaper than linseed oil or China wood oil that it is used as an adulterant for these oils; in fact, many manufacturers would probably use it irrespective of the price up to about 10 per cent in certain classes of mixed paints in order to prevent hardening or settling. A large number of paint manufacturers in the United States who grind heavy paste paints, such as Venetian reds, ochres and white paints containing large amounts of barytes, frequently use from 10 to 70 per cent of corn oil, not because it is any cheaper than linseed oil, but for the reason that the resulting mass never becomes hard in the package as it does where pure linseed oil is used.

Corn oil has a great analogy to soya bean oil, with the one exception that corn oil is not as pale nor can it be bleached as pale as soya bean oil, and when it is bleached by chemical means it dries very badly.

Corn oil is known in England as maize oil. Paint manufacturers in England appear to have very little knowledge of this oil and regard it as a non-drying oil, and yet corn oil is even more than a semi-drying oil, particularly when heated with strong drying oils like China wood oil and cobalt and manganese drier. In the textile arts, such as the manufacture of linoleum and table oilcloth, where flexibility is desired, large quantities of corn oil are from time to time used with excellent results. When an oil like corn oil is used for paint purposes in limited quantities its characteristic of slow drying or tacky drying is eliminated if it is properly manipulated. Corn oil will take up the lead and manganese salts just the same as linseed, but in conjunction with linseed oil. It can be blown and can be thickened by heat, and being very flexible it has a distinct advantage. It has been stated, although the author has not tried this, that for priming new wood half corn oil and half linseed oil with sufficient drier and volatile solvent produce a priming coat to which a second coat of linseed oil paint will adhere perfectly.

The physical and chemical constants of corn oil cannot be given exactly for the reason that samples vary.

Its specific gravity will run from 0.920 to 0.926; its saponification value will average 190; and its iodine value will average 120, although several samples examined by the author have shown as high an iodine value as 130.

CHAPTER XVII

TURPENTINE

TURPENTINE occupies the same relative position among the vehicles of paints and varnishes as white lead does among the pigments. It is impossible to say for how many generations turpentine was the only solvent or diluent known to the paint and varnish industry, and therefore when other solvents were introduced they were looked upon as adulterants.

The methods used in the manufacture of turpentine are very well known; the sap of the Georgia pine and two or three other species of pine trees growing in the southern part of the United States is collected and distilled with steam. The distillate is known as turpentine, and that which remains behind in the still is known as rosin (colophony). American turpentine has a very pleasant odor, and from several combustion analyses made by the author, the composition of turpentine taken directly from the barrel as shipped from the South corresponds absolutely with the theoretical formula $C_{10}H_{16}$. It has absolutely none of the qualities of a paint preservative, but is used only to increase the spreading power and working quality of paint. Entirely too much stress is laid upon the value of turpentine as a paint vehicle, and the sooner the chemist and the consumer realize that turpentine is simply an auxiliary, the sooner will better substitutes be used.

If the forestry department of this government will not interfere with the destruction of the trees, turpentine will become a chemical curiosity within the lifetime of many of us, unless new trees are planted.

American differs from Russian turpentine in odor and in specific gravity, although in chemical composition they are alike. The specific gravity of American turpentine is about .865 when fresh, but it will rise as high as .90 when old. It is supposed to boil at 350° F., but that also depends very largely on the condition of the turpentine and whether it has been exposed to the air. Turpentine flashes according to the text-books, and according to the majority of specifications that are written, at 105° F. As a matter of fact, its flash point is 98° F. Turpentine evaporates very slowly, and on account of this slow evaporation it is very highly prized as a varnish diluent, but there are paraffin products that have lately been invented that evaporate just as slowly and leave no residue behind. Pure turpentine when poured on a sheet of filter paper should leave absolutely no residue behind, and a drop of water poured on the paper after the turpentine has evaporated must be absorbed as readily by the paper as before it was immersed. In this regard the petroleum naphtha solvents are identical. They will be described in the proper chapter.

The following organic analyses of French, American, and wood turpentines show that French turpentine and American turpentine are both represented by the formula $C_{10}H_{16}$, the American turpentine being practically 100 per cent pure. Wood turpentine, however, may be shown to be 97.7 pure, the $2\frac{1}{2}$ per cent of impurities consisting of pyridene bases, formalin, and other wood decomposition products. Since these investigations were made in 1905, samples of wood turpentine have been placed on the market which are so nearly identical with the sap turpentine that it is almost impossible to distinguish them, only an experienced consumer being able to tell the difference, the wood turpentine having a peculiar odor which is lacking in the sap turpentine. No matter how thoroughly a wood turpentine is purified, there is always a smell of sawdust which clings to it and which can be recognized by a person once familiar with the odor. These pure grades of wood turpentine cannot be said to be adulterants of the sap turpentine.

French Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.2040 grams.	0.1870 grams.
CO_2 obtained	0.6558 grams.	0.6009 grams.
H_2O obtained	0.2161 grams.	0.1980 grams.
Hence, percentage composition,		
Carbon	87.67 per cent.	87.63 per cent.
Hydrogen	11.87 per cent.	11.87 per cent.
Total	99.54 per cent.	99.50 per cent.

American Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.1777 grams.	0.1828 grams.
CO_2 obtained	0.5714 grams.	0.5878 grams.
H_2O obtained	0.1923 grams.	0.1968 grams.
Hence, percentage composition,		
Carbon	87.70 per cent.	87.69 per cent.
Hydrogen	12.12 per cent.	12.07 per cent.
Total	99.82 per cent.	99.76 per cent.

Wood Turpentine

	First Analysis	*Second Analysis*
Weight of sample	0.1891 grams.	0.1656 grams.
CO_2 obtained	0.5939 grams.	0.5202 grams.
H_2O obtained	0.2042 grams.	0.1785 grams.
Hence, percentage composition,		
Carbon	85.65 per cent.	85.67 per cent.
Hydrogen	12.10 per cent.	12.08 per cent.
Oxygen	2.25 per cent.	2.25 per cent.
Total	100.00 per cent.	100.00 per cent.

In the Journal of the American Chemical Society[1] for 1904 a very exhaustive treatise is given on spirits of turpentine, in which it is demonstrated that the only reliable chemical test for differentiating between wood turpentine and the old spirits is the determination of the iodine absorption number. But even this is now growing to be very unreliable, for the reason that so much care and skill is exercised in the manufacture of wood turpentine that it is almost impossible to distinguish it from the sap turpentine. A great deal has been written on the optical activity of turpentine when observed through the polariscope. The paint chemist, however, cannot point with any degree of certainty to this test, excepting where a coarse mixture of benzine, rosin oil, etc., is made, and up to the present writing very highly refined turpentine and sap turpentines show little or no difference. The admixture of rosin oil, benzine, benzene, kerosene, and adulterants of that kind are, of course, differentiated with more or less ease.

Turpentine is by no means used as largely as it was prior to 1906. The reason for this, strange to say, is a moral one and not a physical one. Ten years ago it would have been thought impossible to do without spirits of turpentine in paint or varnish. Today it is used by many people who think they have to use it, and by others who use it in high grade piano and other finishing varnishes, because they believe it gives a physical flow to the varnish which cannot be obtained by the use of anything else. This, however, is disputed by many manufacturers. At any rate, the fact remains that several years ago turpentine rose from a price of about 40 cents per gallon to $1.13, for a number of men in the southern part of the United States attempted to corner the market. Before, how-

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[1] "Analysis of Turpentine," by Jno. M. McCandless, p. 981, 1904.

ever, the price reached the abnormal figure of $1.13 some of the officials of the United States Navy made exhaustive experiments and showed that the turpentine substitutes of the petroleum type were absolutely as good and served the same purpose as spirits of turpentine. Not to go into the details of this, about five years ago the United States Navy substituted some 70,000 gallons of turpentine by turpentine substitute, and the resulting paint gave just as good service and the saving in price was very great. The men who had attempted to corner the market and enrich themselves at the expense of others were finally ruined, and the whole turpentine industry received a staggering blow, from which at this date it has not entirely recovered. The price dropped until it hovered around 40 and 50 cents, but in the meantime the paint industry had learned the lesson, which was of tremendous value, that it could do without turpentine entirely.

TURPENTINE[1]

Distillation of Pure Gum Spirits of Turpentine

Will not begin distilling lower than 153° C.

1 to 2%	distills over by	153° C.
50%	" " "	157° C.
80%	" " "	159° C.
85%	" " "	160° C.
95%	" " "	165.5° C.
Sometimes		
50%	" " "	159° C.
80%	" " "	160° C.
85%	" " "	161° C.
95%	should be distilled by	165.5° C.

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[1] Data from J. E. Teeple, New York City.

Distillation of Steam Distilled Wood Turpentine

Usually begins distilling at about 153° C.
50% distills over by 160° C.
80% " " " 164° C.
85% " " " 165.5° C.
95% " " " 175° C.
Sometimes
80% " " " 163° C.
85% " " " 164° C.
90% " " " 165.5° C.
95% " " " 172° C.

This latter would be considered a very good grade.

Sometimes only 60% to 70% will distill by 165.5° C. — Poor grade.

WOOD TURPENTINE

The turpentine in the United States is held in such strong hands that the price is abnormally high, and within the last five years pine, sawdust, shavings, tree stumps, and old logs have been placed in retorts and distilled in the same manner as the sap of the pine tree. A liquid is obtained which is sold under the name of wood turpentine and is guaranteed by many to be absolutely the same material as that obtained from the sap of the tree. It must be frankly admitted that there are some wood turpentines on the market at this writing which are so similar to the real article that it is almost impossible to differentiate between them. And yet there is always a peculiar distinctive odor to these wood turpentines which does not exist in the pure turpentines. Several organic analyses of this variety of wood turpentine by the author have shown that the formula is not $C_{10}H_{16}$, but that it is a most complex mixture containing more than a trace of pyridene bases, formic acid, formaldehyde, and other products from the destructive distillation of wood. But wood turpentine is being improved so continually that these impurities are being largely removed. For exterior painting, wood turpentine that contains only a trace of these impurities is just as good as the sap turpentine, and for indoor painting it is no better than a number of the petroleum products and costs very much more money. It cannot be said that it has advantages in exterior painting over the benzine products. One reason why it can be used on exterior work and not on interior work is that the disagreeable odor it sometimes gives off becomes obnoxious to those who use it on interior work. The pure grades of wood turpentine cost within 5 cents per gallon of the price of sap turpentine, and judging from the large number of concerns that have sprung up within the last five years for the manufacture of wood turpentine and then slowly disappeared, it is reasonable to infer that the industry is not profitable.

AMERICAN SOCIETY FOR TESTING MATERIALS, PHILADELPHIA, PA., U. S. A., AFFILIATED WITH THE INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS

Standard Specifications for Turpentine

Serial Designation: D 13–15

The specifications for this material are issued under the fixed designation D 13; the final number indicates the year of original issue, or in the case of revision, the year of last revision. *Adopted, 1915.*

General. — 1. These specifications apply both to the turpentine that is distilled from pine oleoresins, and commonly known as "gum turpentine" or "spirits turpentine," and to the turpentine commonly known as "wood turpentine" that is obtained from resinous wood, whether by extraction with volatile solvents, or by steam, or by destructive distillation.

2. The purchaser, when ordering under these specifications, may specify whether gum spirits or wood turpentine is desired.

The turpentine shall be clear and free from suspended matter and water.

Color. — 3. The color shall be "Standard"[1] or better.

Specific Gravity. — 4. The specific gravity shall be not less than 0.862 nor more than 0.872 at 15.5° C.

Refractive Index. — 5. The refractive index at 15.5° C. shall be not less than 1.468 nor more than 1.478.

Initial Boiling Point. — 6. The initial boiling point shall be not less than 150° nor more than 160° C.

Distillation. — 7. Ninety per cent of the turpentine shall distill below 170° C.

Polymerization. — 8. The polymerization residue shall not exceed 2 per cent and its refractive index at 15.5° C. shall not be less than 1.500.

METHODS OF ANALYSIS

9. *Color.* — Fill a 200-mm., perfectly flat bottom colorimetric tube graduated in millimeters to a depth of from 40 to 50 mm. with the turpentine to be examined. Place the tube in a colorimeter and place on or under it a No. 2 yellow Lovibond glass. Over or under a second graduated tube in the colorimeter, place a No. 1 yellow Lovibond glass and run in the same turpentine until the color matches as nearly as possible the color in the first tube. Read the difference in depth of the turpentine in the two tubes. If this difference is 50 mm. or more, the turpentine is "Standard" or better.

10. *Specific Gravity.* — Determine specific gravity at any convenient temperature with a plummet, the displacement of which has been accurately determined for that temperature, or by an equally accurate method, using the factor 0.00082 for each degree centigrade that the temperature of determination differs from 15.5° C.

11. *Refractive Index.* — Determine refractive index at any convenient temperature with an accurate instrument, and calculate the results to 15.5° C., using the factor 0.00045 for each degree that the temperature of determination differs from 15.5° C.

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[1] The term "Standard" refers to the color recognized as standard by the "Naval Stores Trade." Turpentine is of "Standard" color when a depth of 50 mm. in a perfectly flat polished bottom tube approximately matches a No. 1 yellow Lovibond glass.

12. *Distillation.* — Use an ordinary Engler flask and condenser,[1] and heat the flask by placing it in a glycerin or oil bath of the general type described in Bulletin No. 135, Bureau of Chemistry. Fit the flask with a thermometer reading from 145° to 200° C. in such a way that the mercury bulb shall be opposite the side tube of the flask and the 175° mark below the cork. Place 100 cc. of the turpentine to be examined in the flask, connect with the condenser, insert stopper bearing thermometer, and heat until distillation of the turpentine begins. Conduct the distillation so that the distillate passes over at the rate of 2 drops per second. Note the initial distilling temperature and the percentage distilling below 170° C.

13. *Polymerization.* — Place 20 cc. of exactly 38 N (100.92 per cent) sulphuric acid in a graduated, narrow-neck Babcock flask, stoppered, and place in ice water and cool. Add slowly 5 cc. of the turpentine to be tested. Gradually mix the contents, cooling from time to time, and not allowing the temperature to rise above about 60° C. When the mixture no longer warms up on shaking, agitate thoroughly and place the bottle in a water bath and heat from 60° to 65° C. for about 10 minutes, keeping the contents of the flask thoroughly mixed by vigorous shaking five or six times during the period. Do not stopper the flask after the turpentine has been added, as it may explode. Cool to room temperature, fill the flask with concentrated sulphuric acid until the unpolymerized oil rises into the graduated neck. Centrifuge at about 1200 r. p. m. from 4 to 5 minutes, or allow to stand for 12 hours. Read unpolymerized residue, notice its consistency and color, and determine its refractive index.

NAVY DEPARTMENT SPECIFICATIONS

TURPENTINE

General Characteristics. — 1. The turpentine must be either a properly prepared distillate of oleo-resinous exudation of the proper kinds of pine, unmixed with any other substance, with the characteristic sweet odor of gum turpentine, or it must be pure wood spirits of turpentine, refined, and freed from heavy oils and empyreumatic or pyroligneous odors by steam distillation; both of the above shall be clear and water-white.

Specific Gravity. — 2. The specific gravity shall not be below 0.862 or above 0.872 at 15.5° C.

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[1] Stillman, "Engineering Chemistry," p. 503.

Refractive Index. — 3. The refractive index shall not be less than 1.468 nor greater than 1.476 at 20° C.

Boiling Point. — 4. The boiling point shall be between 152° C. and 158° C.

Distillation Test. — 5. When 200 c.c. of the turpentine is distilled, 95 per cent should pass over below 170° C.

For this test use a 300 c.c. flask, 8 cm. in diameter, with a side tube 8 cm. from the main bulb, and the neck extending 8 cm. above the side tube. The neck is 2 cm. in diameter and the side tube is 5 m. m. This flask should be fitted with a thermometer (reading from 145° to 200° C.) immersed in the vapor. The mercury bulb should be opposite the side tube of the flask and the reading 175° C. should be below the cork. The distillation should be so conducted that there shall pass over about two drops of the distillate per second.

Polymerization. — 6. When 5 c.c. of the sample is treated with sulphuric acid of specific gravity 1.84, according to the method herein outlined, there shall remain undissolved at the end of thirty minutes not over 0.09 c.c. The residue unpolymerized should show a refraction value between 1.50 to 1.52. It should be viscous in nature. If the residue is water-white, limpid, and does not show proper refraction value, it should be carefully polymerized with 38 N sulphuric acid according to Veitch (see p. 30, Bull. 135, or Cir. 85, Bureau of Chemistry, U. S. Department of Agriculture).

Method of Polymerization. — 7. Add slowly 5 c.c. of the turpentine to 25 c.c. sulphuric acid, 1.84, contained in an ordinary graduated narrow-necked Babcock flask. Shake the flask with a rotary motion to insure gradual mixing. Cool, if necessary, in ice water, not permitting the temperature to rise above 60° to 65° C. Agitate thoroughly and maintain at about 65°, with frequent agitations, for one hour. Cool. Fill the flask with H_2SO_4, bringing the unpolymerized oil into the graduated neck. Allow to stand one hour. Read off unpolymerized content, note its consistency and color, and determine its refractive index.

Color Test. — 8. Shake 10 c.c. of the turpentine with 10 c.c. of concentrated hydrochloric acid in a test tube. The development, after three minutes' standing, of a decided red color is indicative of the presence of other usually heavy resinous oils.

Evaporation Test. — 9. When 10 c.c. of the sample are placed in a glass crystallizing dish, $2\frac{1}{2}$ inches in diameter and $1\frac{1}{8}$ inches high, and evaporated on an open steam bath, with a full head of steam, for three hours, the amount of residue shall not weigh more than 0.15 gram. A single drop allowed to fall on clean white paper must completely evaporate at a temperature of 20° C. without leaving a stain.

Flash Point. — 10. The turpentine must not flash below 34° C. in Abel's enclosed tester.

11. Bidders must state specifically on proposals whether they propose to furnish steam distilled wood turpentine or pure gum spirits of turpentine.

CHAPTER XVIII

Pine Oil[1]

One of the industries which has developed as a result of the policy of conservation in the United States is the manufacture of useful products from resinous woods. Enormous quantities of the latter, which in previous years were considered of little or no use and were deliberately burned in huge burners especially constructed for the purpose, or which were simply allowed to go to waste, are now being economically and profitably manipulated for the recovery of turpentine, pine oil, and rosin, or the production of tar oils, pine pitch, and charcoal.

The two commercially important methods in vogue are, first, the steam and solvent or extraction process, and second, the destructive distillation process.

H. T. Yaryan[2] has taken out letters patent on a process for extracting turpentine and rosin from resinous woods, which very well illustrates the extraction method as practised today. Resinous wood, reduced to fine chips by passing through a wood chipper, is charged into an iron vessel through a charging door at the top. The wood rests upon a false bottom over a coil supplied with superheated steam for producing and maintaining the

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[1] Journal of Society of Chemical Industry, June 15, 1914, No. 11, Vol. xxxiii, by Maximilian Toch.

[2] The following is a list of the Yaryan U. S. Patents:

No. 915,400, March 16, 1909
915,401, March 16, 1909
915,402, March 16, 1909
922,369, May 18, 1909
934,257, September 14, 1909
964,728, July 19, 1910
992,325, May 16, 1911

proper temperature within the iron chamber. The door at the top and the discharge door at the bottom are closed, and the current of superheated steam is driven into the mass of chips. This is continued until the more volatile turpentine has been vaporized and driven over into the condensers. The wood in the extraction vessel is left charged with a small percentage of heavy turpentine, together with pine oil and rosin. Steam is shut off, the excess moisture in the hot wood is removed by connecting the vessel with a vacuum pump, and finally a liquid hydrocarbon (boiling point, 240°–270° F.) is sprayed over the top and allowed to percolate down through the pores of the wood. The resinous materials are thus thoroughly and completely extracted, and passed into a storage tank, from which they are pumped into a still used for separating the component parts of the solution. From the still the hydrocarbon solvent is readily separated from the heavier pine oils by distillation under reduced pressure, on account of the great difference in the boiling point between the pine oils and the hydrocarbon solvent, the former boiling between 350° and 370° F. The pine oils are in turn separated from the rosin by distillation with superheated steam.

Other so-called "low temperature" processes deserve mention as possessing features of merit, although sufficient data does not appear to be available to show their true value when operated on a large commercial scale. The Hough process, for example, is to be considered essentially a preliminary treatment in the manufacture of paper pulp from resinous woods. Chipped wood is placed in a retort and subjected to the action of a dilute alkali. The rosins are saponified and the soap separated from the alkaline liquor by cooling and increasing the alkali concentration to the desired degree. The rosin soap may be sold as such, or treated with acids for recovery of the rosin. The turpentine and pine oils are recovered either by preliminary treatment with steam or during the early stages of the cooking process.

It will be noted that in the low temperature processes the only products recovered are turpentine, pine oils, and rosins, the first two removed by the action of steam, either saturated or superheated, and the latter by extraction by use of a neutral volatile solvent or a saponifying agent. The so-called "spent wood" may be used either for the manufacture of paper pulp or as a fuel to generate the power necessary to carry out the process.

In the destructive distillation process, the wood, in the form of cordwood 4 ft. to 6 ft. in length and 4 in. to 8 in. in diameter, is placed in a horizontal retort and the temperature gradually raised until the wood is thoroughly carbonized. The factor of greatest importance in the successful operation of this process is temperature control, as it is essential that the turpentines and pine oils be removed in so far as is possible before the temperature at which the rosins and wood fibre begin to decompose is reached. The total volume of distillate, as well as the percentage volume of each of the several fractions thereof, is largely dependent on the degree of temperature control.

Destructive distillation of resinous wood was first carried out in earthen trenches, the combustion being controlled by partially covering the wood with earth. Tar and charcoal were the only products recovered. Then came the beehive oven, operated in much the same crude manner, but recovering the more volatile distillates, in addition to tar and charcoal. This was in turn superseded by the horizontal retort, externally heated, hot gases being circulated either through an outer shell or through pipes within the retort. Next came the bath process, wherein the cordwood was immersed in a bath of hot pitch or rosin, thereby volatilizing the turpentine and lighter pine oils and dissolving the heavier oils and rosins. After this preliminary treatment the bath was withdrawn and the wood subjected to straight destructive distillation.

More recently[1] a retort has been devised utilizing the basic principle of the laboratory oil bath. The retort is heated by means of a layer of hot petroleum oil which is kept continually circulating between the retorts and an outer cylindrical shell that completely surrounds the retort proper. In this way it is claimed that the temperature of distillation can be accurately controlled. The turpentine and pine oil obtained are fractionated and rectified by subsequent steam distillation. In running the retort the temperature of the oil bath is so regulated that the heat inside does not exceed 450° F. before all the turpentine and pine oil have been distilled.

The products of destructive distillation by the several processes are in each case of very much the same general nature, namely, turpentine, pine oils, tar oils, pine tar, pitch, and charcoal. In some instances low-grade rosin oils are also produced.

"Light wood" does not refer to woody fibre which has a low specific gravity. The name originated from the fact that this particular wood is so rich in oil and resinous material that it is readily used for lighting fires. In the southern portion of the United States little bundles of "light wood" are for sale in strips about $\frac{1}{4}$ inch in diameter and 1 foot long. When a flame is applied to one of these strips of wood it becomes useful for lighting fires, hence the name "light wood." The author has seen "light wood" so rich in resins and oily material that by transmitted light a thin section looked like translucent

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[1] T. W. Pritchard, Journal of Society of Chemical Industry, 1912, **31**, 418.

ruby glass. It is this particular wood which is most used for the distillation of wood turpentine, pine oil, and rosin.

The product from that type of pine tree from which turpentine is obtained has always been regarded as producing two materials when the sap has been collected and distilled. The one material is turpentine, and the other rosin. About ten years ago, when destructive and steam distillation of pine wood became a practical industry, a third substance was recovered. This material, intermediate between turpentine and rosin, is now known as "pine oil."

As far as the author knows, no one has yet determined the chemical constitution of this intermediate product of the pine tree, which has been designated as "pine oil." Two years ago the writer started this investigation, which is practically finished. There is as yet no standard of purity for pine oil, but that it has a definite chemical composition is now fairly well established. The only original investigation of the chemical composition of pine oil was carried out by Dr. J. E. Teeple[1] on long leaf pine oil.

Dr. Teeple says: "The commercial long leaf oil, as it comes on the market, is either clear and water white, containing 3 or 4 per cent of dissolved water, or it may have a very faint yellow color and be free from dissolved water. The specific gravity ranges from 0.935 to 0.947, depending on freedom from lower boiling terpenes. A good commercial product will begin distilling at about 206° to 210°, and 75 per cent of it will distill between the limits 211°–218° and 50 per cent of it between 213°–217°. A sample having a density of 0.945 at 15.5° showed a specific rotation of about $[a]^{20}_{D} - 11^\circ$, and an index of

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[1] Journal of American Chemical Society, 1908, **30,** 412; Journal of Society of Chemical Industry, 1908, 346.

refraction of N_D 1.4830. In fractional distillation of the oil the specific gravity of the various distillates rises regularly with increasing temperature, becoming steady at about 0.947 at 217°.

"If the oil consists essentially of terpineol, $C_{10}H_{18}O$, it should be easy to convert it into terpin hydrate, $C_{10}H_{20}O_2 + H_2O$, by the method of Tiemann and Schmidt.[1] The conversion was found to proceed easily when the oil was treated with 5 per cent sulphuric acid, either with or without admixture with benzine. If agitated continuously, the reaction is complete within 3 or 4 days. If, on the other hand, the mixture is allowed to stand quietly, the formation of terpin hydrate extends over several months and produces most beautiful large crystals, which, without recrystallizing, melt at 117°–118°. When recrystallized from ethyl acetate they melt at 118°. The yield is about 60 per cent of the theoretical. This forms such a simple, cheap, and convenient method of making terpin hydrate that it will doubtless supersede the usual manufacture from turpentine, alcohol, and nitric acid, and instead of terpin hydrate serving as raw material for the manufacture of terpineol, as heretofore, the reverse will be the case."

The term "pine oil," as now understood, is the heavy oil obtained from the fractionation of crude steam distilled wood turpentine. When the sap of the pine tree is subjected to distillation in a current of steam the volatile liquid — turpentine — consists almost entirely of the hydrocarbon, pinene ($C_{10}H_{16}$). When, however, the trunk, stumps, and roots of the same tree have been allowed to remain on the ground for a number of years and are then steam distilled, there are obtained, in addition to the turpentine and rosin, certain heavier oils formed

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[1] Ber., **28,** 1781.

by hydrolysis and oxidation as a result of exposure to the atmosphere. To the heavier oils thus formed and yielded up in the process of steam distillation the term "pine oil" is properly applied.

Pure pine oil has a very pleasant aromatic odor, similar at times to the oil of caraway seed or the oil of juniper seed. When pine oil is impure it is very difficult to use it for interior work on account of its pernicious odor of empyreumatic compounds. It has been used to a considerable extent for making paints which should dry without a gloss, and as a "flatting" material it has been very successful. It has the excellent quality of flowing out well under the brush and of not showing brush marks, the latter because it evaporates so very slowly. It is a very powerful solvent, and many of the acid resins which have a tendency to separate when they are insufficiently heated with drying oils will remain together when pine oil is added. Pine oil can be used to a considerable extent as a diluent in nitrocellulose solutions, and as a cooling agent for the reduction of varnishes it also has excellent qualities. The author takes this opportunity of stating that on previous occasions his recommendations concerning new and useful materials for the paint and varnish industry have been misunderstood in some instances, and it is to be hoped that these remarks will not be misinterpreted. Pine oil is a new and useful material, but it is by no means a substitute for linseed oil or turpentine or any of the other materials now on the market. It has properties peculiar to itself, and when intelligently used is of considerable value.

Practically all the pine oil obtainable contains a small percentage of water in solution, to which it clings rather tenaciously, and it is by no means a simple matter to dehydrate this material. A rather complex apparatus for dehydrating the material is necessary with temperature control, but the test which the author has devised for the determination of water is quite simple. If 5 c.c. of pine oil are mixed with 1 c.c. of a neutral mineral oil, like benzine, kerosene, or benzol, and a perfectly clear solution is obtained on shaking, no water is present; but if there is any water present in the pine oil the water appears as a colloid, and a milky solution is obtained which does not separate after long standing. The fact that pine oil will take up a considerable quantity of water and still remain clear makes it useful for emulsion paints such as are very much in vogue at the present time for the interior of buildings, and it has been suggested that the addition of water up to 5 per cent for such a purpose is beneficial on new walls. The United States Bureau of Chemistry[1] has developed a method for the determination of moisture by the use of calcium carbide; this is being investigated by the author but on account of its being a gas-volumetric method it is not quite feasible for general use in technical laboratories.

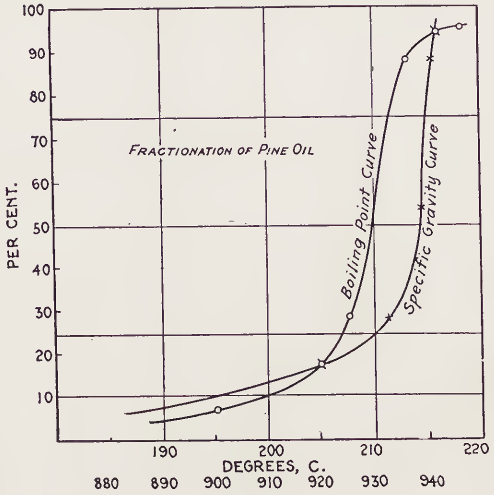

Fig. VI.

A number of commercial samples of pine oil were dehydrated and analyzed. The tables following indicate the results obtained: —

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[1] U. S. Dept. Agriculture, Bureau of Chemistry, Circular 97.

Table I. — Analyses of Pine Oils

Sample	Sp. gr. at 15½° C.	Color	Acid value	Iodine value	Flash (a) point °F.	Evaporation Tests						
						On steam bath (b) Per cent loss after	At room temperature — 65° F. Per cent loss after					
						9 hrs.	2 hrs.	4 hrs.	6 hrs.	8 hrs.	24 hrs.	32 hrs.
1	0.9423	Faintly yellow	0.68	142.5	170	93.4	27.8	43.8	52.2	67.2	96.7	96.7
2	0.9427	Not quite water white	0.29	118.4	175	96.3	20.3	31.8	41.8	50.8	92.4	92.7
3	0.9338	Water white	0.51	125.4	145	97.3	30.4	46.9	58.6	70.0	97.5	97.5
4	0.9330	Straw color	0.59	161.5	160	93.8	...	...	...	...	...	...
5	0.9291	Pale amber	0.49	173.9	148	85.7	...	...	...	...	...	...
6	0.9355	Straw color	0.70	143.2	168	92.7	36.8	56.6	69.8	80.4	95.5	95.5
7	0.9382	Water white	0.17	129.8	175	98.6	39.5	58.9	70.5	82.5	96.5	96.5
8	0.9350	Straw color	0.73	142.7	160	95.1	46.4	68.0	81.0	88.7	94.0	94.0
9	0.9383	Water white	0.27	124.4	176	98.7	24.6	35.3	46.0	53.2	88.8	90.4

(a) Open cup (Tagliabue tester).

(b) After evaporation a small, hard residue, similar in appearance to pale rosin was left. In the case of 4 and 5 the residue was very dark, almost black in color, due probably to impurities in the pine oils.

TABLE II. — FRACTIONAL DISTILLATION OF COMMERCIAL PINE OIL

Temperature	Fraction in %	Total distillate	Sp. gr. 15.5° C.
Water, 100°	2	2	0.882
174 — 194	5	7	0.920
194 — 205	11	18	0.933
205 — 208	10	28	0.939
208 — 210	25	53	0.941
210 — 213	35	88	0.942
213 — 216	6	94	0.942
216 — 218	1	95	
218 —	4	99	

TABLE III. — ULTIMATE ANALYSIS OF PINE OIL

Sample Number.	C.	H.	O.
1	78.1	11.5	10.4
2	77.9	11.4	10.7
3	77.0	11.1	11.9
4	81.8	10.6	7.6
5	80.9	10.6	8.5
6	79.0	11.4	9.6
7	78.4	11.2	10.4
8	79.6	11.5	8.9
9	78.3	11.1	10.6
Average	79.0	11.2	9.8
Terpineol (theoretical)	77.85	11.77	10.38
French turpentine	87.7	11.9	
American turpentine	87.7	12.1	
Wood turpentine	85.7	12.1	2.2
Pine oil, first runnings	84.3	11.8	3.9
Distillate pine oil, 174 — 195° C.	82.6	11.4	6.0

CHAPTER XIX

BENZINE

THE petroleum products are used very largely in the manufacture of all kinds of mixed paints, the principal one used being that known as "benzine." It belongs to the series of organic compounds having the general formula $C_nH_{2n} + 2$. Although it is frequently added to paint in its pure form as a diluent it is just as frequently added in the form of a liquid drier which is a solution of the original thickened drier in benzine.

Within the past ten years benzine has been so made that its odor is not very apparent, and there is much discussion as to whether benzine is a detriment to paint or not. It is hardly necessary to touch upon the moral side of this question. If a man should order a paint made according to a given specification and free from benzine, or to contain only turpentine as a diluent, the addition of benzine would be a palpable fraud. It is, however, unnecessary to discuss this point. The principal questions for discussion are, first, "Is a moderate amount of benzine harmful to paint?" Second, "How much benzine is permissible in paint?"

Answering the second question first, as to how much benzine is permissible in paint, that depends entirely upon the paint. A thick, viscous, ropy paint which is so difficult to apply that it will not flow evenly is undoubtedly improved by the addition of benzine. It would be just as much improved by the addition of turpentine; perhaps it would be improved most by the addition of kerosene, especially in the case of very quick drying paints, since kerosene evaporates more slowly than either benzine or turpentine. In the case of such dilution theory fails and only practice can dictate how much diluent can be added. In the case of a dipping paint where the even spreading of a linseed oil paint is desirable, and the sudden evaporation of the solvent helps to produce a uniform coat, benzine cannot be replaced by any other solvent.

The argument that is held forth by many, that benzine is of no value in a structural iron paint for the reason that its rapidity of evaporation lowers the dew point, as then moisture is deposited as it evaporates, is a most fallacious argument, although in theory it is correct. Turpentine will do exactly the same thing and so will any other solvent, depending entirely upon the hygroscopic condition of the atmosphere. If painting be done in an atmosphere where the humidity is high and the temperature near the dew point, it is always found that it makes very little difference what solvents are used, the condensation being apparent in any case. The metallic structure itself lowers the dew point so that the painting is being conducted on a film of invisible water, to the detriment of the paint and to the detriment of the metal. On the other hand a series of experiments made on this subject showed that where the dew point and the humidity are high, condensation easily occurs even though the percentage of moisture in the atmosphere is relatively small. (See "Causes of Rust in the Subway," Journal of the Society of Chemical Industry, 1905, No. 10, Vol. 24.) A great advantage is to be obtained by the moderate use of benzine, for in brushing on a quick-drying paint containing benzine the evaporation carries with it much of the moisture in the paint.

The low price of benzine in America offers a great temptation for its unlimited use. In France and Germany, where the petroleum products are more expensive than they are in America, and more particularly in France, benzine is not regarded so much as an adulterant. However, the physical effects of benzine have been so thoroughly overcome since turpentine has reached such an abnormal price, that a number of most excellent brands have been placed on the market as substitutes, all of which are equal in physical characteristics to pure spirits of turpentine. The objection, of course, to kerosene as a diluent in paint is that it may carry a small percentage of paraffin oil that has a tendency to produce a "bloom" on paint and particularly on varnish.

Quite a large number of petroleum products have been placed on the market which are so closely analogous to turpentine that were it not for the odor, or lack of odor, it would be very difficult to differentiate them. As an instance it may be cited that turpentine is a better solvent for some of the mixing varnishes and fossil and semi-fossil resin driers than benzine, but the newer petroleum or paraffin compounds, some of which have had marked success, are absolutely identical in solvent power, speed of evaporation, and viscosity, to turpentine, and while the polymerization acid test would clearly show that they are not turpentine, they can by no means be said to be inferior in working quality or solvent power to turpentine. The method by which these benzines are made consists in passing certain paraffin oils over red-hot coke in conjunction with wood turpentine. The product which is obtained has little or no odor. Thick or viscous paints, particularly the varnish and enamel paints, are so much improved by the addition of these materials that even an inexperienced painter will notice the free-flowing qualities of the material to which these diluents have been added.

The petroleum products used in the manufacture of paint are principally 62° benzine, which means benzine having a specific gravity of 62° Baumé. Some of the other naphthas ranging from 71° to 88° are used, but these are so light and bring so much higher prices than the 62° that they are not used as much as the 62° naphtha. The newer grades, however, which approach turpentine in physical characteristics, must be counted on as an important factor in paint on account of the extremely high price of turpentine, and the fact that it is strongly held in a few hands. On account of the decreasing amount of this product, substitutes must be recognized. After all, any solvent, whether it be benzine, turpentine, naphtha, benzol or acetone, is nothing but a solvent and evaporates completely, leaving the other vehicles to protect the paint. Of course, too much solvent is a detriment to paint, no matter what kind it may be.

BENZINE[1]

Engler Distillation of Commercial 88° Naphtha

Sp. Gr. (Westphal)..........15.6° C...........0.651

N_p 25°....................1.3695

Temperature	% Wt.	Sp. Gr. 15.6° C.	N_p 25°
50°	47.7	0.609	1.3605
50° to 75°	29.2	0.65	1.3756
75° to 100°	6.8	0.70	1.3930
Residue	1.4	....	1.4061

Engler Distillation of Commercial 62° Naphtha

Sp. Gr. (Westphal)...........15.6°...........0.732

N_p 25°....................1.4106

[1] Richardson & Mackenzie, Amer. J. of Sc. XXIX, May, 1910.

Temperature	% Wt.	Sp. Gr. 20° /20° C.	N_p 25°
50°	....	......	......
50° to 75°	1.2	......	1.3830
75° to 100°	20.0	0.7029	1.3956
100° to 125°	51.9	0.7286	1.4061
125° to 150°	24.6	0.7462	1.4168
Residue	9.2	......	1.4282

CHAPTER XX

TURPENTINE SUBSTITUTES[1]

WHEN coal is distilled in the dry form volatile hydrocarbon gases are liberated, which when condensed form a liquid which has great value in the arts, and is generally called crude benzol. Its composition really is about 60 per cent of benzol, the balance being toluol, xylol and solvent naphtha. The latter three are homologues of benzol. It is estimated that over forty million gallons of these solvents have been wasted in the United States in smoke and vapor in the manufacture of coke, but at this writing great efforts are being made to collect the vapors economically and to put in additional ovens for the manufacture of these by-products, so that it is very likely that both benzol and toluol will soon be sold again at normal prices. At this writing both benzol and toluol have risen from 25 and 30 cents per gallon to $1.25 and $7.00 per gallon respectively, owing to the great European war and to the small amount of benzol and toluol manufactured in the United States. These materials have been sought for very eagerly for the manufacture of both carbolic and picric acids and trinitrotoluol.

BENZOL

This material was for many years known under the name of benzene, and here it must be noted that the benzene which is equivalent to benzol is always spelled

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[1] In the chapter on "Turpentine" the author has related how turpentine substitutes came into their own on account of the excessive price of turpentine.

benzene, and the light naphtha obtained from paraffin crude oil is spelled benzine.

Benzol is the first volatile liquid which is recovered when coal tar is distilled. Benzol when pure is colorless, has a pleasant odor, a specific gravity of 0.879 and a boiling point of 191° F. It flashes practically at air temperature. It crystallizes into a solid at the freezing point of water and has a peculiar analogy to water inasmuch as it melts again at about 37° F. It is insoluble in water but is soluble in alcohol, ether and petroleum naphtha. Its formula is C_6H_6; it attacks, though it does not dissolve, all forms of linoxyn, which it wrinkles and removes from the base. It is for this reason that it is so valuable as a paint remover.

Benzol has remarkable solvent properties for many things which contain water, such as a number of the soaps, and is therefore invaluable to the paint manufacturer when used in small quantities, for it prevents the livering or saponification of many of the paints which have alkaline tendencies, and which would become unfit for use if it were not for the small quantity of benzol added.

The addition of benzol to mixed paints to be used for priming purposes has been found to be very advantageous, on account of the fact that a firmer bond is formed between a priming coat and the wood, so that when benzol is found in a mixed paint recommended for priming purposes it must be looked upon as a valuable ingredient.

The addition of a very small percentage of benzol to mixed paints does no harm, but if a paint made with benzol and intended as a priming coat be used as a finishing coat it is quite likely to attack the ground coats and produce a shriveled effect.

The theoretical chemist will sometimes make a mistake when he finds benzol in a black mixed paint by reporting the presence of coal tar, from the false reasoning that if benzol is present coal tar must be present, because benzol is a constituent of coal tar. A chemist must, therefore, be very careful in drawing such a conclusion, for the presence of either coal or pine tar in a paint can be determined by other methods.

TOLUOL

Formula, $C_6H_5 \cdot CH_3$

Toluol is very closely related to benzol, has practically the same specific gravity but a trifle lower—.869 to .87—a freezing point of 30° F., and a boiling point of 230°. It does not flash at air temperature, and therefore is of considerable value where high flash paints are wanted.

In the manufacture of turpentine substitutes out of paraffin or petroleum naphthas the addition of toluol is of great value, particularly where refractory gums are to be dissolved. As for instance, cold petroleum naphtha added to a manila varnish will practically throw it out or precipitate it out, whereas the addition of toluol prevents this, depending upon the amount of toluol that the solvent contains.

It has been recommended, and from experiments made it appears to be a fact, that toluol added to a paint in a quantity not over 10 per cent is of great value in the painting of cypress wood, but it is doubtful whether it is any better than pine oil, which can be used more liberally and which has even more penetrative effects and a higher flash point than toluol.

XYLOL

Formula, $C_6H_4(CH_3)_2$

Xylol really consists of three isomers having boiling points of 278° and 287° respectively. It cannot be very well separated by distillation. Xylol has all the characteristics of toluol but is not used to any great extent in the paint industry on account of its high price.

SOLVENT NAPHTHA

This is a mixture of different hydrocarbon compounds which have not yet been very well worked out; but solvent naphtha has a very disagreeable odor, which no one has been able to remove up to the present time, and therefore its use in the paint industry is very limited. When someone will discover a method for deodorizing solvent naphtha it probably will replace many of our solvents, as it is really a better solvent than anything we know of at present, and even dissolves such materials as gutta percha, balatta and many forms of rubber. Its specific gravity is the same as that of xylol and toluol, but it boils at a much higher temperature, depending upon its composition, from 300° F. to 360°.

CHAPTER XXI

COBALT DRIERS[1]

THE cobalt compounds which are generally offered on the market today may be divided into two classes. In the first are cobaltous oxid, acetate, sulphate, chloride, nitrate, hydroxid, and basic carbonate. In the second class are various grades and qualities of resinates (sometimes called sylvinates), both fused and precipitated, oleates or linoleates, oleo-resinates, tungates and resino-tungates, besides some other liquid preparations composed in whole or part of the foregoing.

From the varnish manufacturer's standpoint the substances in the first division are crude materials which are utilized in the production of the compounds in the second class, and also in the preparation of some varnishes, liquid driers, drying oils, and the so-called paint oils. The materials enumerated under the second class are the result of a varnish maker's labor, and when properly made and used in mixtures to which they are adapted give very good results.

The inorganic salts of cobalt do not directly come under the scope of this paper, and thus will not be directly considered except inasmuch as their use as crude material affects the driers into whose composition they enter.

It is only within the past three years that the cobalt driers have been offered to the American paint and varnish

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[1] By V. P. Krauss, 8th Int. Congress of Applied Chem. From the laboratory of Toch Brothers, under the direction of the author.

manufacturers. Up to the present time their use is not general, first, because of the very high price, and second, because their use is not thoroughly understood. Many experimenters have had unsatisfactory results and therefore refused to further consider the introduction of the new material. Furthermore, not all of the cobalt driers, whether liquid, paste, or solid, now offered for sale, are properly made and truly adapted to the purposes for which they are recommended. This situation, in addition to unsatisfactory results obtained by some of those experimenting, would naturally have a retarding effect on the introduction of a new type of material.

The salts of cobalt which are at our disposal in commercial quantities are all of the cobaltous or divalent type. It has been found that although they can be readily used in the manufacture of driers and worked like the various compounds of manganese, lead, zinc, calcium, aluminium, etc., the organic compounds formed, which are the basis and active principles of the so-called driers, are not efficient while in the cobaltous state. The cobaltic combinations, however, are very active driers, and it is for the formation of trivalent cobalt compounds that we strive in the making of driers. This transformation can be effected in several ways. By blowing cold, heated, or ozonized air through the hot cobaltous drier stock, or by the introduction of liquid or solid oxidizing agents. The use of cold or even heated air is a very long and tedious operation if carried out to the extent to which it is necessary in order to get the maximum strength in the drier, and greatly adds to the cost of an already expensive material. The use of the liquid or solid oxidizers can be carried out successfully and in a comparatively short time, although even when great care is exercised the batch of material is in danger of catching fire.

Since driers are used in a number of industries in which drying oils form part of the material produced, and since the operating methods of the various manufacturers are widely divergent, the siccatives or driers adapted to each will in many instances show widely different characteristics, not merely in form but also in composition.

Since the paint manufacturer and also the practical painter who mixes his own paints from paste colors and raw or treated oil are the principal consumers of what are generally known as driers, the materials adapted for their use may be first considered. The driers will, in practically all instances, be in the liquid state either very fluid, of heavy consistency or of a semi-paste nature. In composition, they will mostly consist of resinates, tungates, oleates, or linoleates, or combinations of the three. For the drying of linseed oil, when the proper driers are selected, little or nothing can be asked in addition to those known at present. When the general lead, manganese and other prevalent metallic driers are well chosen raw linseed oil can without any difficulty be made to dry by the addition of from 5 to 10 per cent or even less, the time of drying under average weather conditions being from 10 to 24 hours. By the use of cobalt driers, the same drying effect can be obtained when only from 1 to 3 per cent of a liquid drier is used. The author is not yet prepared to say positively what the ultimate effect of cobalt driers is upon paint films, but from the experiments made it is deduced that cobalt has not the harmful progressive oxidizing action that some of the usual manganese-lead compounds have. It has also been noticed that although a cobalt drier may be fairly dark in color, it will not have as darkening an effect as one of the usual driers of like color would have upon a white paint. The cobalt driers likewise show the same phenomena as some of the others when used in excessive amount; that is, that although the paint film will set up well in the usual time the drying action apparently reverses and the film remains tacky.

The terms applied to liquid driers are often uncertain and apt to be misleading. There are no general standards for strength or consistency, and, it must be admitted, many of the materials found on the market contain more volatile thinners than is conducive to obtaining a maximum drying effect with a minimum quantity of drier.

The value of the cobalt specialties depends not on their power to dry linseed oil, but on their ability to make the lower priced semi-drying oils act like it.

Soya, fish, and even corn and cottonseed oil are adaptable for use in paint, and when correctly treated, increase its durability.

In the making of waterproof fabrics, insulating coatings, etc., both liquid and solid driers are used. In the linoleum, oilcloth, patent leather, artificial leather and similar industries, the semi-liquid, paste, and solid driers are in demand since for these products the manufacturers cook the oils and varnishes in their own factories.

The paste and solid driers must essentially be considered under the caption of crude materials because they must be churned or cooked in the oils or varnishes in which they are used.

The methods of making both the solid and liquid driers are in general similar in the first stage of the process, and thus may be described under the same headings.

Resinate of Cobalt; Precipitated and Fused.—This is correctly made by saponifying rosin or colophony with caustic soda or sodium carbonate, care being taken to avoid an excess of the reagent, and then precipitating with a solution of some salt of cobalt. The chloride or sulphate serve best for this purpose. The precipitated resinate, or as it is sometimes called, rosinate or sylvinate, must then be thoroughly washed, and then pressed and dried. This will yield a pinkish, fairly fluffy powder when ground, which will readily dissolve in oil at a low temperature. The fused variety is made by melting the dried resinate in a kettle and then pouring into cooling pans. The operation is performed more rapidly by taking the cakes from the presses and driving off the water and fusing in one operation.

Cobalt Oleates or *Linoleates.* — The basis of this class is generally linseed oil, although walnut, perilla, soya, and some other oils may be used. The oil is thoroughly saponified with caustic soda, and, like the resinate, precipitated with a salt of cobalt. The material is then carefully washed and pressed. It may be melted to form a dark viscous heavy fluid.

Several samples of cobalt linoleate examined consisted of bodied linseed in which small amounts of inorganic cobalt salts had been dissolved. Another was of the same order with the addition of volatile solvents.

True linoleate of cobalt, when fused with varnish gums and dissolved in volatile oils, yields an excellent drier.

Oleo-resinates. — This type of drier is made by melting together the precipitated resinate and linoleate, sometimes with the further addition of fused fossil gum-resins.

Tungate of Cobalt. — Like the linoleates, the tungate of cobalt is made by saponifying pure China wood oil (tung oil) with caustic soda, care being taken to avoid excess of caustic, and then precipitating with a salt of cobalt. The tungate is then washed thoroughly, pressed and generally dried and fused. Great care is necessary in the preparation of a tungate since it oxidizes very rapidly, and the oxidized material is useless.

Like the linoleate of cobalt, the tungate may be fused with the resinate to form what may be called a resino-tungate.

In general the foregoing substances are incorporated in oils by means of heat, the combining temperature being between 300° and 500° F. The amount necessary will vary from about $\frac{1}{2}$ per cent to 5 per cent. In order to make *liquid driers*, the paste or solid driers can be melted alone or in combination with gum-resins, bodied linseed oil, or both, and then thinned to liquid consistency with volatile oils.

Among other cobalt salts, some of the chemical manufacturers offer the acetate, with directions for its use as a drier. All agree that between two and four tenths of 1 per cent are necessary to dry linseed oil. The oil should be at a temperature between 300° and 400° F., and be carefully stirred until all the salt is dissolved. Soya and China wood oil may be similarly manipulated.

It is still a little too soon to make a positive statement as to how oils thus treated with the acetate withstand wear and exposure.

Cobalt oxide, like the acetate, can be directly added to oil during boiling. It, however, dissolves slowly and necessitates heating to high temperature; the resulting product is also very dark, and mostly consists only of bodied oil. Rosin also will directly combine with cobalt compounds on heating together in a suitable kettle or container. The product possesses a number of objectionable features. It still is mostly unchanged rosin, has become much darker and lost considerably in weight due to volatilization. The effect on oils of quite a number of cobalt compounds was tried, but none equal in efficiency to those described in the foregoing was found.

CHAPTER XXII

COMBINING MEDIUMS AND WATER

Combining Mediums

In certain classes of mixed paints, particularly house paints which are made of corroded lead, sublimed lead, barium sulphate, etc., there is a likelihood or tendency of the pigment to settle. This is more marked in the case of corroded lead than in any of the other pigments. To prevent this, in a measure, water is added, and up to a certain percentage (1 per cent) both the manufacturer and the consumer have accepted the fact that water is not injurious when added for the purpose of combining the paint; but beyond this percentage its effect is likely to be injurious.

Sometimes for the sake of an argument, but more often for the sake of making a paint which contains no more water than the natural moisture of its constituents, a manufacturer feels the necessity of adding a combining medium other than water to prevent the paint from settling hard in the package. Among these are gutta-percha solutions, solutions of balata, para-rubber, gum chicle, etc. The rubber solutions mentioned serve their purpose very well without injuring the paint, and the percentage used is so small that it may be considered negligible. This, however, is not true of many of the mixing varnishes which are made by varnish manufacturers who have no experience in the manufacture of paint. They sell rosin varnishes neutralized with lime, lead, or manganese, and while they assist very well in combining the lead with the oil, the wearing quality of the paint is proportionately reduced.

Within the last few years a new combining medium has appeared on the market which in itself is an improvement on all paints. It is made by melting a mixture of a resin (free from rosin or colophony) and heavy linseed oil, and reducing with China wood oil and naphtha. Where a manufacturer uses a combining medium of this character the paint becomes more viscous as it grows older, and when it dries it produces a satin-like gloss and shows fewer brush marks than a paint containing water.

Water in the Composition of Mixed Paints

The question of how much water shall be added to mixed paints, or how much water mixed paints shall contain, either added or incidental, is not fully decided upon, as there is a difference of opinion as to its value, and likewise a difference of opinion as to the amount necessary for certain purposes. There are some paints in which as high as 2 per cent of water is necessary, and in other paints less than 1 per cent is purposely added. That water is of great benefit in certain paints cannot be disputed, one large railway corporation permitting the addition of 1 per cent of water to its mixed and paste paints.

A chemist in making an examination of a mixed paint must necessarily be careful in giving an opinion as to the amount of water in the paint, and great judgment must be used in a report. For instance, a paint, made according to a certain specification, containing a large mixture of Venetian red and yellow ochre, might contain very nearly 2 per cent of moisture, which was a part of the composition of the pigment. Then again, linseed oil frequently contains more than a trace of water, which the manufacturer cannot extract nor can he afford the time necessary to allow the water to settle out of the oil. A mixed paint should not contain over 1 per cent of water, for it is unnecessary to add more than this amount to any paint.

The proper benefits derived from the addition of water to a pure linseed oil paint are suspension of the pigment and improvement in its working quality. Take the case of artists' tube colors which lie on the dealers' shelves for years and which are prone to get hard and likely to separate so completely that the color will be found on one side of the tube and the oil be entirely free on the other. Water is an absolute necessity in this case and is an improvement for both seller and user. The colors made with the correct addition of water are known to "pile," and artists prefer a color which "piles" properly.

There are many ways of adding water to a paint. In some instances the required amount of water, together with the oil and the drier, are placed in a churn or mixer and the paste paint stirred in. Where materials like calcium sulphate, calcium carbonate, ochre, Venetian red, silicate of magnesia, silicate of alumina, white lead, etc., are used, there is no necessity for adding any combining material which will form a soap with the linseed oil, there being sufficient action between these materials and the water. It is an additional advantage that there is less likely to be complete saponification in a mixed paint to which no "emulsifier" has been added.

The following materials are used for emulsifying paints:

Saturated solutions of hypochlorite of lime.
Five per cent solution of carbonate of soda.
One-quarter of one per cent solution caustic soda.
One per cent solution of carbonate of potash.
Emulsion mixtures of half water and half pine oil.
Solutions of hypochlorite of lime containing twenty per cent wood alcohol.
Ten per cent solution of borax.
Five per cent solution zinc sulphate.
Seven per cent solution lead acetate.
Five per cent solution manganese sulphate.
Solutions of ordinary laundry soap or rosin soap in half alcohol and half water.
Weak solutions of casein dissolved in ammonia water.
Ordinary lime water emulsified with linseed oil.

There is no license whatever for the addition of much water to paint. Some authorities state that as high as 1½ per cent is permissible, but the author does not by any means subscribe to that, as 1½ gallons of water in 100 gallons of paint are far in excess of any desirable amount. Three-quarters of 1 per cent or at most 1 per cent would probably be a maximum, and as an explanation of this it must be understood that materials like ochre, clay, silicate of magnesia, white lead, calcium sulphate and many of the pigments which contain moisture or water of crystallization may carry a small amount of water into paint.

Yet there may be cases where water is permissible up to 5 per cent, but only for interior purposes. Flat wall paints which have a tendency to settle hard can be emulsified so as to prevent them from settling, and in a case of this kind where the wear of the paint is not taken into consideration there may be some excuse or license for the addition of water.

To detect water in paint, particularly in light-colored paints, is a comparatively simple matter. The method devised by the author is almost quantitative for some purposes. The first method ever published by the author consisted in placing a strip of gelatin in a mixed paint. When a measured or weighed amount of mixed paint was taken and the strip of gelatin allowed to remain immersed for twenty-four hours a fairly correct quantitative determination was obtained. Another method described some years ago involved the use of anhydrous sulphate of copper, a bluish white powder, which on the addition of water returns to the natural dark blue color of crystallized copper sulphate.

The author has, however, devised the scheme of using a glass plate and mixing a paint with a dyestuff such as "Erythrosine B." When about ½ gram of the dye and 5 grams of mixed paint are rubbed together with a palette knife on a sheet of glass, a paint containing no water will produce a distinct pearl-gray color; if there is water in the paint the mixture changes almost immediately to a brilliant cerise red, and if there is much water in the paint (over 2 per cent) the color changes into a crimson, so that the reaction is clearly marked. The test must not be allowed to stand more than four minutes, since even paints which contain no added water but which naturally contain traces of moisture will begin to change into a rosy color, in which the presence cannot be reported. In red, black or dark colored paints Erythrosine B is just as indicative of water in paint, particularly when the mixture is viewed by transmitted light. Even in the case of black paint the erythrosine emulsion paint will produce a beautiful purple color.

CHAPTER XXIII

FINE GRINDING

THERE is a great difference of opinion on the question of how paints should be ground, and a careful canvas on this subject reveals the fact that most paint manufacturers believe that all paints should be very finely ground. This is a great error, for there are many conditions where a paint should be slightly coarse in order to give proper results, for if paints do not have a slight amount of coarseness, or "tooth" as it is called, one coat will not hold successfully on the other, and it is for the very reason of producing a mechanical bond that fillers are used which have a distinct grain. Without making any general rule on the subject, all priming coats should have sufficient tooth to enable the succeeding coat to hold.

Those familiar with the subject are aware of the fact that a gloss coat on a gloss coat very frequently peels, and the same is sometimes true of a gloss coat on a priming coat which is too finely ground. This does not apply to a finishing coat, because the finer a finishing coat the longer it lasts and the cleaner it remains, for a coarse finishing coat will hold dust and dirt which even a heavy rainstorm will not always dislodge, while a smooth, finely ground finishing coat acts like a glaze and remains clean until it perishes. It may therefore be taken as a general statement that priming coats should be slightly coarse and finishing coats should always be fine.

If you take the case of the finishing of a very fine object like a piano or an automobile, rubbing varnishes are used on the undercoat, and these varnishes are scarified with pumice stone for two reasons: first, so as to smooth the coat thoroughly because the succeeding coat when applied will then itself produce a smooth and glossy effect, and secondly, so that the next coat which is applied can bind itself mechanically to the undercoat. If, therefore, rubbing is a practice where varnished objects are to be finished, it must be taken as a rule that where paints are applied and rubbing is not practiced a slight grain is of great benefit, so that the question of fine grinding does not apply to every case.

CHAPTER XXIV

THE INFLUENCE OF SUNLIGHT ON PAINTS AND VARNISHES[1]

It may properly be said that direct sunlight has a very destructive action on paint and varnish films, and the author had noted as far back as 15 years ago that many of the paint materials that were perfectly waterproof in places where sunlight never reached became permeable to water and disintegrated very rapidly when exposed to direct sunlight. As an example of this, it might be cited that pure asphaltum, when applied in a good continuous coat on cast iron pipes in a cellar, will last from three to four years, yet the same asphaltum when applied on the roof of a building will show almost complete decomposition within 20 days. In order, therefore, to determine the cause, the first experiments with a series of bitumens were made as follows: Sheets of clean steel and wood were painted with a variety of bitumen compounds and exposed to direct sunlight under various colored glasses, finally reduced to the three colors, violet, green, and red; for obvious reasons these three served all purposes. It was found at the end of four weeks that the bitumens exposed under the blue rays showed marked signs of decomposition, those under the green showed some signs, and those under the red none whatever. The same experiments were tried again by cementing the glass to the painted surface, when little or no decomposition followed in any case. A large

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[1] Reprinted from the Journal of the Society of Chemical Industry, April 15, 1908. No. 7, Vol. XXVII, Maximilian Toch.

variety of experiments was then tried by mixing the bitumens with various pigments, and a preservative action was obtained in direct ratio to the pigment used, so much so that a sample of paint made to contain 80 per cent of bitumen, 15 per cent of linseed oil, and 5 per cent of finely divided carbon, showed only slight deterioration at the end of six months; this was easily accounted for by the fact that the finely divided carbon prevented the absorption of many actinic rays. While these experiments were very conclusive, it was necessary to determine the cause, and to this end a large variety of experiments was conducted, all of which were productive of excellent results.

All asphaltums are bitumens, but all bitumens are not asphaltums, and it is necessary to look into the composition of the asphaltums which decompose in the sunlight and of those resins which do not. The difference between a resin and an asphaltic bitumen may generally be stated as follows: — Asphaltums and bitumens are composed principally of carbon and hydrogen, whereas the resins are semi-fossilized, and composed of carbon, hydrogen, and oxygen. Asphaltums, whether they be natural or artificial, consist largely of hydrocarbons of the series of C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-8}, etc., and according to Clifford Richardson[1] and others, these hydrocarbons are probably polymethylenes. From a large number of combustion determinations made with bitumens, it may be safely stated that many of the bitumens are probably polymethylenes of various series, as above. There are, of course, substances in bitumens such as sulphur and nitrogen, which probably exert very little influence on the material from an actinic point of view. Assuming,

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[1] See "The Modern Asphalt Pavement" and "Origin of Asphalt," by Clifford Richardson.

therefore, that the hydrocarbons are of the character described, we should have under the combined action of the oxygen of the air and the actinic rays of the light, sometimes, in conjunction with moisture, a favorable condition where oxygen would combine with hydrogen, and carbon be set free. Therefore, if this reaction takes place, all bitumens in a short time ought to become carbonized and deposit relatively pure carbon on their surfaces, and this is exactly what takes place, the action of the sunlight probably resulting in a combination of the hydrogen with oxygen, and a deposit of what appears to be carbon takes place. If this, then, is the first lucid explanation of the decomposition of bitumens in sunlight, it is the explanation of the cause of the valuelessness of pure bitumens as protective paints for exterior purposes. Even the addition of a small amount of bitumen to a large percentage of otherwise good paint will result in the decomposition of this paint when exposed to the direct action of moisture and light.

We have no such action when materials are used which are glycerides of fatty acids, such as fish oil, Chinese wood oil, and linseed oil. Indeed, any one of these three oils are light-proof in a very large degree, and fish oil and Chinese wood oil are both heat-proof and light-proof. Linseed oil, however, unless prepared with fossil resins, is not water-proof, but fish oil is more water-proof, and Chinese wood oil most water-proof of all. At the same time, pure Chinese wood oil is less light-proof, next comes fish oil, while linseed oil is most light-proof, and there would appear to be an established ratio that a paint or varnish containing the least amount of oxygen is the least light-proof and the most water-proof, and the paint containing the largest amount of oxygen is most proof against light, and least water-proof.

In conclusion, and as evidence of the correctness of these statements, if a sheet of metal or wood be painted with asphaltum or bitumen-paint and exposed to sunlight and air, the coating will be rapidly decomposed, and after a lapse of 20 days probably carbon will be set free. At least, this is a deduction from the nature of the bitumens. Minute scrapings from the surface of exposed bitumens show that the principal constituent is carbon, and, whereas the original material contains much less, the exposed bitumen shows over 95 per cent of carbon, the remainder being principally hydrogen, with a small difference, which is evidently oxygen. This shows that the general reaction tends to produce carbon.

The painting of concrete to preserve it against the action of moisture and frost is destined to become as large an industry as the painting of wood, and those who have tried asphaltum paints for this purpose have already found to their sorrow that disintegration takes place in a very short time, even though the material be perfectly proof against the alkaline action of the lime in the concrete, and as linseed oil paint is rapidly destroyed by concrete itself, owing to the interaction of the lime and the linseed oil, we have to look for other materials with which we can coat concrete in order to preserve not only its appearance, but the very structure itself.

Regarding the action of sunlight on pigments, it is well known that lithopone is rapidly acted upon by light, and direct sunlight turns it a dark gray, but frequently overnight the color leaves it and it is brilliant white again in the morning. English vermilion (mercuric sulphide) is also acted upon by sunlight, and forms first a brown compound and then a black compound of mercury. This has been regarded as mercurous sulphide or as a sub-sulphide of mercury, but on this question the writer has doubts. Some of the oxids of iron, particularly the bright red ferric oxids, are affected by light, and a compound results which from bright red turns to brown, probably a change tending towards the formation of ferrous oxid.

We know that a large number of the organic dyestuffs tend to bleach in the sunlight, but sunlight alone is never very active regarding the decomposition of colors when air is excluded, for even mercury vermillion is regarded as permanent when it is covered by a coat of varnish. This is largely true of the organic lakes and finer colors used for coach painting. Linseed oil itself is bleached by sunlight, but this is a chemical change produced by the actinic rays in which the green chlorophyll is changed to pale yellow.

CHAPTER XXV

PAINT VEHICLES AS PROTECTIVE AGENTS AGAINST CORROSION [1]

A CAREFUL search of the literature of the past twenty years has failed to reveal anything like a systematic investigation of the relative value of different vehicles used in the manufacture of paints for structural steel and the prevention of corrosion. There are a few isolated cases in which boiled linseed oil,[2] Kauri linseed oil varnish[3] and spar varnish as protective coatings on structural steel were studied. For many years past much has been written and many investigations have been made on the protective quality of the pigments, but no one has apparently made any study of the vehicles.

It is quite obvious that without a vehicle a pigment is useless, and the author knows of no instance where a pigment could be used alone, with perhaps the single exception of Portland cement, if that may be classed as a pigment; even then, Portland cement would be useless unless water were used as a vehicle. The example need hardly be called to your attention of taking a dry pigment and using water as a vehicle to show you that when the water evaporated it would leave the pigment, and the pigment in turn would leave the metal; and yet, to the best of the author's

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[1] Journal of Society of Chemical Industry, June 15, 1915. No. 11, Vol. XXXIV, by Maximilian Toch.

[2] C. Von Kreybig, *Farben Ztg.*, **17,** 1766–8; J. N. Friend, Carnegie Scholarship Report, Iron and Steel Inst., May, 1913, pp. 1–9.

[3] Address of Prof. A. H. Sabin before American Society of Civil Engineers, Nov. 4, 1896, reported in *Engineering News*, July 28, 1898.

knowledge, nobody has paid any attention to the very important rôle that is played by the vehicle itself. There is an old proverb which says, "One hand is useless, for one hand washes the other," and it seems that the same is true with reference to vehicle and pigment, for one is of little value without the other, and if any value is to be attached to either of them the vehicle has by far the advantage, because there are some vehicles which protect for a considerable length of time.

With this end in view exposure tests were made in 1913, in which fifty-two steel plates (in duplicate) were carefully freed from grease by washing with benzol, dried, sanded, and rubbed clean with pumice, and then coated with all the paint vehicles or protective vehicles to the extent of fifty-two in number, many of which, of course, are seldom, if ever, used alone, and some of which are failures a short time after they are put on. However, the author wanted to do this thing thoroughly, and for this purpose selected the same quality of steel, known as cutlery steel, which has been used by him for many years for his exposure tests. It is a steel which rusts very rapidly.

Those plates must be eliminated which have shown no rusting in the year and five months that they have been exposed. These were coated with the paraffin or machinery oil compounds, and it would be poor advice to any engineer to coat steel with paraffin compounds, for the method of cleaning before the application of any good paint would have to be very carefully followed out, since no protective paint would hold on steel that retained the least trace of a paraffin coat. Then the paraffin, or non-drying oils, all collect a great deal of dirt, which showed that this would have to be entirely removed before any paint could be applied.

Plate No. 41 showed excellent results, and a material of this kind would not be so very expensive where engineers demand that steel be coated with a clear liquid in the shop so that the steel may be inspected in the field. This was composed of half spar varnish and half stand oil. Stand oil is practically a polymerized linseed oil. Linseed oil when heated to 550° F., with a drier like Japanner's Prussian brown or borate of manganese will produce a very thick viscous liquid, which is largely used as a patent leather finish. This can be reduced with 50 per cent of thinner and still have the fluidity or viscosity of raw linseed oil, and is, therefore, inexpensive.

Plate No. 50 was coated with a material containing 10 per cent of paraffin oil, which might be classed as an adulterated linseed oil, and while it showed up very well, it could not be recommended because on an exposed structure like a bridge a coat of good protective paint would not adhere very thoroughly.

Plate No. 52 has taught a valuable lesson with regard to the use of raw China wood oil which is heated to a sufficient degree of heat to take 10 per cent of a tungate drier, and then thinned with 15 per cent of benzine. This made a material which is hardly more expensive than good, boiled linseed oil, and left a most excellent surface for repainting. In fact, this has proved itself the equal of plates No. 22 and No. 23, with the addition of a better surface for repainting.

Plate No. 46 was coated with kettle-boiled linseed oil, and is very good, but this material might be regarded by some engineers as too expensive for application, as it took all day to make this oil. A carefully selected linseed oil was chosen to start with, to which was added 5 per cent of litharge and no other drier. This oil dried very badly, but when it did dry produced a good flexible film which lasted. This must not be confounded with the average boiled linseed oil of commerce.

The various coatings used in these exposure tests have been divided according to their protective value into five classes:

1 and 1 b — Those vehicles which have little or no value for the prevention of rusting.

(*a*) The raw and refined drying and semi-drying vegetable oils. (Plates Nos. 1, 7, 8, 13, 35, 36, 47, 48.)

(*b*) The same oils to which 10 per cent of drier had been added. (Plates Nos. 2, 3, 4, 6, 9, 10, 11, 12, 14, 34.)

(*c*) The more or less volatile paint thinners. (Plates Nos. 17, 18, 19, 20, 33.)

(*d*) Solutions of celluloid and pyroxylin. (Plates Nos. 24, 25.)

(*e*) The liquid (at room temp.) paraffin oils. (Plates Nos. 21, 30.)

2 — Those vehicles which showed some degree of protection, though not very much at best.

(*a*) Wood-oil varnishes containing a certain percentage of rosin. (Plates Nos. 26, 29.)

(*b*) Copal-wood-oil varnishes. (Plates Nos. 27, 28.)

(*c*) Varnishes made from linseed oil which had been thickened and oxidized by blowing with air, oxygen or ozonized air. (Plates Nos. 32, 37.)

This compared with the results obtained below with cooked-oil varnishes proves conclusively that the film yielded by a blown oil is not nearly as waterproof and resistant to severe weather conditions as that formed by a boiled or polymerized oil.

3 — Varnishes or varnish mixtures which protected the steel very nicely as long as weather conditions were

not severe and temperature changes not very rapid and pronounced. (Plates Nos. 39, 40, 42, 43, 44, 45, 49.)

4 — The semi-solid and solid paraffin oils. These show a very high degree of protection from rusting. (Plates Nos. 15, 31.)

5 — Those varnishes and vehicles which afford a high degree of protection against corrosion. To be set down in this class a material must be extremely waterproof; it must dry with a film which is very elastic and yet tough in order to be able to withstand "weathering." A film which cannot remain intact against condensed moisture, snow and ice and despite comparatively wide and sometimes rapid changes in temperature (as between day and night even in rather warm climates), will of necessity afford very little protection for the steel to which it is applied. As the table on pages 272–273 shows, this class comprises:

(*a*) Spar varnish. (Plate No. 16.)

(*b*) Varnishes made from linseed oil, or China wood oil, which have been thickened by a heat process. (Plates Nos. 22, 23, 52.)

(*c*) Open kettle-boiled oil. (Plate No. 46.)

In Plate No. 50 we find a rather anomalous case. It seems that raw linseed oil which has been dried with a small percentage of a liquid paraffin oil proved to be an excellent coating for rust prevention.

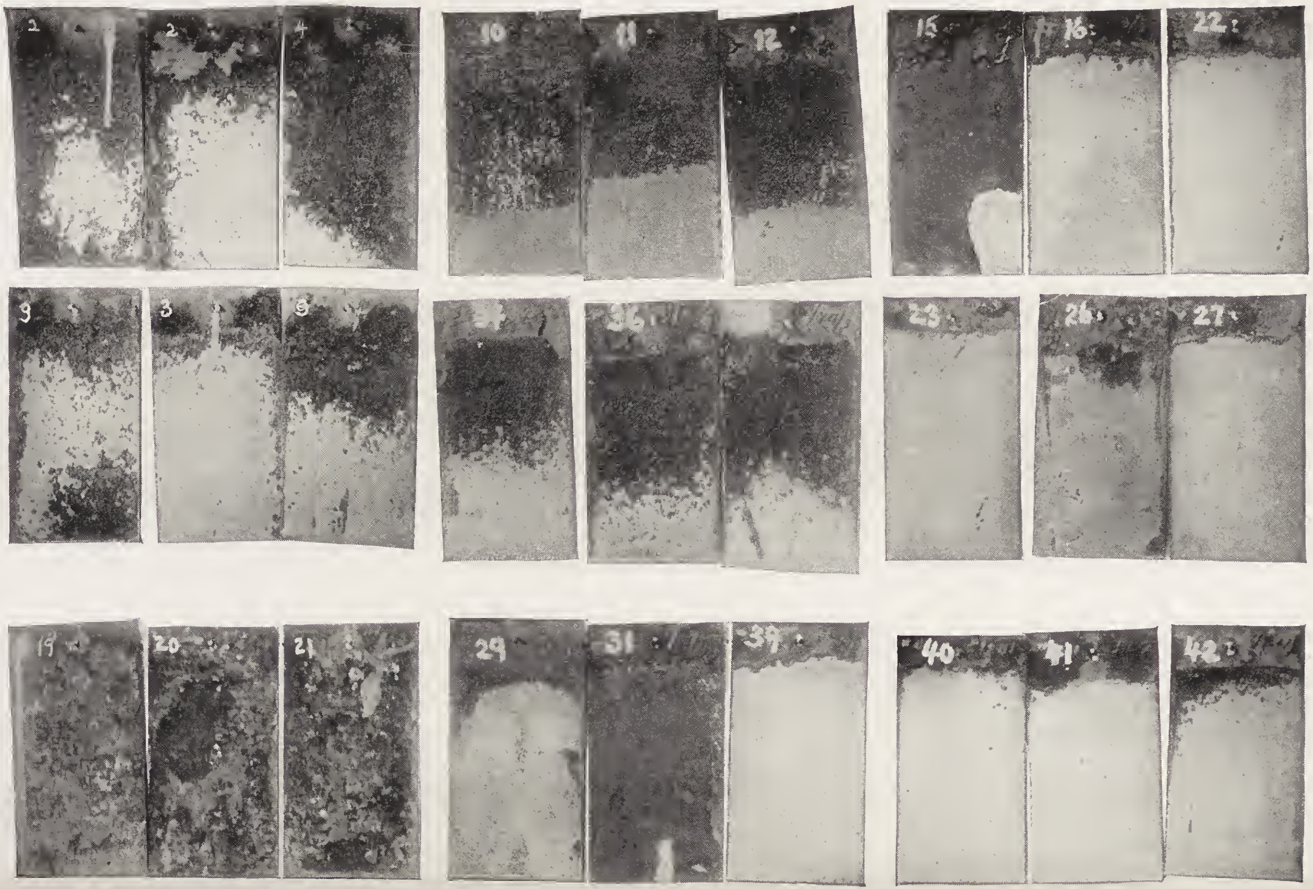
The addition of any paraffin or non-drying oil, even in such a small quantity as is shown in Plate No. 50, is dangerous in case repainting becomes necessary. Although the matter is not settled in the author's mind as to whether linseed oil and paraffin oil dissolve in each other, his idea at present is that, although they apparently make a clear solution, separation takes place. Several experiments were conducted, and it was found that a film of linseed oil which contains paraffin oil in some quantities when apparently dry shows minute globules of paraffin oil in wet condition when the film is heated over 100° C. A film of linseed oil containing 10 per cent of paraffin oil after it is six months old can be extracted with naphtha and shows uncombined paraffin oil. These experiments prove conclusively that it is dangerous to mix a paraffin oil with linseed oil for any purpose, excepting where it is not necessary, or not the intention, to repaint subsequently.

NOTE: All the photographs submitted (see pages 274–275) were taken during December, 1914.

INSPECTION REPORT ON STEEL PLATES EXPOSED DECEMBER 8TH, 1913

Pl. No.	Coating	April 14th, 1914	December, 1914	April, 1915	Value
1	Raw linseed oil	Completely rusted	Completely corroded	Completely corroded	1
2	Raw linseed oil plus 10% linoleate drier	About $\frac{1}{2}$ rusted	Badly rusted along edges; partly protected in middle	Completely corroded	1B
3	Raw linseed oil plus 10% Japan drier	Slight rusting	(1) Slight rust along edges; fairly protected over rest of film	Completely corroded	1B
			(2) Badly rusted along edges; partly protected in middle	Completely corroded	
4	Raw linseed oil plus 10% Japan drier	Almost completely rusted	Almost completely corroded	Completely corroded	1
5	Japan drier	Completely rusted	Completely corroded	Completely corroded	1
6	Menhaden oil plus 10% Japan drier	Completely rusted	Completely corroded	Completely corroded	1
7	Menhaden oil	Almost completely rusted	Completely corroded	Completely corroded	1
8	Soya bean oil	Completely rusted	Completely corroded		1
9	Soya bean oil plus 10% light drier	About $\frac{1}{2}$ rusted	Much corroded on upper half, free from rust on lower half	Completely corroded	1B
10	Soya bean oil plus 10% linoleate drier	About $\frac{1}{2}$ rusted	Much corroded on upper half, free from rust on lower half	Completely corroded	1B
11	$\frac{1}{2}$ raw oil, $\frac{1}{2}$ menhaden oil plus 10% linoleate drier	About $\frac{1}{2}$ rusted	Much corroded on upper half, free from rust on lower half	Completely corroded	1B
12	$\frac{1}{2}$ raw oil, $\frac{1}{2}$ soya bean oil plus 10% linoleate drier	About $\frac{1}{2}$ rusted	Badly rusted $\frac{3}{4}$ way down; fairly good on lower fourth of plate	Completely corroded	1B
13	Perilla oil	Completely rusted	Completely corroded	Completely corroded	1
14	Perilla oil plus 10% Japan drier	Almost completely rusted	Completely corroded	Completely corroded	1
15	Petrolatum	Much dirt, slight rusting	Collected much dirt; but well protected from rust	Still very good	4
16	Spar varnish	No rusting	Slight rusting	Unchanged; very good	5
17	Turpentine substitute	Completely rusted	All corroded	All corroded	1
18	Anhydrous pine oil	Completely rusted	All corroded	All corroded	1
19	Benzine	Completely rusted	All corroded	All corroded	1
20	Turpentine	Completely rusted	All corroded	All corroded	1
21	Paraffin oil	Completely rusted	All corroded	All corroded	1
22	Bodied linseed oil and turpentine substitute thinner	No rusting	No rusting	Unchanged; very good	5
23	Bodied linseed oil and turpentine substitute. thinner	No rusting	Very slight rusting	Unchanged; very good	5
24	Pyroxylin lacquer	Completely rusted	All corroded	All corroded	1
25	Celluloid solution	Completely rusted	All corroded	All corroded	1
26	No. 38 China wood oil varnish	Slight rusting	Rusted appreciably under whole film	Rather badly corroded	2
27	No. 5 copal, China wood oil varnish	No rusting	No rusting	Rather badly rusted	2
28	No. 6 copal, wood oil varnish	Slight rusting	Rusted much over whole plate	All rusted	2
29	No. 39 China wood oil varnish	Slight rusting	Rusted under whole film to small extent	All rusted	2
30	Steam cylinder oil	Completely rusted	Completely corroded	All rusted	1
31	Gear case oil	Much dirt; slight rusting	Collected very much dirt; shows but little rusting	Still protected	4

32	Blown linseed oil plus turpentine	Slight rusting	(1) Slight rusting in few spots (2) Badly rusted all over		2
33	Kerosene oil	Completely rusted	Completely corroded	Completely corroded	1
34	Raw oil plus 2% cobalt drier	About ½ rusted	Rusted badly ½ way down	Completely corroded	1B
35	Raw China wood oil	About ½ rusted	Almost completely corroded	Completely corroded	1
36	½ raw oil, ½ raw China wood oil	About ½ rusted	Badly corroded ¾ way down	Completely corroded	1
37	Blown linseed oil, turpentine substitute, 10% linoleate drier	Slight rusting	Partly rusted in quite a few isolated spots	All corroded	2
38	Raw oil, 10% paraffin oil, 10% Japan drier	About ½ rusted	Badly rusted ¾ way down	All corroded	1B
39	China-wood-oil rosin varnish	No rusting	No rusting; very good	Badly corroded	3
40	½ heavy boiled linseed oil, ½ raw oil	No rusting	No rusting; very good	Badly corroded	3
41	½ spar varnish, ½ stand oil	No rusting	No rusting; very good	Still good	5
42	80% raw oil, 15% spar varnish, 5% linoleate drier	No rusting	Rusted a little along upper edge and in several other spots	Badly rusted	3
43	½ raw oil, ½ No. 6 copal-wood oil varnish, 5% Japan drier	No rusting	No rusting; very good	Badly rusted	3
44	½ heavy boiled linseed oil, ½ menhaden oil, 5% Japan drier	No rusting	Very slight rusting	Badly rusted	3
45	½ heavy boiled linseed oil, ½ soya bean oil, 5% Japan drier	No rusting	No rusting: very good	Badly rusted	3
46	Kettle boiled oil	No rusting	Practically no rusting	Still very good	5
47	Pale refined varnish oil	Completely rusted	Completely corroded	All corroded	1
48	Pale refined linseed oil	Completely rusted	Completely corroded	All corroded	1
49	80% wood oil, 10% No. 38 China-wood-oil varnish, 10% Japan drier	No rusting	Practically no rusting	Corroded	3
50	90% raw oil, 10% paraffin oil, 1% cobalt drier	No rusting	Somewhat rusted on top; perfectly good at bottom	Still good	5
51	95% spar varnish, 5% petrolatum in turpentine substitute	No rusting	Slight rusting underneath film along edges	Still good	5
52	China wood oil, heated with Tox-tungate and thinned with benzine	No rusting	No rusting at all; very good	Still very good	5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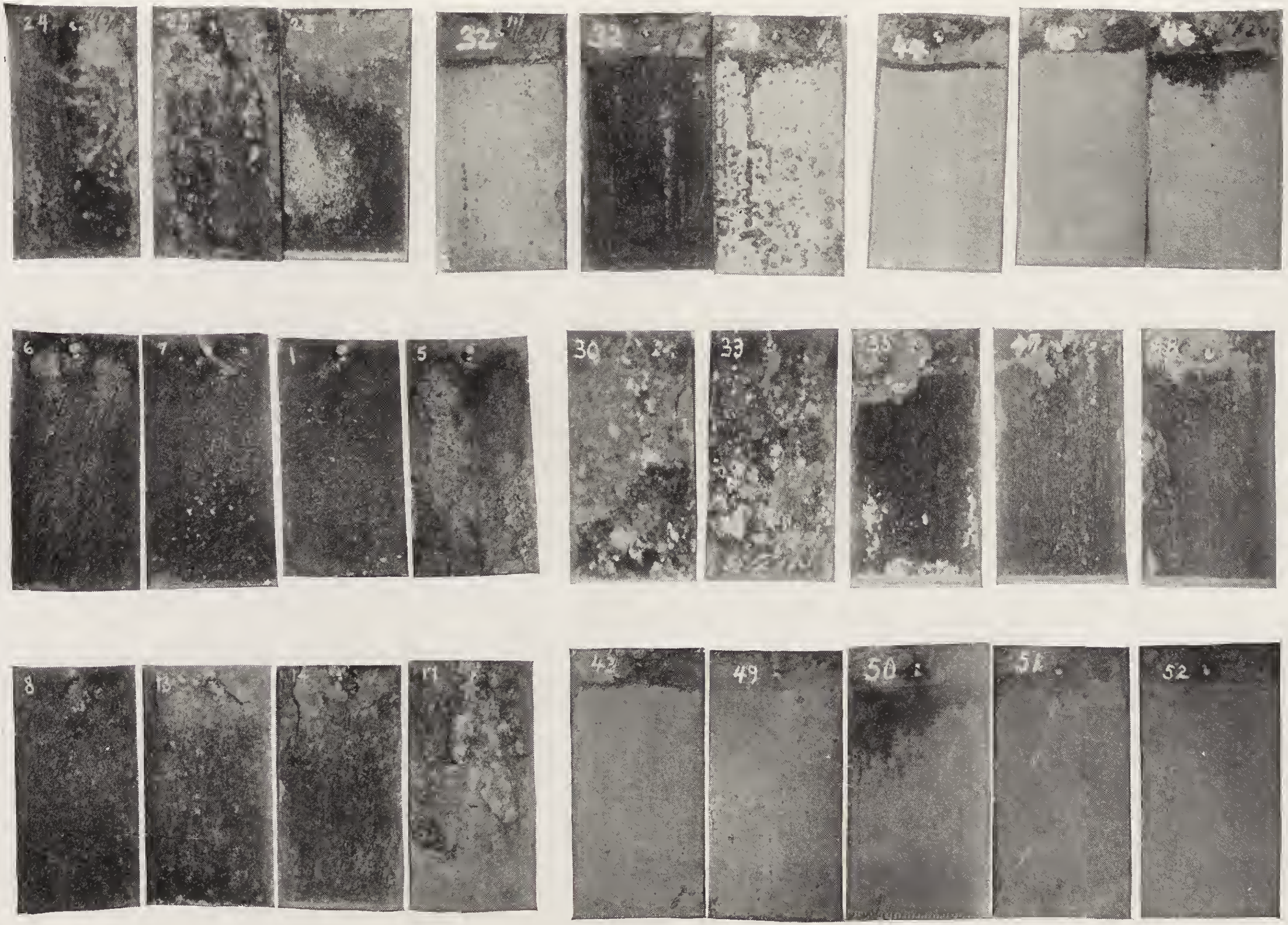
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CHAPTER XXVI

THE ELECTROLYTIC CORROSION OF STRUCTURAL STEEL[1]

ENGINEERS have commented publicly on the electrolytic corrosion of structural steel, particularly those parts known as grillage beams, supporting columns and base posts, which are either in the ground or surrounded by concrete and partly above the ground, with a view of determining beyond question at which of the poles corrosion occurs, and whether one pole is more active than the other.

The author performed an experiment by taking two sheets of high grade watch spring steel, which is extremely susceptible to corrosion, and connecting them with the ordinary bluestone telegraphic cell. A volt ammeter was placed in the circuit and the two pieces of steel buried up to 5 in. in sand. Careful observation was made every day to see that the current was uniform, and the sand was first moistened with salt water and then continually moistened with distilled water so that the same strength of salt solution was maintained. This experiment was conducted for 100 days, and assuming that the current travels from plus to minus, or from anode to cathode, the anode being connected with the copper and the cathode being connected with the zinc, corrosion was noticed almost immediately at the anode, and the plates showed violent corrosion at the anode and practically no corrosion at the cathode. These plates indicated some

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[1] By Maximilian Toch. Reprinted from Proceedings of American Society for Testing Materials, Volume VI, 1906.

slight corrosion on the cathode, which, however, was principally chemical corrosion.

The strength of the current was .05 of a volt and the distance between the plates, varying in the damp sand, was 1½ inches, and the amperage varied from .02 to .05.

The current was measured by a "Pignolet," direct reading, continuous current volt-ammeter, and the amount of current which produced this corrosion was exceptionally small.

Another experiment was tried exactly in the same manner, for a shorter period of time, but instead of using two plates, three plates were used, the third one being designated as the "free" plate, in which chemical corrosion had full sway. At the end of six days these plates were removed; the anode showed marked corrosion, the cathode plate showing practically no corrosion at all, and the "free" plate showed a fair average between the cathode and the anode, and it can be deduced that the difference between the cathode and the anode corrosion is equal to the "free" corrosion. In other words, there is many times more corrosion on the anode than there is on the "free" plate, and no corrosion on the cathode plate.

The rust first produced was the green ferrous oxid, $Fe(OH)_2$, which, being a very unstable product, was quickly converted in the air into Fe_2O_3, $N(H_2O)$.

The current was .1 of a volt and .1 of an ampere which produced this result. The salt solution was four times as strong as that produced in the first experiment.

A third experiment was, however, of the greatest importance, owing to the fact that the author attempted to imitate the conditions exactly as they existed in buildings. The same kind of steel was taken and bedded in various mixtures of concrete, starting from neat cement and going up to 1:3:5. There is a well-known law in physical chemistry that reactions which take place with an increase of pressure are retarded by an increase of pressure, and the question has come up as to whether it is possible for steel to corrode when surrounded by concrete, many engineers holding that the alkaline nature of the cement will prevent the corrosion, and others holding that in conjunction with this condition the pressure exerted by the concrete prevents chemical decomposition. The author is glad to be able to throw some light on this subject, and the following experiment was carried out:

In the first place cement was taken of known composition, agreeing practically with the definition as quoted in the Journal of the American Chemical Society, July, 1903, when the question of the permanent protection of iron and steel by means of cement was thoroughly gone into. The cement for these experiments was what might be termed the tri-calcic silicate and calcium aluminate. This is in contradistinction to the general classes of Portland cements containing dicalcium ferrite as a part of their composition and free calcium sulphate in excess. A cement of the calcium aluminate class, free from iron and free from calcium sulphate, is a well-known protector of steel and iron against corrosion, and this class of cement was used in these experiments. The pieces of steel were connected up with six elementary cells of sufficiently high voltage and amperage, and it was impossible to get a direct reading from the volt-ammeter, the instrument being too sensitive. The seven parts of cement containing the steel strips were then put into the circuit and wet every few hours with solutions of 5 per cent sodium chloride and 1 per cent nitric acid, and water, in order to increase their conductivity and produce corrosion as rapidly as possible. The average strength of the current was .05 volts and .05 amperes throughout the entire experiment. Corrosion was immediately noticed at the anode pole, and the pat of neat cement, which should have protected the steel most perfectly against all kinds of corrosion, showed a hair line split colored with rust at the end of the third day, which demonstrated that the chemical reaction of rusting had taken place at the anode; that the molecular increase had likewise taken place, and the pressure caused by the molecular increase had split the block. The steel in each alternate pat was painted half the length which was embedded in the cement with an insulating paint of known composition having a voltage resistance of 625 volts per millimeter. The results obtained after these various briquettes were broken open demonstrated that electrolytic corrosion takes place most violently at the anode unless the steel be coated with an insulating medium.

Cement, concrete, or even neat cement, is therefore no protection against electrolytic corrosion, unless the steel be insulated as heretofore mentioned, and there was absolutely no corrosion where coated with insulating material. It must be noted that the cathode in all these experiments was perfectly free from any signs of oxidation.

The result of this entire series of experiments is to prove conclusively that electrolytic corrosion of structural steel embedded in concrete or sand takes place only at the anode and there with great violence; and furthermore, that the cathode is protected by the electrical current. The popular impression that cement is a protector against all kinds of corrosion is fallacious. The anode does not only rust very violently, but a molecular increase of volume may take place which will split the concrete shell.

Another conclusion arrived at is that the electrolytic rusting of grillage beams of buildings need not be feared if the structural steel be protected by a good insulating material, but the insulating medium should form a bond with concrete.

CHAPTER XXVII

PAINTERS' HYGIENE

ALL paints should be regarded as poisonous, and even though it may be understood as a general rule that materials like ultramarine blue are non-toxic or that silica has no effect upon the system, it is unwise for the paint manufacturer to permit his men either to breathe these in dry dust form or to allow his workmen to eat their meals before washing themselves thoroughly. We are all very familiar with the fact that white lead produces lead poisoning, but in any well-regulated factory there is no excuse for this, and the amount of lead poisoning produced in factories like the large lead manufactories in the United States is reduced to a minimum because the workmen are looked after most thoroughly. Workmen who are employed in a dusty atmosphere should always wear respirators, and workmen who work with lead products should not be permitted to grow moustaches, as the dust of many of the poisonous pigments settles in the moustache and is then absorbed through the nose. White lead under the finger nails is absorbed into the system, and a careful watch of these things will prevent any disease among the men; but all in all there is more sensationalism and hysteria on this subject than is warranted by the results, for in paint factories where sufficient care is taken there is practically no illness among the men.

Paint vapors are all toxic, and any painter who is ignorant enough to apply any paint material in a closed room does not deserve to be a painter. Even materials like pure spirits of turpentine, which are known to have medicinal qualities, when breathed in large quantities are supposed to produce headache and vertigo, and the fumes of benzol, benzine and alcohol give the same results; therefore all people who apply paint should do so in well-ventilated rooms. Large vats which are varnished on the interior like brewers' vats, or water tanks which are painted on the inside, are generally ventilated by the engineers in charge by having fresh air pumped in continually to the men from the top and by simply pumping out the vapors from below, as practically all of the materials used in the manufacture of paint give off vapors which are heavier than air.

Paint vapors are also inflammable, and any fire resulting from careless smoking or throwing lighted matches near paint is likely to produce disastrous results, but much information has been disseminated on this subject, particularly through the railroads, who now demand caution labels printed on each package before it is shipped with the result that many lawsuits which were instituted formerly against the manufacturer are not permitted today. The same is true with regard to the vapors arising from paint. It has been a practice among certain questionable lawyers to institute suits against paint manufacturers for illness, headaches, nausea, vertigo and such other physical ills as have resulted from the fumes of paint, and few of these lawsuits have ever been tried, because the paint manufacturer in former times has been inclined to settle a suit of this kind rather than go to court, but these cases are not as frequent as they formerly were on account of the wide-spread knowledge of the subject. Fumes arising from paint are not dangerous in the open air, but if a painter is careless in a closed room it is certainly his fault, and a man who knows so little about paint should not be permitted to use it.

CHAPTER XXVIII

The Growth of Fungi on Paint

Fungi must not be confounded with bacteria. Bacteria are invisible micro-organisms, and whether they thrive on paints has never yet been established. Their existence in oil or paint media has never been proved. Experiments made by the author in which various bacteria were grown in gelatin or agar agar have demonstrated that when turpentine, benzine, linseed oil, varnish or paints of any character, excepting those containing water, were added, they rapidly perished. Fungi, however, are totally different organisms. A fungus is derived from a spore which floats in the air and which practically is a microscopic seed. When this falls on fertile ground it sprouts and becomes a white downy mass, which is known as the hypha. This downy mass later on assumes a color, which may be either gray, green, yellow or black, and is known under the popular title of mildew, which is in reality a fungus or micro-organic growth of the vegetable type.

No. 71. Olive Green Fungus, growing on paint — Photomicrograph ×600. Penicilium Crustaceum.

What may be poisonous to a human being is evidently non-poisonous or neutral to a fungus, for fungi can grow and do grow on practically all of the barium precipitates, which are known to be highly poisonous.

A fungus needs both warmth and moisture for its propagation, and so we will frequently find that on the south side of a house at the seashore, where moisture will collect and the temperature will be fairly uniform, fungi will sprout on a painted surface and frequently destroy the paint. This is more noticeable in the tropics than it is in the North, and more noticeable in the European countries than it is in America, for the humidity in the United States is way below normal for more than half of the year whereas the humidity is fairly constant in Europe and in the tropics. Some of these fungi are very disagreeable, particularly the black types, which will grow on the interior of houses, and which always propagate better in a cellar than they do in a garret, for light has a tendency to kill them.

No. 72. Penicilium Crustaceum — Photomicrograph ×600, a common green or cellar fungus which grows on many forms of paint.

No. 73. Aspergillus Niger — Photomicrograph ×100, old fungus found on paint.

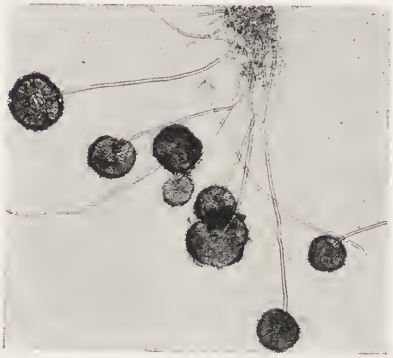
The fungi that are found on paint may be classified into the following varieties:

1. Penicilium Crustaceum types, of which there are many varieties, but all of which are greenish or olive grayish.

2. Aspergillus Niger, which is distinctly black and very tenacious.

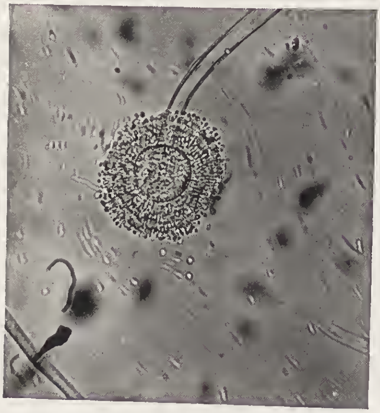
3. Rhizopus Nigricans, which is brown and black, and which appears generally in the Fall of the year.

4. Aspergillus Flavus, which is yellow and orange, and which grows freely on a putrid soil or near decaying vegetable matter.



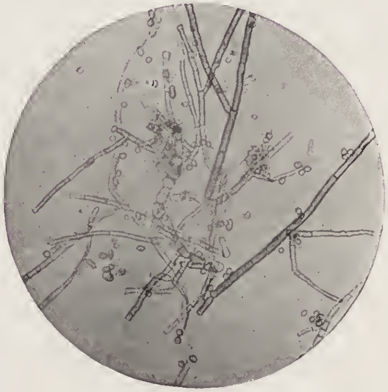
No. 74. Aspergillus Niger — Photomicrograph ×100, black fungus frequently found on paint in cellars.

It must be generally understood that the use of fungicides is not always to be recommended, for in breweries, malt houses, rooms which have swimming pools, and cellars which have been used for storage, these fungi grow at times, and it seems as if there is nothing which kills them. The best way to get rid of them is to wash the surface copiously with soap and water and then spray a mixture of carbolic acid and formaldehyde and afterward bichloride of mercury, but a man applying a material of this kind must use a mask and a respirator.



No. 75. Aspergillus Flavus — Photomicrograph ×600, yellow fungus frequently found in breweries and dairies, thriving on paint.

Many a complaint has reached a paint manufacturer that his paint has turned black in spots under the eaves of a roof or in a ground-floor room, and the manufacturer on account of ignorance has supplied fresh paint free of charge, or the painter has done the work over again, when as a matter of fact the fault was due entirely to fungus growth. It is well, therefore, for the paint chemist to familiarize himself with at least these few fungi, as they are the principal types which flourish on paint.



No. 76. Cladosporium Herbarum — Photomicrograph ×600, a pale fungus growing on damp walls.

ANALYSIS OF PAINT MATERIALS

Analysis of White Lead

Gravimetric Methods — Estimation as $PbSO_4$

Lead. — Dissolve 1 g. in dilute acetic acid, filter, wash and weigh the insoluble residue. To the filtrate add 10 c.c. of dilute sulphuric acid (1:1) and evaporate on the steam bath. Allow to cool, dilute cautiously to 100 c.c., add 10 c.c. of alcohol and stir well. Filter on a Gooch or alundum crucible, wash with water containing 1 per cent of sulphuric acid and 10 per cent of alcohol, and finally with alcohol alone. Dry at 110° C.

Lead sulphate is appreciably soluble in concentrated sulphuric acid and slightly soluble in water. It is practically insoluble, however, in 1 per cent sulphuric acid and in alcohol. It is very soluble in hot, concentrated ammonium acetate solution.

Estimation as $PbCrO_4$

Treat 1 g. in a beaker with hot water and just sufficient acetic acid to dissolve the white lead, using no more than 5 c.c. of acetic acid in excess. Filter off from the insoluble residue. Dilute to 100 c.c., heat to boiling and add an excess of a neutral, saturated solution of potassium dichromate solution. Allow to cool. Filter on a Gooch or alundum crucible, wash and dry at 130° C.

Volumetric Methods — Estimation as Molybdate

Dissolve 0.5 g. of white lead in 5 c.c. of concentrated hydrochloric acid by boiling. Add 25 c.c. of cold water and proceed as indicated below, under "Standardization of Ammonium Molybdate."

Lead is precipitated as $PbMoO_4$ by a standard solution of ammonium molybdate from hot solutions slightly acid with acetic acid. The solutions required are:

(*a*) Ammonium molybdate — Dissolve 4.25 g. in 1 litre of water
(*b*) Tannic acid solution — Dissolve 0.1 g. in 20 c.c. of water

Standardization of Ammonium Molybdate. — Weigh off about 0.2 g. pure lead foil in a small Erlenmeyer flask and dissolve in 6 c.c. of nitric acid (1:2). Evaporate the solution just to dryness. Treat the residue with 30 c.c. of water and 5 c.c. of concentrated sulphuric acid and shake well. The precipitated lead sulphate is allowed to settle, filtered and washed with dilute sulphuric acid (1:10). Filter and precipitate are placed in an Erlenmeyer flask and boiled with 10 c.c. of concentrated hydrochloric acid until completely disintegrated. Then add 15 c.c. more of concentrated hydrochloric acid, 25 c.c. of cold water and neutralize with ammonia until slightly alkaline to litmus paper. Reacidify with acetic acid. Dilute to 200 c.c. with hot water and heat to boiling. Titrate, using the tannic acid solution as outside indicator, until a brown or yellow coloration is obtained with the latter.

Precautions. — Titration must be carried out hot, at about 90° C. If the solution should cool down in the course of titration, reheat it. Here, as in the case of the titration of zinc with potassium ferrocyanide, the scheme of dividing the solution into two unequal parts may be used.

To determine the excess of ammonium molybdate necessary to affect the indicator, place in an Erlenmeyer flask 25 c.c. of hydrochloric acid, neutralize until slightly alkaline to litmus, then reacidify with acetic acid. Dilute to 200 c.c., heat to boiling, and add ammonium molybdate drop by drop until the outside indicator is affected.

Antimony and bismuth do not affect the results obtained by this method. Barium and strontium give very low results, while calcium yields but slightly low results. The alkaline earth sulphates tend to retard the solution of the lead. This difficulty can be overcome by thoroughly washing the lead sulphate and then boiling it with sufficient ammonium acetate.

Carbon Dioxid and Combined Water. — 1 g. of white lead is weighed off in a porcelain boat. The latter is then placed in a combustion tube and heated in a current of dry air free from carbon dioxid. The water is collected in calcium chloride tubes, and the carbon dioxid in potash bulbs or soda lime tubes.

Carbon dioxid may be determined by evolution by treating white lead with dilute nitric acid. Use a reflux condenser in connection with the evolution flask and dry the carbon dioxid by passing through calcium chloride before absorbing in the potash bulbs or soda lime tubes.

Basic Lead Sulphate

Lead and Zinc (gravimetric). — Digest 1 g. for ten minutes in the cold with 20 c.c. of 10 per cent sulphuric acid. Filter, keeping most of the residue in the beaker, and wash twice by decantation with 1 per cent sulphuric acid. The filtrate from the sulphuric acid teatment is reserved for the determination of zinc which is carried out by any of the methods outlined under "Zinc Oxid." Preferably precipitate as phosphate. Calculate the zinc to ZnO.

Dissolve the residue in the beaker with hot concentrated slightly acid ammonium acetate solution pouring the solution through the filter. Wash the latter with ammonium acetate and then with hot water. Dilute to 200 c.c., add an excess of a neutral saturated solution of potassium dichromate and bring to boiling. Allow to cool, and filter on a Gooch or alundum crucible. Dry at 130° and weigh as $PbCrO_4$.

Lead (volumetric). — Treat 0.5 g. sample with 30 c.c. of water and 5 c.c. of concentrated sulphuric acid, and proceed as outlined under "Estimation as Molybdate."

Sulphates.[1] — Dissolve 0.5 g. by boiling in a mixture of 25 c.c. water, 10 c.c. aqua ammonia and enough concentrated hydrochloric acid to give a slight excess. Dilute to 200 c.c. and add a piece of pure thick aluminium foil large enough to nearly cover the bottom of the beaker. This should be kept at the bottom by means of a glass rod. Boil gently until the lead is precipitated. When the lead no longer adheres to the aluminium, the precipitation may be considered complete. Filter and wash with hot water. A little sulphur-free bromine water is added to the filtrate, the latter is boiled, and sulphates determined by precipitation with barium chloride in the ordinary way.

If desired the sulphates may be determined as indicated under Analysis of "Zinc Lead."

Sulphur Dioxid. — Digest about 2 g. in the cold with 5 per cent sulphuric acid, and titrate with $\frac{N}{100}$ iodine solution, using starch as indicator.

ANALYSIS OF ZINC LEAD

Lead. — 1 g. of the material is heated on the steam bath with 20 c.c. of hydrochloric acid (1:1) and 5 g. of ammonium chloride. The solution is diluted to 250 c.c. with hot water and boiled. This treatment should suffice to dissolve a pure zinc lead.

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[1] Holley, "Analysis of Paint and Varnish Products," 1912, p. 104.

The insoluble residue, if any, is filtered, weighed, and examined for impurities. Neutralize the filtrate with ammonia, reacidify slightly with hydrochloric acid, and precipitate the lead with hydrogen sulphide.

Allow the precipitate to settle, filter off the liquid, and wash the precipitate several times by decantation with hydrogen sulphide water. The precipitate is finally dissolved in hot, dilute nitric acid, treated with an excess of sulphuric acid, and evaporated to SO_3 fumes.

Allow to cool, dilute cautiously with 100 c.c. of cold water, filter off the precipitated lead sulphate on a Gooch crucible, wash several times with dilute sulphuric acid, and finally once with alcohol. Dry at 130° C., and weigh as $PbSO_4$.

Zinc. — The filtrate from the lead sulphide precipitate is boiled to expel hydrogen sulphide, treated while hot with a few drops of HNO_3, then rendered slightly ammoniacal, and any precipitate which is formed is filtered off. The filtrate is then slightly acidified with acetic acid, heated to boiling and a stream of sulphuretted hydrogen passed in to precipitate the zinc. The latter is filtered and washed with water containing a small amount of acetic acid saturated with hydrogen sulphide, using a Gooch or alundum crucible for filtering.

In filtering zinc sulphide, keep the crucible full of liquid or wash water until the precipitate is completely washed. Only then may the precipitate be allowed to drain free from wash water.

The zinc sulphide is then dissolved in dilute hydrochloric acid, the sulphuretted hydrogen expelled by boiling, and the zinc determined either volumetrically by the ferro-cyanide method or gravimetrically by precipitation with a slight excess of sodium carbonate, and ignition to oxid.

Calcium and Magnesium. — The filtrate from the zinc sulphide is evaporated to a small bulk and the calcium determined by precipitating hot from a slightly ammoniacal solution with ammonium oxalate. Magnesium is determined as usual.

Soluble Salts. — To determine the presence of zinc sulphate, 1 g. is digested with 100 c.c. of water, filtered, and the sulphate determined in the filtrate as usual, with barium chloride.

Total Sulphates. — Dissolve 2½ g. of sodium carbonate in a beaker with 25 c.c. of water, add 0.5 g. of the sample, boil gently for about ten minutes and allow to stand for several hours. Dilute with hot water, filter and wash until the filtrate is about 200 c.c.

Render the filtrate slightly acid with hydrochloric, boil to expel carbon dioxid and precipitate the sulphate with a slight excess of barium chloride solution.

Filter, wash and weigh as $BaSO_4$. Calculate the latter to $PbSO_4$.

ZINC OXID

Insoluble. — Dissolve 1 g. in hot dilute acetic acid. Filter, wash and weigh any insoluble residue. If the latter is very small in quantity, it should be determined by dissolving a proportionately larger quantity of zinc oxid.

Zinc. — Neutralize the filtrate with ammonia, then make faintly acid with acetic acid, dilute to 300 c.c., and precipitate with sulphuretted hydrogen. The solution should be kept hot during the precipitation, and should smell strongly of hydrogen sulphide at the end. Allow the precipitate to settle, decant through an alundum or Gooch crucible, keeping the crucible full of liquid during the filtration, wash the precipitate in the beaker with a hot 2 per cent acetic acid solution saturated with hydrogen sulphide, finally transferring the zinc sulphide to the crucible and allowing the last wash water to drain completely. The zinc sulphide is dissolved in dilute hydrochloric acid and boiled to expel H_2S (test with lead acetate paper held in the escaping vapors from the beaker or flask to show the presence of hydrogen sulphide).

Gravimetric Methods for Zinc. — (*a*) Precipitation as Phosphate

The solution is rendered very *faintly acid* by almost completely neutralizing with ammonia, diluted to 150 c.c. and heated on the steam bath. Add to the solution on the steam bath about ten times as much di-ammonium phosphate[1] as zinc present. Heat for 15 minutes longer. The crystalline zinc ammonium phosphate is filtered through a Gooch or alundum crucible, washed with hot 1 per cent ammonium phosphate solution until free from chlorides, then with cold water and finally with 50 per cent alcohol. Dry at 120° C. for one hour and weigh as $ZnNH_4PO_4$.

(*b*) Precipitation as Carbonate

The zinc chloride solution is carefully neutralized in the cold with sodium carbonate solution until a precipitate begins to form. The solution is then heated to boiling, and precipitation completed by adding a slight excess of sodium carbonate (use phenolphthalein as indicator). *Ammonium salts must not be present.* Filter on a Gooch crucible, wash, ignite and weigh as ZnO.

Volumetric Method. — Zinc is precipitated from hot somewhat acid solutions by the addition of potassium ferro-cyanide according to the following reaction:

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[1] Dissolve in cold water and add dilute ammonia until faintly pink with phenolphthalein.

$$3ZnCl_2 + 2K_4FeC_6N_6 = Zn_3K_2Fe_2(CN)_{12} + 6KCl$$

The end point is indicated by a solution of uranium nitrate as outside indicator. A brown coloration is produced when a drop of the solution containing the excess of potassium ferrocyanide is added to a drop of uranium nitrate solution on a spotting tile.

Solutions Potassium Ferrocyanide. — Dissolve 21.6 g. of crystallized salt, $K_4FeC_6N_6 \cdot 3H_2O$ in cold water and dilute to one liter. One c.c. of this solution is equivalent to about 0.005 g. zinc.

Uranium nitrate	5% solution
Ammonium chloride	10 g. per liter

Standardization of Ferrocyanide. — Weigh out two or three portions of 0.2 to 0.25 g. of pure ignited zinc oxid. Dissolve in 10 c.c. of hydrochloric acid (1:2), add sodium carbonate solution or ammonia until a *slight* permanent precipitate is formed, redissolve the latter with one or two drops of hydrochloric acid, add 6 c.c. of concentrated hydrochloric acid and 10 g. of ammonium chloride. Dilute to 180 c.c., heat to 70° C. and titrate with ferrocyanide solution until the end point is reached. To determine the end point rapidly divide the zinc solution into two unequal parts. Titrate the smaller part running in the ferrocyanide solution 1 c.c. at a time. When an excess has been added pour in the rest of the zinc solution, run in 1 c.c. less than the quantity of potassium ferrocyanide previously added, and finish the titration drop by drop.

A blank must be deducted because of the excess of potassium ferrocyanide required to develop the brown coloration with uranium solution.

To determine the allowance, add 6 c.c. of concentrated hydrochloric acid and 10 g. of ammonium chloride to 200 c.c. of water in a beaker, heat to 70° C., and add the ferrocyanide solution until the brown coloration is obtained with the outside indicator. The correction should be less than 0.5 c.c. Deduct this amount from all future titrations.

Determination of Zinc. — To determine zinc in the solution obtained by dissolving ZnS in hydrochloric acid and expelling hydrogen sulphide, neutralize with ammonia or sodium carbonate, reacidify slightly with dilute hydrochloric acid, and proceed as outlined under "Standardization of Ferrocyanide." The presence of a small amount of lead does not interfere with the accuracy of the above method.

Soluble Impurities. — Most zinc oxids are contaminated with small quantities of cadmium and traces of iron, copper and lead. The cadmium [1] is best determined by dissolving a relatively large amount, 25 to 50 g., of zinc oxid in dilute sulphuric acid, filtering, diluting to 400 c.c. and precipitating as sulphide in the presence of an excess of about 5 c.c. of concentrated sulphuric acid in 100 c.c. of solution. Filter, wash, redissolve in sulphuric acid and reprecipitate as sulphide. Dissolve into a crucible with as small an amount of sulphuric acid as possible. Evaporate cautiously and ignite to $CdSO_4$.

LITHOPONE

METHOD I

Zinc Oxid. — Digest 1 g. with 100 c.c. of 1 per cent acetic acid at room temperature for one half hour. Filter, wash and weigh the insoluble. The loss in weight represents the zinc oxid present.

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[1] For electrolytic method of determining Cadmium, see E. F. Smith's "Electro-Analysis."

Insoluble and Total Zinc. — Treat 1 g. in a 200 c.c. beaker with 10 c.c. of concentrated hydrochloric acid, mix, and add in small portions 1 g. of potassium chlorate (this should be carried out under a hood); evaporate on the steam bath to ½ the volume. Dilute with hot water, add 5 c.c. of dilute sulphuric acid (1:10), boil, filter, and weigh the insoluble. The latter is barium sulphate. The zinc is determined in the filtrate by the methods outlined under "Zinc Oxid."

METHOD II

Soluble Salts. — Treat 2 g. of lithopone with 100 c.c. of hot water. Digest for a few minutes and filter on a Gooch crucible (test the filtrate for Ba, Zn and SO_4). Wash with hot water and finally once with alcohol. Dry the crucible in the air oven at 100° C. and determine loss in weight. The latter is equal to the percentage of moisture present plus the water soluble salts.

Zinc Oxid. — Digest for ½ hour, without warming, a 1 g. sample with 100 c.c. of 1 per cent acetic acid. Filter, wash, and determine the zinc in the filtrate gravimetrically or volumetrically, as outlined under "Zinc Oxid." Calculate to ZnO.

Zinc Sulphide. — Transfer the filter paper and residue to a beaker, treat with dilute hydrochloric acid (1:4) and boil to drive off H_2S. Filter, wash with hot water, and determine the zinc in the filtrate by the usual methods. Report as ZnS.

Barium Sulphate. — The residue is dried, ignited, treated with a few drops of concentrated sulphuric acid in the crucible, again ignited and weighed as $BaSO_4$. Test the latter for clay or silica. Should any be present, treat the residue with hydrofluoric and sulphuric acids in a platinum crucible and evaporate to dryness. The loss in weight represents silica.

RED LEAD AND ORANGE MINERAL

Lead Peroxid (*Method I*). — Dissolve 0.5 g. in a beaker with 30 c.c. of 2N nitric acid, heat to boiling to complete solution. Add 25 c.c. N/5 oxalic acid, accurately measured from a pipette or burette, boil and titrate hot with $KMnO_4$.

A blank containing the same quantities of nitric acid and oxalic acid is also titrated against the permanganate. The difference between the two titrations represents the amount of PbO_2 reduced by oxalic acid.

$$Pb_3O_4 + 4HNO_3 = 2Pb\,(NO_3)_2 + H_2O + H_3PbO_3$$
$$PbO_2 + H_2C_2O_4 = PbO + H_2O + 2CO_2$$

Lead Peroxid (*Method II*). — Mix together in a small beaker 1.2 g. of potassium iodide, 15 g. sodium acetate and 5 c.c. of 50 per cent acetic acid. Weigh off 0.5 g. of red lead in a 150 c.c. Erlenmeyer flask and add the above mixture to it. Stir until the lead is completely dissolved. Dilute to 25 c.c., and titrate with N/10 sodium thiosulphate, using starch as indicator.

A little red lead, especially when it is not very fine in texture, at first resists solution in the potassium iodide mixture, but dissolves, on mixing, toward the end of the titration. Proceed with the titration as soon as the lead is in solution, so as to avoid loss of iodine by volatilization.

The reaction involved in the above method is

$$PbO_2 + 4HI = PbI_2 + 2H_2O + I_2$$

The lead peroxid is reduced in the presence of an excess of sodium acetate when treated with potassium iodide in acetic acid solution.

ANALYSIS OF IRON OXIDS

Moisture. — Heat 2 g. in the air oven at 105° C. for two hours.

Loss on Ignition. — Ignite 1 g. in a porcelain crucible to a red heat. The loss in weight consists of hygroscopic moisture, water of combination, sometimes organic matter, and carbon dioxid due to the presence of carbonates.

Insoluble. — Digest 1 g. of the oxid with 20 c.c. of hydrochloric acid (1:1) on the hot plate for 15 minutes. Filter, wash and weigh the insoluble residue. The latter may be examined to determine the presence of barytes, clay or silica.

Iron Oxid. — Weigh off from 0.3 to 1.0 g., depending upon the amount of iron oxid present, treat with 20 c.c. of hydrochloric acid (1:1) on the hot plate until the residue is white, and while hot reduce with a strongly acid stannous chloride solution until the iron solution is colorless, using only one or two drops in excess. Wash down the sides of the beaker and the cover glass with a little water, add all at once 10 c.c. of a saturated solution of mercury bichloride, stir, and wash the whole into a large beaker containing 400 c.c. of cold distilled water to which has been added 10 c.c. of preventive solution. Titrate with N/10 potassium permanganate to a faint pink.

In the case of magnetic oxids and certain purple oxids, solution is facilitated by the addition of 1 to 3 c.c. of a 25 per cent stannous chloride solution. Should the residue after digestion on the hot plate still show greenish or black, filter, wash, and determine the iron in the soluble portion as outlined below.

To determine iron in the insoluble portion, fuse in a porcelain crucible with five times its weight of potassium bisulphate for about ½ hour. Cool, dissolve in water and filter. Determine iron in the filtrate after reduction as outlined below.

Stannous Chloride Solution.—Dissolve 50 g. of stannous chloride in 100 c.c. of hydrochloric acid and dilute to 1000 c.c. To preserve the solution, always keep a few pieces of metallic tin at the bottom of the bottle.

PREVENTIVE SOLUTION:

Crystallized Manganese Sulphate	67 g.
Water	500 c.c.
Syrupy Phosphoric Acid (Sp. Gr. 1.7)	138 c.c.
Concentrated Sulphuric Acid	130 c.c.

Dissolve in the order named and dilute to 1 liter.

ANALYSIS OF UMBERS AND SIENNAS

To 0.5 to 1.0 g., depending upon the amount of iron oxid present, in a casserole, add 20 c.c. of hydrochloric acid (1:1) and 0.35 g. potassium chloride (or 0.25 g. ammonium chloride), and evaporate to dryness on the steam bath. Heat for 10 minutes longer to expel hydrochloric acid. Dissolve the soluble salts in about 25 c.c. of hot water, filter and wash the insoluble residue. The latter is dried, ignited and weighed, and reported as insoluble or silicious matter. (When necessary analyze this separately as indicated under "Analysis of Silica, Asbestine or Clay".)

To the filtrate, heated almost to boiling, there is added 3.0 g. of sodium acetate for every 0.3 g. of iron in solution, and 400 c.c. of boiling water. Heat to incipient boiling. By this means the iron is quantitatively precipitated as a basic acetate, while manganese and other divalent metals of the group stay in solution. The precipitate is allowed to settle, the solution decanted off and filtered; the precipitate is washed several times with hot water, dissolved in a small amount of hot dilute hydrochloric acid, and either precipitated with ammonia or determined volumetrically as under "Analysis of Iron Oxids." The filtrate is evaporated to about half its volume, treated with an excess of bromine water, and then boiled until the precipitated manganese dioxid becomes floccular. The precipitate is then filtered off, washed, and ignited to Mn_3O_4.

Calcium and magnesium are determined in the filtrate in the usual way. When appreciable quantities of these two elements are present, it is best to separate the manganese by precipitation as sulphide.

To determine manganese as sulphide, heat the neutral solution to boiling, add an excess of ammonia and ammonium sulphide, and continue the boiling until the manganese sulphide becomes a dirty green. Decant through a Gooch crucible, using gentle suction, keeping the crucible filled all the time. Wash the precipitate twice by decantation with 5 per cent ammonium nitrate solution containing a little ammonium sulphide, add to the crucible and filter, allowing the crucible to drain. The filtrate is acidified with dilute acetic acid boiled to expel hydrogen sulphide, and the calcium and magnesium determined as usual. The precipitated manganese sulphide is dissolved in a little hot dilute hydrochloric acid, evaporated to expel hydrogen sulphide, and precipitated as carbonate or phosphate. In the first case the manganese is ignited and weighed as Mn_3O_4.

Colorimetric Determination of Manganese.[1] — Dissolve

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[1] Treadwell, Volume II, pages 127, 128. Marshall, Chem. News, 83, 76 (1904). Walters, Chem. News 84/239 (1904).

0.5 g. of umber or sienna in about 10 c.c. of hydrochloric acid (1:1) in a casserole, add an excess of nitric acid and evaporate to dryness to drive off the hydrochloric acid. Cool, add 20 c.c. of cold nitric acid (specific gravity 1.2) filter and wash with the least quantity of cold water into a 100 c.c. graduated flask. Make up to the mark. Remove 10 c.c. by means of a pipette to a graduated test tube, add 10 c.c. of silver nitrate[1] solution, and 2.5 c.c. of ammonium persulphate[2] solution, mix, and place the tubes in water at 80 to 90° C. until bubbles of gas arise, and remain at the top for a few seconds. Cool the test tubes and compare against standard tubes made with known amounts of manganese.

MERCURY VERMILION

This pigment is very expensive and therefore quite often adulterated. The possible adulterants are organic lakes, orange lead chromes, red lead, and iron oxids, as well as barytes, silica or clay.

Its high specific gravity (8.2) and its insolubility in alkalies, and in any one acid, distinguish it from all other pigments of like color.

A pure vermilion can be volatilized completely on heating, leaving no residue. On account of the extremely toxic properties of mercury vapors, such volatilization should be carried out in a hood having a good draft.

Barytes, Silica or Clay. — Dissolve 2 g. in aqua regia, or hydrochloric acid with a little potassium chlorate, and after evaporating to dryness take up with boiling water and a little hydrochloric acid. Filter and weigh the residue.

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[1] 1.38 g·$AgnO_3$ in 1000 c.c. of water.

[2] 20% solution.

Lead. — Evaporate the filtrate from the above with an excess of dilute sulphuric acid to SO_3 fumes, and determine lead as $PbSO_4$. (Calcium must be absent.)

Free mercury, free sulphur and iron may be identified by dissolving the mercury vermilion in potassium monosulphide (1:1), in which it dissolves readily. The solution is colorless after the iron sulphide has settled out. Free mercury settles to the bottom of the dish as a gray sediment.

Free sulphur is recognized by the yellow coloration of the solution. It may also be detected in the usual way by digesting with potassium hydroxid or extraction with carbon disulphide (if present in crystalline form). The quantitative determination is carried out by extracting with soda solution and oxidation to sulphate.

For separating foreign adulterations such as barytes, clay, litharge, chrome red, brick dust, etc., potassium sulphide may be used to advantage. After filtering, wash with dilute KOH solution and not with water, otherwise the Brunner's salt decomposes with separation of black HgS.

The coal tar colors are identified by extraction with alcohol; carmines by the drop test with ammonia on filter paper.

For detecting arsenic sulphide, boil with caustic soda, acidify with hydrochloric acid and introduce H_2S gas into the solution.

Analysis of Chrome Yellows and Oranges

Organic Matter. — Test with alcohol to determine presence of organic coloring matter.

Insoluble. — Boil 1 g. for about 5 minutes with 20 c.c. of concentrated hydrochloric acid, adding 1 or 2 c.c. of alcohol drop by drop. Dilute with about 100 c.c. of boiling water. Boil a few minutes longer. Filter, wash with boiling water, and weigh the insoluble. Test the latter for barium sulphate, clay or silica.

Lead. — Neutralize the filtrate with ammonia until a *slight* permanent precipitate appears. Reacidify slightly, using an excess of not more than 1.5 c.c. of concentrated hydrochloric acid in 100 c.c. of solution. Dilute to 200 c.c. Precipitate the lead with hydrogen sulphide. Filter, wash with H_2S water, dissolve the PbS in hot dilute nitric acid, boil to expel H_2S, add 10 c.c. of dilute H_2SO_4 (1:1), evaporate to fumes of SO_3 and determine lead gravimetrically or volumetrically as outlined under "White Lead."

Chromium. — Evaporate the alcoholic filtrate from the $PbSO_4$ almost to dryness and mix with the filtrate from PbS. The chromium is determined by precipitating hot with a slight excess of ammonia. Filter, wash, ignite and weigh as Cr_2O_3.

Zinc. — The filtrate from chromium hydroxid is analyzed for zinc by precipitating with hydrogen sulphide. See "Zinc Oxid."

Chrome Greens

Preliminary Test. — Determine the presence of organic coloring matter by extraction with alcohol.

Insoluble. — In a small evaporating dish heat 1 g. sample at as low a temperature as possible until the blue color is completely discharged. Transfer to a beaker, and boil with 20 c.c. of concentrated hydrochloric acid and a little alcohol to dissolve the soluble portion. Dilute with hot water, boil, filter, wash, and weigh the insoluble portion. Examine the latter for silica, clay or barytes.

Lead. — Determine in the filtrate after neutralizing with ammonia and reacidifying slightly with hydrochloric acid as under "Chrome Yellows."

Chromium, Iron and Aluminium.—Boil the filtrate from the lead sulphide to expel hydrogen sulphide, add a few drops of nitric acid and about 2 g. of ammonium chloride. Heat to boiling, and precipitate iron, aluminium, and chromium as hydroxids with ammonia in slight excess. Filter and wash the precipitates. Dissolve the mixed hydroxids in a small amount of hot dilute hydrochloric acid and dilute to 150 c.c. Heat to boiling and treat with an excess of sodium hydroxid, and bromine water. Filter and wash. Redissolve the ferric hydroxid in dilute hydrochloric acid, and determine iron by the usual methods.

The filtrate is acidified faintly with hydrochloric acid and aluminium hydroxid precipitated with a slight excess of ammonia.

The filtrate from aluminium hydroxid is carefully acidified with acetic acid, and the chromium precipitated by the addition of barium acetate to the hot solution. Allow to stand for some time, and filter through a Gooch or alundum crucible (using gentle suction). Wash with alcohol, and dry in hot closet. Finally ignite at a dull red heat by suspending the crucible inside a larger porcelain crucible by means of an asbestos ring. If desired the chromium present as alkali chromate may be reduced to chromic salt by evaporating with hydrochloric acid and alcohol. The chromium may then be precipitated by ammonia and weighed after ignition as Cr_2O_3.

Calcium and Magnesium.—Determine as usual in the filtrate from iron, aluminium and chromium hydroxids.

Sulphates.—Treat 1 g. as mentioned in the second paragraph of this section. Determine sulphates as under "Zinc Lead."

Nitrogen.—Determine by the Kjeldahl-Gunning method.

PRUSSIAN BLUE

Hygroscopic Moisture.—Determine on a 1 g. sample by heating for 2 hours at 105° C.

Water of Composition.—Determine by difference after the other constituents have been obtained.

Ferrocyanic Acid.[1]—Treat 0.5 g. with 10 c.c. of normal potassium hydroxid solution in a flask. Boil for 5 minutes, dilute with 50 c.c. of hot water, filter, and wash the ferric hydroxid.

The filtrate containing a solution of potassium ferrocyanide is slightly acidified with sulphuric acid, 2 to 3 g. of ammonium persulphate are added, and the liquid boiled from 20 to 30 minutes. Any blue color which persists is removed by the addition of hydrochloric acid and a little more persulphate.

The iron is precipitated with ammonia by the usual method gravimetrically or volumetrically. Calculate as FeC_6N_6.

Cyanogen.—If desired, the total nitrogen in Prussian blue may be determined by the Kjeldahl-Gunning method as outlined in Bulletin 107, Bureau of Chemistry, U. S. Dept. of Agriculture.

To determine the amount of Prussian blue, multiply the total iron content by 3.03 or nitrogen content by 4.4. The results thus obtained are fairly approximate. They are not exact since the composition of Prussian blue is variable. The pure Prussian blue should contain about 20 per cent of nitrogen and 30 per cent of iron, and less than 7 per cent of moisture. The sulphuric acid used in determining the nitrogen by the Kjeldahl-Gunning method should not be blackened due to the presence of organic adulterants.

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[1] Ber. 1903, 36, 1929.

Iron. — To determine the total iron in Prussian blue, ignite 1 g. gently until the blue color is completely discharged. Dissolve the residue in 10 c.c. of hydrochloric acid (1 : 1), filter, make up to 100 c.c. in a graduated flask. Determine Fe_2O_3 in 50 c.c. in this solution (calculate to metallic iron).

In the other 50 c.c. of the filtrate determine $Fe_2O_3 + Al_2O_3$ by the usual methods. Calculate Al_2O_3 by difference. Report as metallic aluminium.

Calcium. — Determine as usual in the filtrate from $Fe_2O_3 + Al_2O_3$.

Alkali Metals. — Determine by the usual methods.

ANALYSIS OF ULTRAMARINE

I

The ultramarine is finely powdered and dried at 100°. 2 to 10 g. are weighed off, digested with water, filtered, the filtrate diluted to 500 c.c., and 100 c.c. taken for each of the following determinations.

(*a*) $Na_2S_2O_3$ — determine with iodine solution and starch. Calculate to $Na_2S_2O_3 + Ag$.

(*b*) Na_2SO_4 — determine by precipitating with barium chloride in acid solution.

(*c*) NaCl — determine by precipitating with $AgNO_3$ (NaCl is rarely present in ultramarine).

10 to 20 grams of ultramarine are washed two or three times by decantation (to obtain a clear filtrate, alcohol is added). Evaporate almost to dryness with a dilute solution of sodium sulphite[1] on the water bath. Wash until a test of the ultramarine moistened with water and filtered gives no trace of turbidity with barium chloride.

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[1] In order to remove free S, for CS_2 extracts only 40 to 60% of the same.

The ultramarine dried at 130 to 140° is again powdered and placed hot into a glass stoppered flask.

II

Estimation of silicic acid, silica, clay and total sulphur.

1 g. of the dried substance is weighed into a porcelain dish, stirred up with water and treated with 1 to 2 c.c. of bromine. If it is partially dissolved (as shown by the yellow coloration of the liquid) 15 to 20 c.c. of nitric acid are added and the whole evaporated to dryness on the water bath.

Take up with water, add 20 c.c. of hydrochloric acid and evaporate again (to remove nitric acid which would increase the $BaSO_4$ precipitate, and to render silicic acid insoluble). Treat with hydrochloric acid, digest warm for a few hours, dilute with water and filter. On the filter are left silicic acid and sand.

To determine total sulphur, the filtrate is heated to boiling and precipitated with barium chloride.

III

Estimation of alumina and of soda.

1 g. of ultramarine, washed and dried as in number I, is carefully mixed with water and treated with an excess of hydrochloric acid. After standing for a while it is heated until the solution settles clear. It is then filtered, leaving sulphur, sand and silicic acid undissolved. The residue is weighed after ignition. The filtrate is evaporated to dryness, the residue moistened with water and hydrocloric acid and again dried. Take up with hydrochloric acid, dilute with water after standing for some time and filter. On the filter is left silicic acid, which, added to the residue obtained in the first filtration, gives the content of total silicic acid and sand. The filtrate is evaporated to dryness to remove excess hydro-

chloric acid. The residue is dissolved in water, precipitated with ammonia and the whole thoroughly dried in the water bath. (This facilitates complete washing of the alumina.)

Take up the residue with hot water, add a few drops of ammonia, heat and filter. Alumina on the filter is determined and weighed.

For determining soda, the filtrate is treated with sulphuric acid and a little fuming nitric acid and evaporated to dryness. The residue is strongly ignited and the Na_2SO_4 calculated to Na.

Black Pigments

(Carbon Black, Lampblack, Vine Black, Bone Black)

Moisture. — Determine on a 2 g. sample by heating for two hours at 105° C.

Volatile. — Heat for 10 minutes over a Bunsen flame in a well-covered porcelain crucible.

Ash. — Determine on a 1 g. sample, ignite over a Bunsen burner with free access of air. When the ash is large in quantity, cool, moisten with a solution of ammonium carbonate and ignite again gently.

Soluble and Insoluble Ash. — Treat the ash obtained by the above procedure with 5 to 10 c.c. of dilute hydrochloric acid, heat, filter, wash and weigh the insoluble portion. Calculate the percentage of acid-soluble ash from the total ash and the acid-insoluble ash.

Certain blacks are sometimes adulterated with Prussian blue. To detect the latter, boil with dilute caustic soda, filter, acidify the filtrate with dilute hydrochloric acid, and add a mixture of ferric chloride and ferrous sulphate. The formation of a blue precipitate indicates the presence of Prussian blue.

Graphite

Heat 1 g. of the finely powdered graphite to a dull red heat and calculate the loss in weight as water. The dried substance is intimately mixed with 3 g. of a mixture of equivalent parts of K_2CO_3 and Na_2CO_3 and placed in a crucible. 1 g. of KOH or NaOH is sprinkled over the surface of this mixture and the whole heated slowly to redness. The mass fuses, swells and forms a crust on top, which must be broken with a stout platinum wire.

After fusing for one half hour, the melt is cooled, heated with water for $\frac{1}{4}$ hour almost to boiling, filtered, washed well and the liquids set aside. The insoluble is dried, placed in a dish, the filter ash added and about 3 g. of HCl (specific gravity 1.18) poured in. After several minutes a slight gelatinization sets in due to the decomposition of the small residue of alkali silicate. The addition of a little more hydrochloric acid brings the silicic acid into solution. After digestion for one hour, dilute with water, filter and wash out. The residue on the filter is pure carbon, which, after drying and gentle ignition, is weighed. The acid filtrate is united with the alkaline one obtained above, more HCl added until weakly acid, evaporated to dryness, and silicic acid, alumina and iron oxid determined as usual.

Blanc Fixe

Water Soluble Salts. — Owing to the variety of methods employed in the technical production of blanc fixe, a preliminary qualitative examination of the material is always essential before proceeding with the quantitative analysis.

Digest about 5 g. with 150 c.c. of hot water and filter. Examine the filtrate to detect the presence of water soluble salts. Determine the amount of water soluble salts, by difference, on a 1 g. sample.

Acid Soluble.— Digest 1 g. of blanc fixe with hot water, wash by decantation and filter, keeping as much of the residue as possible in the beaker. Discard the filtrate and treat the residue in the beaker with about 25 c.c. of hot dilute HCl (1:3); filter through the filter paper used above, wash and ignite. Add 1 drop of nitric and 2 drops of sulphuric acid, evaporate, ignite again and weigh. Calculate % acid soluble from loss in weight, % water soluble and % moisture.

$BaSO_4$.— Proceed as outlined below under barytes (fusion in platinum with Na_2CO_3) to determine barium sulphate and silica (Page 314).

Iron. — Determine colorimetrically.

Silica. — To determine qualitatively[1] whether a sample of blanc fixe is free from silica or clay, heat about 0.5 g. with 10 to 15 c.c. of concentrated sulphuric acid. A pure blanc fixe or barytes dissolves completely. Silicious matter remains undissolved. Determine the amount of silicious matter on a 1. g. sample by evaporating with a few c.c. of hydrofluoric acid and several drops of sulphuric acid.

Analysis of Whiting

Carbon Dioxid. — Determined as outlined under "White Lead."

Calcium. — Determined by the usual methods.

Gypsum or Calcium Sulphate

Calcium and Sulphates. — Determine by the usual methods.

Moisture. — Dry 2 g. in a vacuum dessicator over sulphuric acid to constant weight.

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[1] Method developed in the laboratory of Toch Brothers.

Combined H_2O and Moisture. — Heat 1 g. in a covered porcelain crucible on an asbestos plate for 15 minutes, then heat the bottom of the crucible to dull redness for 10 minutes over a Bunsen burner, remove the cover and heat for 30 minutes at a slightly lower temperature. Cool and weigh rapidly.

SILICA, ASBESTINE, CLAY (BARYTES)

Hygroscopic Moisture. — Determine on a 2 g. sample by heating for 1 hour at 105° C.

Loss on Ignition. — Determine on a 1 g. sample. This is largely water of composition, unless carbonates are present.

Complete Analysis. — Mix 0.5 g. in a platinum crucible intimately with about 5 g. of anhydrous sodium carbonate. Add a thin layer of the latter on top, cover the crucible and heat gently over a Tirrill or Tech burner for a short time. Raise the temperature gradually to the full heat of the burner. Finally heat for a short time over the blast lamp. Allow to cool, then heat the lower part of the crucible to dull redness, and cool again. Add a little water, heat carefully to boiling and the melt will readily separate from the crucible. Place the melt in an evaporating dish; wash the crucible with a little hot water, and add to the dish. If barytes, or blanc fixe is present, the melt is digested with hot water until completely disintegrated, the barium carbonate is filtered off and washed, and the barium determined as outlined under barium carbonate. The filtrate is then treated in a large covered beaker with concentrated hydrochloric acid. After a certain amount of acid has been added, the silicic acid separates out as a gelatinous mass, which has to be broken up in order to obtain intimate admixture with the acid. After an excess of acid has been added, the solution is heated to boiling, transferred to a porcelain or platinum dish and evaporated to dryness.

It is essential that dehydration of the silica be carried out twice[1] at the temperature of the steam bath and that the insoluble silica be filtered off before evaporating the second time.

Filter, wash, combine the insoluble residues from the two dehydrations, ignite in a platinum crucible and weigh. Drive off SiO_2 with a few c.c. of HF and several drops of H_2SO_4. Ignite and reweigh. The loss in weight is silica.

Iron and Aluminium Oxids. — Treat the filtrate from the silicic acid with a few drops of concentrated nitric acid and 10 to 20 c.c. of a cold saturated solution of ammonium chloride. Heat to boiling and precipitate with a slight excess of ammonia. Allow the precipitate to settle, filter off the clear liquid and wash twice by decantation with hot water. Redissolve the ferric and aluminium hydroxids by running hot dilute hydrochloric acid through the filter paper into the beaker containing the major portion of the precipitate. Reprecipitate with ammonia, as before, filter, wash and ignite wet in the platinum crucible containing the residue obtained after SiO_2 was volatilized with HF and H_2SO_4. Weigh as $Fe_2O_3 + Al_2O_3$.

For the determination of iron in the mixed oxids, see Treadwell and Hall, Vol. II, p. 109.

Calcium. — Evaporate the filtrates from the ferric and aluminium hydroxids to a small volume. Heat to boiling and precipitate with a boiling solution of ammonium oxalate. Allow to stand for several hours. Filter and wash. Puncture the filter paper with a glass rod, wash the precipitate into a beaker with a stream of water from the

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[1] Hillebrand, "Analysis of Silicate and Carbonate Rocks."

wash bottle, and pass 20 c.c. of hot dilute sulphuric acid (1:1) over and through the filter paper. Heat to 90° C. and titrate with N/10 $KMnO_4$.

Magnesium. — Evaporate the filtrate from the calcium oxalate to dryness, and ignite in a porcelain dish. Moisten the residue with a little concentrated hydrochloric acid and dissolve in hot water. Filter and determine magnesium in the filtrate. Heat to boiling and treat with an excess of sodium or ammonium phosphate. Add an amount of 10 per cent ammonia equal to $\frac{1}{3}$ of the volume of solution. Allow to cool and set aside for a few hours. Filter through an alundum crucible, wash with 2.5 per cent ammonia, dry, ignite slowly at first and finally strongly until the precipitate is white. Weigh as $Mg_2P_2O_7$.

Alkalies. — See J. Lawrence Smith (Bulletin 422, U. S. Geologic Survey).

BARYTES

Make a preliminary test for lead compounds. In the absence of the latter weigh off 1 g. sample and mix with 5 g. anhydrous sodium carbonate in a platinum crucible. Fuse over the blast lamp for a half hour, occasionally imparting a rotary motion to the crucible to insure thorough reaction. Allow to cool, then heat the lower part of the crucible to dull redness, and cool again. Add a little water, bring carefully to boil, and the melt will readily separate from the crucible. Place in an evaporating dish, add 100 c.c. of water, and digest on the steam bath until completely disintegrated. Filter and wash the insoluble residue ($BaCO_3$) until free from soluble salts. Dissolve the $BaCO_3$ with 25 c.c. of hydrochloric acid (1:3), catching the filtrate and passing it through the filter to insure complete solution of the barium carbonate. Boil to expel carbon dioxid, neutralize the filtrate with ammonia, reacidify with a few drops of hydrochloric acid, heat to boiling, and precipitate with dilute sulphuric acid. Filter and wash on a Gooch crucible, dry at 130° C. and report as $BaSO_4$.

In the presence of lead, first extract the barytes with hot concentrated ammonium acetate solution before proceeding with the sodium carbonate fusion, since the presence of metallic lead in the fusion will ruin the platinum crucible.

Iron. — Determine colorimetrically.

Clay and Silica. — Acidify the filtrate from the barium carbonate with hydrochloric acid, evaporate to dryness on the steam bath, heat for 20 minutes longer on the steam bath, and extract with hot water and a little hydrochloric acid. Filter, wash and weigh the insoluble SiO_2. Determine alumina in the filtrate from SiO_2 as usual. See also determination of silica in blanc fixe (p. 311).

In reporting the presence of silica and alumina, it must be remembered that the reagents used in the above determination, sodium carbonate and ammonia, almost always contain appreciable quantities of silica and alumina. Especially is this true of aqua ammonia, except when kept in bottles lined with ceresin or paraffin wax.

ANALYSIS OF BARIUM CARBONATE

Water Soluble Salts. — Determine by difference in a 1 g. sample, treat with hot water, filter, wash, and weigh the insoluble.

Insoluble. — Dissolve about 10 g. in dilute hydrochloric acid. Heat to boiling, filter, wash and weigh the insoluble residue. The latter is generally silicious, but should be examined to determine the presence of barium.

Barium. — Dissolve 0.5 g. in dilute hydrochloric acid, neutralize with ammonia, then reacidify faintly with hydrochloric acid. Dilute to 100 c.c., heat to boiling, and precipitate with hot dilute sulphuric acid. Filter on a Gooch crucible, wash, and dry at 130° C. Calculate $BaSO_4$ to $BaCO_3$. For the separation of barium, calcium, and strontium from each other, see Treadwell and Hall, Anal. Chem., Vol. II, p. 79.

Carbon Dioxid. — Determine by evolution as outlined under "White Lead."

Iron.[1]— Treat 2 g. in a beaker with 15 c.c. of water and sufficient nitric acid to dissolve the barium carbonate. Boil for several minutes to expel carbon dioxid and to convert all the iron to the ferric state. Filter and wash the residue. Cool the filtrate, neutralize with ammonia and acidify faintly with nitric acid.

Wash the contents of the beaker into a 100 c.c. Nessler cylinder, add 15 c.c. of dilute ammonium thiocyanate (1:20) and dilute to the mark. The depth of the blood red color developed is a measure of the amount of iron present. Compare with a blank made as follows:

Prepare a standard solution of ferric ammonium sulphate by dissolving 0.7022 g. of ferrous ammonium sulphate in water. Acidify with sulphuric acid, heat to boiling and oxidize the iron by the addition of a solution of potassium permanganate. Only the faintest excess of permanganate should be added. The faint pink tinge due to the latter soon disappears. The solution is cooled and diluted to 1 liter. One c.c. of this solution is equivalent to 0.0001 g. of iron.

Into a 100 c.c. Nessler cylinder add about the same amount of nitric acid as was used to dissolve the barium

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[1] Modified Thompson & Schaeffer method. J. Ind. Eng. Chem. 1912, 659.

carbonate, and 15 c.c. of ammonium thiocyanate solution. Dilute to 100 c.c. and add the standard ferric ammonium sulphate solution, drop by drop, until the color exactly matches that developed in the sample being tested. One c.c. of the solution is equivalent to 0.01 per cent iron when a 1 g. sample is used. Not more than 2 or 3 c.c. of the standard should be required to equal the color; otherwise, the color becomes too deep for comparison.

Sulphur.— For colorimetric determination see Treadwell & Hall, Vol. II, pages 354–7.

Chlorine. — Determine in the water soluble portion (acidified with nitric acid) by precipitating hot in the presence of a slight excess of silver nitrate, filter on a Gooch or alundum crucible, wash, and weigh the insoluble AgCl after drying at 130° C.

Analysis of Mixed White Paints

I. *By use of Acetic Acid*

Treat 1 g. of the mixed white pigment with 22 c.c. of water and 10 c.c. of glacial acetic acid. Boil, filter, and wash with water. The filtrate is heated to boiling, and precipitated with hydrogen sulphide. Filter off the lead and zinc sulphides, dissolve in hot dilute nitric acid, and determine lead and zinc as usual. Calculate the lead to white lead, and zinc to oxid. The filtrate from lead and zinc sulphides is tested for Ba, Ca, and Mg. Determine and calculate to carbonates.

To the residue from the acetic acid treatment add 10 c.c. of water, 10 c.c. of strong hydrochloric acid, and 5 g. ammonium chloride. Heat on steam bath for 5 minutes, dilute with boiling water to 400 c.c., boil, filter, wash, ignite and weigh the insoluble. Examine for silica, clay, barytes or asbestine.

Precipitate the lead in the filtrate with hydrogen sulphide, filter and wash. Dissolve in hot dilute nitric acid, and determine as usual. Report as $PbSO_4$. The filtrate is boiled to expel hydrogen sulphide, a few drops of nitric acid, ammonium chloride, and ammonia in excess are added to precipitate iron and aluminium. Calcium is determined in the filtrate as usual. Report as $CaSO_4$.

II. *By G. W. Thompson,* (*Jour. Soc. Chem. Ind. 15, 432*)

"The qualitative examination for the elements present may be determined as follows: Effervescence with concentrated hydrochloric acid indicates carbonic acid, sulphuretted hydrogen if zinc sulphide is present, or sulphurous acid if lead sulphite is present. These latter two may be recognized by their odors. Boil a portion of the paint with acid ammonium acetate and test a portion of the filtrate for sulphuric acid with barium chloride. Test another portion of the same solution with sulphuric acid in excess for lead and test filtrate for zinc by making alkaline with ammonia, and adding ammonium sulphide. Test another portion of the ammonium acetate solution for lime by making alkaline with ammonia, adding ammonium sulphide, filtering and adding ammonium oxalate to filtrate. The portion insoluble in ammonium acetate, in the absence of sulphite of zinc and sulphate of lead may be barytes, China clay, or silica. The qualitative examination of this residue is best combined with quantitative examination given further on."

"The oxids and elements, the presence of which is usually possible in a white paint, are: carbonic acid, water (combined), sulphuric acid, sulphurous acid, sulphur (combined as sulphide), silica, barium oxid, calcium oxid, zinc oxid, and zinc combined as sulphide, lead oxid, aluminium oxid."

"In the absence of sulphuric acid, the lead soluble in acetic acid may be directly calculated to white lead."

"Sulphuric acid may exist in two conditions, in one it is soluble in ammonium acetate, and in the other, as in barytes, it is insoluble in ammonium acetate. That soluble in ammonium acetate may be determined by precipitating with barium chloride in that solution. Sulphuric acid in barytes is best calculated from the barium present, and determined as described later on. Sulphurous acid may be determined by oxidation to sulphuric acid, or its determination may be based on the insolubility of lead sulphite in ammonium acetate. For instance, one portion of the sample is oxidized with nitric acid and the total lead determined. Another portion is treated directly with ammonium acetate, and the lead soluble in that menstruum determined. The difference between the two determinations is the lead present as sulphite, from which we may calculate the sulphurous acid present. Sulphur as sulphide is always present as zinc sulphide, which is never used in the presence of lead compounds. It may be determined by oxidation with bromine water and precipitation with barium chloride, or by determining the zinc insoluble in ammonium acetate. Silica may be determined by treating the matter insoluble in ammonium acetate with hydrofluoric acid and sulphuric acid. The loss on ignition is silica, or it may be determined by fusing the residue in the regular way. Barium oxid is determined by precipitation with sulphuric acid from hydrochloric acid solution of that part of fused residue insoluble in water."

Rapid Methods for White Pigments

"Sample 1 is a mixture of barytes, white lead, and zinc oxid.

"Two 1-gram portions are weighed out. One is dissolved in acetic acid and filtered, the insoluble matter ignited and weighed as barytes, the lead in the soluble portion precipitated with dichromate of potash, weighed in Gooch crucible as chromate, and calculated to white lead.

"The other portion is dissolved in dilute nitric acid, sulphuric acid added in excess, evaporation carried to fumes, water added, the zinc sulphate solution filtered from barytes and lead sulphate and precipitated directly as carbonate, filtered, ignited, and weighed as oxid.

"Sample 2 is a mixture of barytes and so-called sublimed white lead.

"Weigh out three 1-gram portions. In one determine zinc oxid as in Case 1. Treat a second portion with boiling acetic acid, filter, determine lead in filtrate and calculate to lead oxid. Treat third portion by boiling with acid ammonium acetate, filter, ignite, and weigh residue as barytes, determine total lead in filtrate, deduct from it the lead as oxid, and calculate the remainder to sulphate. Sublimed lead contains no hydrate of lead, and its relative whiteness is probably due to the oxid of lead being combined with the sulphate as basic sulphate. Its analysis should be reported in terms of sulphate of lead, oxid of lead, and oxid of zinc.

"Sample 3 is a mixture of barytes, sublimed lead, and white lead.

"Determine barytes, zinc oxid, lead soluble in acetic acid and in ammonium acetate, as in Case 2; also determine carbonic acid, which calculate to white lead, deduct lead in white lead from the lead soluble in acetic acid, and calculate the remainder to lead oxid.

"Sample 4 is a mixture of barytes, white lead, and carbonate of lime.

"Determine barytes and lead soluble in acetic acid (white lead) as in Case 1. In filtrate from lead chromate precipitate lime as oxalate, weigh as sulphate, and calculate to carbonate. Chromic acid does not interfere with the precipitation of lime as oxalate from acetic acid solution.

"Sample 5 is a mixture of barytes, white lead, zinc oxid, and carbonate of lime.

"Determine barytes and white lead as in Case 1. Dissolve another portion in acetic acid, filter and pass sulphuretted hydrogen through the boiling solution, filter, and precipitate lime in filtrate as oxalate; dissolve mixed sulphides of lead and zinc in dilute nitric acid, evaporate to fumes with sulphuric acid, separate, and determine zinc oxid as in Case 1.

"Sample 6 is a mixture of barytes, white lead, sublimed lead, and carbonate of lime.

"Determine barytes, lead soluble in acetic acid and in ammonium acetate, as in Case 2, lime and zinc oxid, as in Case 5, and carbonic acid. Calculate lime to carbonate of lime, deduct carbonic acid in it from total carbonic acid, calculate the remainder of it to white lead, deduct lead in white lead from lead soluble in acetic acid, and calculate the remainder to oxid of lead.

"Sample 7 contains sulphate of lime.

"Analyses of paints containing sulphate of lime present peculiar difficulties from its proneness to give up sulphuric acid to lead oxid if white lead is present. Sulphate of lime and white lead boiled in water are more or less mutually decomposed with the formation of sulphate of lead and carbonate of lime. A method for the determination of sulphate of lime is by prolonged washing with water with slight suction in a weighed Gooch crucible. This is exceedingly tedious, but thoroughly accurate. A reservoir containing water may be placed above the crucible, and the water allowed to drop slowly into it. This may take one or two days to bring the sample to constant weight, during which time several liters of water will have passed through the crucible. Another method for separating the sulphate of lime is by treatment in a weighed Gooch crucible with a mixture of nine parts of 95 per cent alcohol and one part of glacial acetic acid. Acetates of lead, zinc, and lime being soluble in this mixture, the residue contains all the sulphate of lime and any sulphate of lead and barytes which may be present. Determine the lead and lime as in sample 4, and calculate to sulphates. Sulphate of lime should be fully hydrated in paints. To determine this, obtain loss on ignition; deduct carbonic acid and water in other constituents; the remainder should agree fairly well with the calculated water in the hydrated sulphate of lime, if it is fully hydrated. If, after washing a small portion of the sample with water, the residue shows no sulphuric acid soluble in ammonium acetate, the sulphate of lime may be obtained by determining the sulphuric acid soluble in ammonium acetate and calculating to sulphate of lime. The difficulty is in determining the sulphate of lime in the presence, or possible presence, of sulphate of lead. To illustrate the analysis of sample of white paint containing sulphate of lime and the difficulty attending thereon, we would mention a sample containing sublimed lead, white lead, carbonate of lime, and sulphate of lime. In such a sample we would determine the lead, lime, sulphuric acid, carbonic acid, loss on ignition, the portion soluble in water, and the lime or sulphuric acid in that portion, calculating to sulphate of lime. Deduct the lime in the sulphate of lime from the total lime, and calculate the remainder to carbonate of lime;

deduct the carbonic acid in the carbonate of lime from the total carbonic acid, and calculate the remainder to white lead; deduct the sulphuric acid in the sulphate of lime from the total sulphuric acid, and calculate the remainder to sulphate of lead. The lead unaccounted for as sulphate or white lead is present as oxid of lead. Deduct the carbonic acid and water in the carbonate of lime and white lead from the loss on ignition, the remainder being the water of hydration of the sulphate of lime.

"Sample 8 contains as insoluble matter, barytes, China clay and silica.

"After igniting and weighing the insoluble matter, carbonate of soda is added to it, and the mixture fused. The fused mass is treated with water, and the insoluble portion filtered off and washed. This insoluble portion is dissolved in dilute hydrochloric acid, and the barium present precipitated with sulphuric acid in excess. The barium sulphate is filtered out, ignited, weighed, and if this weight does not differ materially — say by 2 per cent, — from the weight of the total insoluble matter, the total insoluble matter is reported as barytes. If the difference is greater than this, add the filtrate from the barium sulphate precipitate to the water-soluble portion of fusion. Evaporate and determine the silica and the alumina in the regular way. Calculate the alumina to China clay on the arbitrary formula $2SiO_2 . Al_2O_3 . 2H_2O$, and deduct the silica in it from the total silica, reporting the latter in a free state. It is to be borne in mind that China clay gives a loss of about 13 per cent on ignition, which must be allowed for. China clay is but slightly used in white paints as compared with barytes and silica."

"Sample 9 contains sulphide of zinc.

"Samples of this character are usually mixtures in varying proportions of barium sulphate, sulphide of zinc, and oxid of zinc. Determine barytes as matter insoluble in nitric acid, the total zinc as in Case 1, and the zinc soluble in acetic acid, which is oxid of zinc. Calculate the zinc insoluble in acetic acid to sulphide."

"Sample 10 contains sulphite of lead.

"This is of rare occurrence. Sulphite of lead is insoluble in ammonium acetate, and may be filtered out and weighed as such. It is apt on exposure to the air in the moist state to become oxidized to sulphate of lead.

"There are certain positions which the chemist must take in reporting analyses of white paints:

"*First.* White lead is not uniformly of the composition usually given as theoretical $2PbCO_3 \cdot Pb(OH)_2$, but in reporting we must accept this as the basis of calculating results, unless it is demonstrated that the composition of the white lead is very abnormal.

"*Second.* In reporting oxid of lead present this should not be done except in the presence of sulphate of lead, and if white lead is present, then only where the oxid is more than 1 per cent; otherwise calculate all the lead soluble in acetic acid to white lead.

"*Third.* China clay is to be calculated to the arbitrary formula given.

"In outlining the above methods we have in mind many samples that we have analyzed, and the combinations we have chosen are those we have actually found present."

ANALYSIS OF PAINTS

Separation of Pigment from Vehicle.—The can of paint is weighed off and if free from water, heated on the steam bath for 15 to 30 minutes. Owing to the marked decrease in the specific gravity and the viscosity of the paint vehicle at the higher temperature, the pigment generally settles to the bottom very quickly.

In the case of paints which show the presence of water, it is best to allow the pigment to settle out in the cold in order to avoid any saponifying action which the pigment might exert on the vehicle. The clear liquid is then drawn off as far as possible and set aside for analysis. The can is carefully wiped and weighed again.

About 25 g. of the residue in the can are weighed into a tall weighing tube. A mixture of benzol and alcohol 1:1 is added and the contents carefully stirred up with a glass rod. Another tube containing a similar weighed quantity of the same material is balanced to within 0.1 of a gram against the first tube, after adding the solvent and stirring.

The two are then placed in the opposite receivers of a centrifuge and whirled at a moderate or high speed, (depending upon the facility with which the pigment settles out) for about five or ten minutes. The clear liquid is then drawn off, the tubes balanced, and after the addition of fresh solvent, stirred and again centrifuged. This is continued until no more of the vehicle can be extracted.

The tubes are then placed in an air oven first at 80° C. and then at 100° C. until dry. From the weights of the tubes before and after extraction, the weight of paint extracted, and the weights of the can with and without the supernatant liquid, the percentage of vehicle and pigment can be calculated.

There is generally left with the extracted pigment a small percentage of unextracted matter (probably soaps resulting from the interaction of pigment and vehicle, or linoxyn), for which allowance must be made.

The extracted pigment is analyzed as outlined in the chapter on "Methods of Analysis of Pigments."

Determination of Volatile Matter.[1]—Weigh off into a round bottomed flask, 50 to 75 g. of the ready mixed paint. Connect with a condenser by means of a steam trap. Pass live steam through until no more of the volatile oil comes over. Allow the distillate to separate from the water and analyze separately. Shut off the steam and drive air through the apparatus. At the same time, heat the contents of the flask to 130° C. The residue is analyzed for non-volatile oils. Acetone, if present, will be found in the aqueous as well as oily layers of the distillate.

Analysis of Non-volatile Portion Extracted from the Ready Mixed Paint, as Previously Outlined.—As a rule, very little information can be obtained, in the present state of our knowledge of this subject, from the analysis of a varnish or the non-volatile portions of a paint vehicle.

Most of the constants or characteristics of the various ingredients which go to make up the varnish are so altered in the process of cooking that it is often extremely difficult, if not impossible, to distinguish them in the final material.

Rosin can generally be determined qualitatively and quite often, quantitatively, but even here it is sometimes impossible to detect it in admixture with other varnish resins.

DETERMINATION OF ROSIN

(*Twitchell Method*)[2]

Fatty or aliphatic acids are converted into ethyl esters when acted upon by hydrochloric acid gas in their

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[1] Amer. Soc. Testing Mat. Report of Comm. on Preservative Coatings for Structural Materials, 1903–1913.

[2] J. Soc. Chem. Ind. 1891, 10, 804.

alcoholic solution; rosin acids undergo little or no change, abietic acid separating from the solution.

Weigh off 2 to 3 g. of the mixed fatty or rosin acids in a flask, dissolve in 10 volumes of *absolute alcohol* and pass a current of dry, hydrochloric acid gas through the solution, the flask being kept cool by immersion in cold water. After about 45 minutes the reaction is complete, when unabsorbed HCl gas escapes.

The flask is allowed to stand for one hour to permit complete esterification and separation of the ethyl esters and rosin acids. Dilute the contents of the flask with five times its volume of water and boil until the aqueous solution has become clear.

Gravimetric Method.—Mix the contents of the flask with a little petroleum ether (b.p. below 80°) and transfer to a separatory funnel. The flask is washed out with the same solvent. The petroleum ether layer should be about 50 c.c. in volume.

After shaking, the acid solution is removed, the petroleum ether layer washed once with water, then treated in the same funnel with 45 c.c. N/5 KOH and 5 c.c. of alcohol. The liquids in the funnel then separate into: 1° a petroleum ether solution floating on top, and 2° an aqueous solution containing rosin soap. The soap solution is run off, the rosin esters liberated by decomposition with dilute hydrochloric acid, dissolved in ether, and separated by evaporating the solvent on the steam bath.

Volumetric Method.—The acidified mixture is poured into a separatory funnel and the flask washed a few times with ether. The mixture is thoroughly agitated, then allowed to separate, the acid layer run out, and the remaining ethereal solution containing the mixed ethyl esters and rosin acids washed with water until free from hydrochloric acid. 50 c.c of alcohol is then added and the solution titrated with standard alkali, using phenolphthalein as indicator. The rosin acids react immediately, forming rosin soaps; the ethyl esters remain unaffected.

The number of c.c. of N alkali is multiplied by 0.346, giving the amount of rosin acids in the sample.

The gravimetric method is the more accurate one, due to the difference in combining weights of the rosin acids in different samples of rosin. The results obtained by the Twitchell method are only approximately accurate.

In the case of a mixture of rosin acids, fatty and unsaponifiable, saponify with alcoholic KOH and drive off the alcohol (after dilution with water) by continued boiling. Disregarding the undissolved unsaponifiable, the aqueous soap solution is transferred to a separatory funnel and shaken out with petroleum ether; this removes the unsaponifiable. On treating with mineral acids, the soap solution yields a mixture of rosin and fatty acids which are separated by the Twitchell process.

In the volumetric method, the unsaponifiable need not be separated as above. 2 g. of the mixed acids and unsaponifiable are weighed off accurately, titrated with N alkali and the number of c.c. (a) noted. Another 2 g. are treated with HCl gas and titrated with N alkali, using (b) c.c.; taking 346 as the combining weight for rosin and 275 for the fatty acids (palmitic, stearic and oleic), the weight of the rosin acids is $b \times 0.346$; the weight of fatty acids is $(a - b) \times 0.275$, and the weight of the unsaponifiable equals $100 - \{b \times 0.346 + (a - b) \times 0.275\}$.

Separation of Rosin Acids from Fatty.—After the esterification process, we get a mixture of free acid and esters, and after titration (e.g. in the volumetric process) we get a mixture of rosin soap and ethyl esters of fatty acids. If the alcohol is distilled off and the remaining mixture treated with water, the soap is dissolved, leaving the esters floating on top of the soap solution. The two layers are separated and the soap solution, after washing with ether to remove traces of esters, yields rosin acids on acidulating. The ethyl esters are saponified by caustic alkali and the fatty acids separated.

DETERMINATION OF ROSIN

(*Wolff & Scholze Method*)[1]

Quick Titrimetric Determination.— 2 to 5 g. of the rosin — fatty — acid mixture, according to the quantity weighed off, are dissolved in 10 to 20 c.c. of absolute methyl or ethyl alcohol, treated with 5 to 10 c.c. of a solution of one part of sulphuric acid in four parts alcohol (methyl or ethyl) and boiled for *two minutes* with reflux condenser.

The reaction liquid is then treated with 5 to 10 volumes of 7 to 10 per cent sodium chloride solution and the fatty acid esters together with the rosin acids extracted with ether or a mixture of ether and a little petroleum ether. The aqueous solution is drawn off and agitated once or twice with ether. The ethereal solutions are united, washed twice with dilute sodium chloride solution (or when the washed water is not neutral, to neutrality), and after the addition of alcohol, titrated with N/2 KOH.

Assuming an average of 160 as the acid value of the rosin acids and a correction for unsaponifiable fatty acids of 1.5, and further taking "m" as the amount of the weighed fatty — acid — rosin mixture and "a" as the number of c.c. of KOH used for neutralization, we obtain as the rosin acid content in per cent, the following:

$$\frac{a.\ 17.\ 76}{m} - 1.5$$

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[1] Chem. Ztg. 38 (1914), 369, 382.

The amount of rosin is approximately obtained by multiplying this value by 1.07.

Gravimetric. — 2 to 5 g. of the fatty acid mixture are treated as in the first method. After neutralization, 1 to 2 c.c. more of alcoholic KOH are added and the ethereal solution repeatedly washed with water. The wash water and soap solution are concentrated to a small volume, transferred to a separatory funnel, acidified, and after the addition of the same amount of sodium chloride solution, extracted two to three times. The ethereal solution is dried with fused sodium sulphate and the ether distilled off in a small flask.

The residue on cooling is dissolved in 10 c.c. of absolute ethyl alcohol, and 5 c.c. of a mixture of 1 part sulphuric acid with 0.4 parts alcohol are added. The mixture is allowed to stand for 1½ to 2 hours at room temperature. It is then treated with 7 to 10 volumes of 10 per cent sodium chloride solution, extracted with ether two to three times, and the united ether extracts (after twice washing with dilute sodium chloride and drying with fused sodium sulphate) distilled off.

The percentage of the thus isolated rosin acids may be multiplied by 1.07 in order to yield approximately the rosin content.

Rosin and Rosin Oils

Liebermann-Storch Reaction.—Dissolve the washed and dried mixed acids (obtained by saponification of the material to be analyzed and liberating the acids with dilute hydrochloric or sulphuric acid) in acetic anhydride on the water bath, cool and add a few drops of sulphuric acid (specific gravity 1.53).

This acid is made by mixing 34.7 c.c. of concentrated sulphuric acid with 35.7 c.c. of water, yielding 62.53

per cent sulphuric acid. The presence of rosin or rosin oil is detected by a very fine reddish violet coloration produced on the addition of the acid.

Detection.—Rosin oil may be detected by the Liebermann-Storch reaction already mentioned, or by the following:[1]

Stannic bromide is prepared by adding bromine dropwise to granulated tin in a dry flask immersed in cold water until an excess is present. Then a little more bromine is added and the whole diluted with three to four volumes of carbon disulphide. The reagent thus obtained is stable.

To carry out the test, a few drops of the rosin oil are placed in a dry test tube and dissolved in 1 c.c. of carbon disulphide. Add the stannic bromide reagent gradually. If rosin oil is present, the liquid assumes an intense, brilliant, violet coloration.

It may be necessary to dilute with more carbon disulphide in order to bring out this color.

On standing, a violet sediment is formed in the tube from which, after removing the liquid and warming the residue with carbon disulphide, the purple coloration is again obtained free from impurities.

In the presence of much mineral oil, mix the sample with the solution of stannic bromide in carbon disulphide, and then add, drop by drop, a solution of bromine and carbon disulphide. This yields the coloration unmasked by any due to the mineral oil.

ROSIN OIL

Rosin Spirit.—This is the lighter and more volatile portion obtained in the dry distillation of rosin. It is separated from the aqueous acetic acid layer, purified with

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[1] Allen, "Commercial Organic Analysis."

sulphuric acid and caustic soda, and then re-distilled. It is insoluble in water or alcohol, but soluble, in all proportions, in ether, petroleum-ether and turpentine. The specific gravity varies from 0.856 to 0.883.

Composition.—The hydro-carbons,[1] of which this is principally composed, include pentane and pentene and their homologues, toluene and its homologues, tetra and hexahydrotoluene and their homologues, terpenes, etc. The characteristic constituent of rosin spirit is heptine, C_7H_{12}, (methyl-propyl-allene). The compound boils at 103° to 104° C., and has a specific gravity of 0.8031 at 20° C. It is soluble in alcohol and ether, absorbs oxygen very readily, but does not affect ammoniacal cuprous chloride or silver nitrate.

Rosin Oil.—This is the heavier and less volatile portion obtained after the rosin spirit has been collected. It generally has a strong fluorescence although the latter can be more or less destroyed by hydrogen peroxid, the addition of nitro-benzol, nitro- or dinitrotoluene, dinitronaphthalene, or by heating with sulphur. The specific gravity of the crude rosin oil varies from 0.96 to 1.1 while the refined generally has a specific gravity of 0.97 to 0.99.

DETERMINATION OF WATER

Qualitative.—Water in an oil, paint, dryer or varnish may be detected by adding a few c.c. of dry mineral oil to an equal quantity of the sample in a test tube and shaking vigorously with a few grains of a strong dye like erythrosine, rhodamine or methylene blue. Coloration proves the presence of water. Solvents like alcohol, acetone or amyl acetate which dissolve these dyes must of course be absent.

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[1] Renard, Amer. Chem. Phys. 1884 (6) 1, 323.

The presence of an appreciable quantity of water in an *oil* is indicated by the crackling produced when some of it is heated in a test tube beyond 212° F.

Quantitative.—(1) In the case of non-volatile oils, about 5 g. are accurately weighed into a small evaporating dish or watch-glass and dried in the air oven at 100–110° C. for two hours. The loss in weight (except where volatile fatty acids are present) is reported as moisture.

For accurate determinations, however, the above method is open to serious objection. In the case of soya bean oil, for example, owing to its comparatively high content of volatile acids and glycerides, the results obtained may be somewhat high; whereas in the case of linseed oil the loss due to moisture may be more than counter-balanced by the gain in weight due to oxidation.

With drying oils, the following method[1] is therefore recommended:

(2) A small Erlenmeyer flask fitted with a cork through which pass two tubes, a long tube reaching down to the bottom of the flask and a short one ending just below the cork, is carefully dried and weighed. 5 g. of oil are then introduced, the flask placed upon a steam bath, and dry carbon dioxid, hydrogen or coal-gas passed through the oil for 1 or 2 hours by connecting the short tube to an air pump or aspirator. The flask is then carefully dried and weighed.

(3) For the determination of water in oils like pine oil, which always contain an appreciable quantity of water, as well as in ready mixed paints, the method[2] outlined on the next page is very useful:

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[1] Determination of moisture in oils in a current of air—Sonnenschein-Zeit. anal. Chem. 25, 373. J. Soc. Chem. Ind. 1886, 508.

[2] Michel, Chem. Ztg., 1913, 353.

The substance containing water is distilled in an inert, water-insoluble medium, lighter than water and having a higher boiling point. For this purpose a mixture of toluene and xylene (1:2) is found most suitable. On condensing the water separates quantitatively from the toluene-xylene mixture.

150 c.c. of a dry mixture of $\frac{1}{3}$ pure toluene (b. p. 110° to 112° C.) and $\frac{2}{3}$ commercial, pure xylene are placed in a 300 c.c. Jena flask, and the substance to be examined added. It is well to add a small spiral of aluminium to produce uniform ebullition. The distillate is collected in a separatory funnel about 10 cm. in diameter, and provided with a glass cock having a bore of at least 5 mm. A 10 c.c. tube, graduated in 0.1 or 0.05 c.c., in which the water is collected is attached. The distillate, which is milky in appearance on account of suspended water, is best separated by centrifuging. The amount of water is then read off on the graduated tube. The toluene-xylene may be dried over calcium chloride and used again.

(4) Determination of water by means of calcium carbide (see U. S. Circular No. 97, of the Bureau of Chemistry).

Analysis of Oils

Specific Gravity.—This is determined at 15.5° C. (60° F.). For most technical purposes the hydrometer is universally used. Where, however, a greater degree of accuracy is desired or where the amount of oil available is rather small, the Westphal or Mohr's balance, the specific gravity bottle, Sprengel's picnometer or finally the analytical balance may be used. In the latter case the specific gravity is determined by means of a plummet suspended from one of the balance beams and immersed in the oil maintained at 15.5° C. The latter is contained in a beaker or short cylinder placed upon a bridge so as not to interfere with the balance pans.

If the plummet weighs in air a grams, in water w grams, and in the oil at 15.5° C. o grams,

$a - w$ = loss in weight of plummet when immersed in water
= weight of vol. of water equal to vol. of plummet
$a - o$ = wt. of vol. of oil equal to vol. of plummet

$$\frac{a-o}{a-w} = \text{sp. gr. of oil}$$

For the determination of the specific gravity of viscous oils Lewkowitsch mentions the use of Bruhl's picnometer.

Eichhorn's araeopicnometer is used in the case of very small quantities of oil.

In the latter case also the specific gravity of the oil may be obtained by preparing a mixture of alcohol and water so that a drop of the oil remains in suspension wherever it is placed in the mixture. The sp. gr. of the alcohol-water mixture is then determined by means of a hydrometer.

It is advisable to determine the specific gravity at 15.5° C. Where, however, this is not feasible a correction[1] must be made. This has been found by Allen to be *approximately* the same for most vegetable and hydrocarbon oils, and is equal to 0.00064 for 1° C. or 0.00035 for 1° F.

Saponification Value.—This expresses the number of mgms. of potassium hydroxid necessary to completely saponify the glycerides and fatty acids in 1 g. of oil.

Weigh off in a 200 c.c. Erlenmeyer flask about 2 g. of oil, add 25 c.c. (from a pipette) of N/2 alcoholic potash, and heat on the steam bath for $\frac{1}{2}$ to 1 hour with reflux condenser. The contents of the flask should boil gently, and should be agitated occasionally. When saponification is complete, cool, add 5 drops of 1 per cent phenolphthalein solution, and titrate the excess of alkali with N/2 hydrochloric acid solution. A blank titration is made with

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[1] Allen, Comm. Org. Anal. 1910, Vol. 2, pp. 49–51.

25 c.c. N/2 alcoholic potash which has been heated as outlined above. The difference between the two titrations shows the number of c.c. of N/2 HCl equivalent to the KOH required to saponify the oil.

The alcoholic potash must be prepared from pure grain alcohol (95 per cent) and chemically pure caustic potash. Dissolve 40 g. of the stick potash in about 25 c.c. of water and dilute with alcohol to 1 liter. After standing for one day the solution may be filtered from the precipitated potassium carbonate (which the stick potash always contains) and set aside in a uniformly cool place.

The saponification value of an oil is valuable as a criterion of its freedom from adulteration with mineral oils. It does not, however, assist in detecting adulteration with other vegetable oils, since most of the naturally occurring vegetable oils have saponification values which vary between rather narrow limits. (See table, page 343.)

Acid Value.—This expresses the number of mgms. of potassium hydroxid necessary to neutralize the free fatty acids in 1 g. of oil.

Weigh off 5 to 15 g. of oil in an Erlenmeyer flask, add 50 c.c. of alcohol, amyl alcohol, or ether-alcohol mixture (1:1), add 2 to 3 drops of phenolphthalein and titrate against N/10 or N/5 caustic potash or soda. Of the above solvents amyl alcohol and ether-alcohol dissolve most oils and resins almost completely. They are especially valuable in the case of viscous oils. Where alcohol alone is used it is generally best to heat it with the oil for a short time on the steam bath before titrating in order to completely extract the free fatty acids. Titrate cold.

In the case of resins, and especially fossil resins, the method must be modified somewhat. Dissolve about 1 g. of the sample in 50 c.c. of a mixture of absolute alcohol and benzol (1:1) or a similar mixture of alcohol and ether by boiling, with reflux condenser, on the steam bath. Titrate against N/2 or N/5 *alcoholic* alkali. It has been found in this laboratory that aqueous alkali yields acid values much higher than those obtained with alcoholic alkali.

Oils which have been thickened by blowing generally have a lower acid value. On the other hand we have found that boiled bodied oils show a fair content of free fatty acids.

Varnish Oil		Same Oil Boiled and Bodied
Sp. gr.	0.933	0.973
Acid. Val.	3.1	14.8
Sapon. Val.	194.2	194.2
Iodine Val.	193.2	93.5

Iodine Value.—This figure represents the percentage of iodine chloride (expressed in terms of iodine) absorbed by the unsaturated glycerides and acids in 1 g. of oil.

Hübl Method.—About 0.15 g. of drying oil, 0.25 g. of semi-drying oil or 1 g. of non-drying oil is weighed off in a capsule, placed in a 500 to 1,000 c.c. glass-stoppered bottle, and dissolved in 10 c.c. of chloroform or carbon tetrachloride. 25 c.c. of mercury iodochloride prepared as shown below are added from a pipette. Empty the pipette each time in exactly the same way, draining until one or two drops have fallen. Moisten the glass stopper with potassium iodide solution, and set the bottle aside in the dark. If after two hours the color of the solution in the bottle is not a deep brownish red, add another 25 c.c. of mercury solution. When the reaction is complete the solution should contain an excess of iodine at least equal to the amount absorbed. For semi-drying oils allow 8 hours for complete absorption of the iodine; for drying oils allow 18 hours. 15 c.c. of 10 per cent potassium iodide solution (or more in case a red ppt. of mercuric iodide is formed) are added, and the contents of the flask diluted to about 500 c.c., at the same time washing in any volatilized iodine trapped by the potassium iodide solution on the stopper. The excess iodine in the aqueous and chloroformic layers is titrated against N/10 sodium thiosulphate with frequent agitation until the color of both layers is but faintly yellow. A few c.c. of freshly prepared starch solution are then added, and the titration continued until the blue color is discharged. A blank containing exactly the same quantities of solvent and mercury iodochloride solution must be set aside along with the oil, and then titrated after the addition of the same quantity of potassium iodide and water.

The difference between the number of c.c. of sodium thiosulphate required to neutralize the free iodine in the blank and the excess iodine with the oil represents the amount of iodine absorbed by the oil; from the latter the iodine value can be calculated.

To prepare the mercury iodochloride solution (1) 25 g. of pure resublimed iodine are dissolved in 500 c.c. of pure alcohol; (2) 30 g. of mercuric chloride are dissolved in the same quantity of alcohol in another bottle. On mixing the above two solutions and allowing to stand for 12 to 24 hours a solution of mercury iodochloride is formed containing 1 molecule of iodine (I_2) to one molecule of $HgCl_2$. The mixed solution cannot be used for making iodine value determinations when it is older than 24 hours. However, the two solutions in themselves will keep indefinitely. It is therefore best to prepare only as much iodochloride solution as is required.

The sodium thiosulphate solution is made by dissolving 25 g. of the crystals in 1,000 c.c. of water. It may be standardized by either of the following methods:

(*a*) *Against Potassium Permanganate*

Dissolve 1 or 2 g. of pure potassium iodide in a 400 c.c. flask, using a small amount of water; add 5 c.c. of hydrochloric acid (1:1) and then 20 or 25 c.c. of an accurately standardized N/10 potassium permanganate solution; the liberated iodine is titrated with the sodium thiosulphate solution after diluting to 200 c.c. The reaction involved is indicated below:

$$2KMnO_4 + 10KI + 16HCl = 12KCl + 2MnCl_2 + 8H_2O + 10I.$$

(*b*) *Against Potassium Dichromate*

$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 6I$$

Weigh off accurately 3.8633 g. of pure potassium dichromate and dissolve in exactly 1,000 c.c. of water. This quantity of dichromate solution is equivalent to exactly 10 g. of iodine liberated according to the above equation. In a 600 c.c. Erlenmeyer flask place 10 c.c. of 10 per cent potassium iodide solution and 5 c.c. of hydrochloric acid (1:1), and add exactly 20 c.c. of the dichromate solution from a burette. Dilute to 300–400 c.c. and titrate against sodium thiosulphate after adding starch solution. The end point is indicated by a change in the color of the solution from deep blue to pale green.

The starch solution is best prepared, as needed, by shaking up about 0.5 g. starch with 50 c.c. of water, heating, and boiling for 1 or 2 minutes. The solution should be cooled before being used. The dichromate solution keeps indefinitely and may be used for standardizing the thiosulphate solution, the strength of which varies slightly with age.

Wijs Method. — Dissolve 13 g. of iodine in glacial acetic acid, and determine accurately the amount of iodine present, using 25 c.c. for the determination. Then pass dry chlorine gas into the solution until the color changes suddenly from deep reddish brown to pale yellow, due to the complete transformation of the iodine into iodine chloride. The iodine equivalent of this solution must be exactly twice that of the original iodine solution. If a titration shows more than double the iodine equivalent, there is an excess of chlorine and enough iodine should be added to combine with it. If the analysis shows less than double the amount of iodine there is still an excess of iodine and more chlorine should be added.

The iodine value determination is carried out exactly as in the case of the Hübl method; the time of absorption, however, is very much less, being ½ hour for non-drying oils, 1 hour for semi-drying oils, and 2 to 6 hours for drying oils and marine animal oils.

According to Allen, absorption in the case of oils of low iodine value is complete in 4 minutes, while those of higher value require not more than 10 minutes, provided too much oil is not taken. In this laboratory we have made it a practice to allow about 1 hour for semi-drying and drying oils.

The values obtained by the Wijs method are as accurate as those obtained by the Hübl method, and agree very closely with the latter.

BROMIDE TEST

It has been found[1] that on treating the ethereal solutions of certain oils with a slight excess of bromine, an insoluble precipitate is obtained.

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[1] Hehner & Mitchell, Analyst, 1898, 23, 313.

Method.—Dissolve 1 or 2 g. of oil in 40 c.c. of ether, add a few c.c. of glacial acetic acid (the precipitate formed with bromine is more granular when the acid is used), stopper the flask, and cool to 5° C. Add bromine, drop by drop, from a very fine pipette until the brown coloration persists. The temperature must not be allowed to rise.

Allow to stand for 3 hours at 5° C., filter (preferably by suction), and wash four times with ice-cold ether. The residue is dried in the water oven and weighed.

The insoluble bromides obtained from linseed oil melt at 140 to 145° C. and contain about 56 per cent bromine. Those obtained from marine animal oils decompose before melting. This property, therefore, furnishes a good method of detecting small amounts of the latter in linseed oil.

The bromide test is useful in the examination of boiled and bodied oils. Lewkowitsch[1] has found that the process of boiling linseed oil decreases the yield of insoluble bromides.

On the other hand, an oil which has been bodied by blowing at a low temperature will give as high a yield of bromides as the oil from which it is prepared.

Lewkowitsch recommends that the mixed fatty acids, carefully prepared in an atmosphere of carbon dioxid or hydrogen, be used in making the bromide test. The precipitate then obtained is much easier to filter than when the oil is used.

According to Eibner and Muggenthaler,[2] the bromide test is carried out as follows:

2 g. of the mixed fatty acids are dissolved in 20 c.c. of dry ether, and cooled to minus 10° C.; 0.5 c.c.

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[1] Farben Ztg., 1912, 33 ff.

[2] Muggenthaler, Inaug. Dissert., 1912, Augsburg.

of bromine are added, drop by drop, from a very fine pipette, allowing about 20 minutes for the addition of this amount of bromine. Another 0.5 c.c. of bromine are then added in 10 minutes' time. The temperature must not go beyond − 5° C. The flask is corked and set aside for 2 hours at − 10° C. The solution is then filtered through a weighed asbestos filter, and washed 5 times with dry ice cold ether, using 5 c.c. each time.

The precipitate is then dried for 2 hours at 80 to 85° and cooled in a dessicator.

Hexabromides by the above Method

Fatty Acids from	*Per Cent*
Perilla Oil	64.12
Linseed Oil (Baltic)	57.96
Linseed Oil (Dutch)	51.73
Linseed Oil (La Plata)	51.66
Linseed Oil (Indian)	50.50
Tung Oil	nil
Soya Bean Oil	up to .78
Poppy Seed Oil	nil

The melting point of the bromides obtained by Eibner and Muggenthaler from the mixed fatty acids of linseed oil was 177° C.

The following table will give an idea of the yield of bromides obtained from various oils:

Material	*Per Cent*[1]
Perilla Oil	53.6
Linseed (iodine value 181.)	23.14 : 23.52
Linseed Oil (iodine value 186.4)	24.17
Linseed Oil (iodine value 190.4)	37.72
Tung Oil	nil
Hempseed Oil	8.82
Walnut Oil	1.42 : 1.9
Soya Bean Oil	3.73
Poppy Seed Oil	nil

[1] Lewkowitsch, Vol. I, p. 477.

Material	*Per Cent*
Soya Bean Oil	3.62
Corn Oil	nil
Cottonseed Oil	“
Menhaden Oil	61.8
Cod Oil	32.68 : 30.62
Seal Oil	27.54 : 27.92
Whale Oil	15.54 : 25.

Some Characteristics and Variables of Commercial Boiled Oils

Description	Specific gravity at 15.5° C	Acid value	Saponification value	Iodine value
				Per cent
Somewhat thin and fluid	.....	13.4	.....	101.3
Very viscid	.....	24.9	.....	77.3
Tacky, yielding strings	.....	32.6	.....	73.7
	.....	.....	188.1–192	145.1–157.2
	.....	.....	.....	149.7–153.4
Very thin	0.947	8.85	182.2	.....
Thin	0.948	7.06	180.9	.....
Thin	0.961	12.43	179.5	.....
Stout	0.972	19.69	189.3	.....
Stout	0.982	20.89	185.6	.....
Very stout	0.983	24.97	183.0	.....
Solid	.....	14.02	193.9	.....
Varying in consistence in the same order, from thin to very viscous	.....	4.8	188.7	159.0
	.....	5.2	189.1	100.7
	.....	7.8	189.1	95.6
	.....	9.5	186.6	83.6
	.....	9.1	187.2	79.1
	.....	11.7	187.2	76.2
	.....	18.8	192.3	71.1
Double boiled oil, I	0.9493	.....	191.0	161.0
“ “ “ II	0.9595	0.98	192.3	.....
“ “ “ III	0.9621	3.00	192.8	.....
Commercial boiled oils, 8 samples	0.9355–0.9474	2.8–6.4	187.5–192.2	180.4–183.3

Characteristics of Boiled Oils (Lewkowitsch)

Name	Specific gravity	Iodine value	Ether-insoluble bromides from glycerides
			Per cent
Linseed oil (raw)	0.9308	186.4	24.17
Pale boiled linseed oil	0.9429	171.0	20.97
Double “ “ “	0.9449	169.96	13.03
Ozonised “ “	0.9310	180.1	36.26–36.34
“ “ “	0.9388	171.2	25.73
“ “ “	0.9483	169.7	30.19

The Conversion of French (Metric) into English Measure

1	cubic centimeter	=	17	minims.							
2	cubic centimeters	=	34	“							
3	“	=	51	“							
4	“	=	68	“	or	1	dram	8	minims.		
5	“	=	85	“	“	1	“	25	“		
6	“	=	101	“	“	1	“	41	“		
7	“	=	118	“	“	1	“	58	“		
8	“	=	135	“	“	2	drams	15	“		
9	“	=	152	“	“	2	“	32	“		
10	“	=	169	“	“	2	“	49	“		
20	“	=	338	“	“	5	“	38	“		
30	“	=	507	“	“	1	ounce	0	dram	27	minims.
40	“	=	676	“	“	1	“	3	drams	16	“
50	“	=	845	“	“	1	“	6	“	5	“
60	“	=	1014	“	“	2	ounces	0	“	54	“
70	“	=	1183	“	“	2	“	3	“	43	“
80	“	=	1352	“	“	2	“	6	“	32	“
90	“	=	1521	“	“	3	“	1	“	21	“
100	“	=	1690	“	“	3	“	4	“	10	“
1000	“	=	1 liter = 34 fluid ounces nearly, or 2⅛ pints.								

The Conversion of French (Metric) into English Weight

The following table, which contains no error greater than one-tenth of a grain, will suffice for most practical purposes:

1	gram	=	15⅖	grains.					
2	grams	=	30⅘	“					
3	“	=	46⅕	“					
4	“	=	61⅘	“	.... or	1	dram	1⅘	grain.
5	“	=	77⅕	“	.... “	1	“	17⅕	grains.
6	“	=	92⅗	“	.... “	1	“	32⅗	“
7	“	=	108	“	.... “	1	“	48	“
8	“	=	123⅖	“	.... “	2	drams	3⅖	“
9	“	=	138⅘	“	.... “	2	“	18⅘	“
10	“	=	154⅖	“	.... “	2	“	34⅖	“
11	“	=	169⅘	“	.... “	2	“	49⅘	“
12	“	=	185⅕	“	.... “	3	“	5⅕	“
13	“	=	200⅗	“	.... “	3	“	20⅗	“
14	“	=	216	“	.... “	3	“	36	“
15	“	=	231⅖	“	.... “	3	“	51⅖	“
16	“	=	247	“	.... “	4	“	7	“
17	“	=	262⅖	“	.... “	4	“	22⅖	“
18	“	=	277⅘	“	.... “	4	“	37⅘	“
19	“	=	293⅕	“	.... “	4	“	53⅕	“
20	“	=	308⅗	“	.... “	5	“	8⅗	“
30	“	=	463	“	.... “	7	“	43	“
40	“	=	617⅕	“	.... “	10	“	17⅕	“
50	“	=	771⅗	“	.... “	12	“	51⅗	“
60	“	=	926	“	.... “	15	“	26	“
70	“	=	1080⅕	“	.... “	18	“	0⅕	“
80	“	=	1234⅗	“	.... “	20	“	34⅗	“
90	“	=	1389	“	.... “	23	“	9	“
100	“	=	1543⅕	“	.... “	25	“	43⅕	“
1000	“	=	1 kilogram = 32 oz., 1 dr., 12⅖ gr.						

Metric System of Weights and Measures

Measures of Length

Denominations and Values		Equivalents in Use
Myriameter	10,000 meters.	6.2137 miles.
Kilometer	1,000 meters.	.62137 mile, or 3,280 ft. 10 ins.
Hectometer	100 meters.	328. feet and 1 inch.
Dekameter	10 meters.	393.7 inches.
Meter	1 meter.	39.37 inches.
Decimeter	1-10th of a meter.	3.937 inches.
Centimeter	1-100th of a meter.	.3937 inch.
Millimeter	1-1000th of a meter.	.0394 inch.

Measures of Surface

Denominations and Values		Equivalents in Use
Hectare	10,000 square meters.	2.471 acres.
Are	100 square meters.	119.6 square yards.
Centare	1 square meter.	1,550. square inches.

Measures of Volume

Denominations and Values			Equivalents in Use	
Names	No. of Liters	Cubic Measures	Dry Measure	Wine Measure
Kiloliter or stere.	1,000	1 cubic meter.	1.308 cubic yards.	264.17 gallons.
Hectoliter	100	1-10th cubic meter.	2 bu. and 3.35 pecks.	26.417 gallons.
Dekaliter	10	10 cubic decimeters.	9.08 quarts.	2.6417 gallons.
Liter	1	1 cubic decimeter.	.908 quart.	1.0567 quarts.
Deciliter	1-10	1-10th cubic decimeter.	6.1023 cubic inches.	.845 gill.
Centiliter	1-100	10 cubic centimeters.	.6102 cubic inch.	.338 fluid oz.
Milliliter	1-1000	1 cubic centimeter.	.061 cubic inch.	.27 fl. drm.

Weights

Denominations and Values			Equivalents in Use
Names	Number of Grams	Weight of Volume of Water at its Maximum Density	Avoirdupois Weight
Millier or Tonneau	1,000,000	1 cubic meter.	2204.6 pounds.
Quintal	100,000	1 hectoliter.	220.46 pounds.
Myriagram	10,000	10 liters.	22.046 pounds.
Kilogram or Kilo	1,000	1 liter.	2.2046 pounds.
Hectogram	100	1 deciliter.	3.5274 ounces.
Dekagram	10	10 cubic centimeters.	.3527 ounce.
Gram	1	1 cubic centimeter.	15.432 grains.
Decigram	1-10	1-10th of a cubic centimeter.	1.5432 grains.
Centigram	1-100	10 cubic millimeters.	.1543 grain.
Milligram	1-1000	1 cubic millimeter.	.0154 grain.

For measuring surfaces, the square dekameter is used under the term of ARE; the hectare, or 100 ares, is equal to about 2½ acres. *The unit of capacity* is the cubic decimeter or LITER, and the series of measures is formed in the same way as in the case of the table of lengths. The cubic meter is the unit of measure for solid bodies, and is termed STERE. *The unit of weight* is the GRAM, which is the weight of one cubic centimeter of pure water weighed in a vacuum at the temperature of 4 deg. Cent. or 39.2 deg. Fahr., which is about its temperature of maximum density. In practice, the term cubic centimeter, abbreviated c.c., is generally used instead of milliliter, and cubic meter instead of kiloliter.

Specific Gravity of Various Materials

Acetic Acid	1.0607 $\frac{15}{4}$
Acetone	.788–.790
Acetylene	.92
Acrylic Acid	1.0621 $\frac{16}{4}$
Agate	2.5–2.8
Alabaster	2.3–2.8
Aluminium Oxid	3.75–3.99
“ Sulphate	2.71
“ “ $18H_2O$	1.62
Alum, Potassium	1.75
“ Soda	1.65
“ Ammon. Chrome	1.719
“ Potass. Chrome	1.81278 (0.°)
Amber	1.0–1.1
Ammonia (gas)	.5971
“ (liq.)	.6234 (0.°)
Ammonium Carbonate NH_4HCO_3	1.586
“ Chloride	1.520 (17.°)
“ Nitrate	1.725 (15.°)
“ Sulphate	1.7687 $\frac{20}{4}$
“ “ acid	1.787
Amyl Acetate	.8792 (20.°)
“ Alcohol	.8144–.8330
“ Valerianate	.8812 (0.°)
Aniline	1.0276 (12.°)
Anthracene	1.147
Anthracite	1.4–1.7
Antimony Oxid, Tri	5.2–5.7
“ “ Tetra	4.07
“ “ Penta	3.78
“ Pentasulphide	4.120 (0.°)
Arsenic Disulphide	3.4–3.6
“ Pentoxid	3.99–4.25
“ Trioxid	3.646
Asbestos	1.2
Asphalt	1.1–1.5
Barium Carbonate	4.27–4.37
“ Chloride $2H_2O$	3.097 $\frac{24}{4}$
“ Peroxid	4.958
“ Sulphide	4.25
“ Sulphate	4.33–4.476
Barley	.51–.69
Barytes	4.476
Basalt	2.7–3.2
Bees Wax (see wax).	
Beefsuet m.p. 31.°–31.5° C.	.968
Bellmetal	8.81
Benzene b. p. 80.5° C.	.8799(20.°C.)
Benzoic Acid	1.201 (21.°)
Blanc Fixe	4.02–4.53
Blue Vitriol	2.27
Bones	1.7–2.0
Boric Acid	1.46
Butter	.865–.868
Butyric Acid	.9599 $\frac{19}{4}$
admium Sulphide (artif.)	3.9–4.8 C
“ “ (Greenockite)	4.8–4.9
Calcium Carbide	2.22
“ Carbonate	2.72–2.95
“ Chloride (6 H_2O)	1.654
“ “	2.26
“ Fluoride	3.15–3.18
“ Hydroxid	2.078
“ Oxid	3.15–3.40
“ Sulphate	2.964
“ (Gypsum)	2.32
“ Sulphide	2.8
“ Tungstate	6.062
Camphor	.992
Caoutchouc	.92–.96
Carbolic Acid	1.0597 (33.°)
Carbon (Amorphous)	1.75–2.10
“ (Graphite)	2.10–2.585
“ (Diamond)	3.47–3.5585
“ Dioxid	1.529
“ Disulphide	1.28
“ Monoxid	0.967
“ Tetrachloride	1.59
Cast Iron	7.25
Cellulose	1.27–1.45
Charcoal (Airfilled)	0.4
“ (Airfree)	1.4–1.5
Chlorine	2.491
Chloroform	1.5264
Chrome Alum $Cr_2(SO_4)_3.K_2SO_4.24H_2O$	1.81278
Chromic Oxid	5.04
Chromium	6.92
Chromium Trioxid	2.67–2.82
Citric Acid	1.542
Clay	3.85
Cobalt Chloride	2.94
Cobaltic Oxid (Co_2O_3)	4.81–5.6
Cocoabutter (m. p. 33.5°–34.° C)	.89–.91
Copal	1.04–1.14
Copper	8.91–8.96
Copper Carbonate, Basic	3.7–4.0
Cork	.24
Corundum	4.0
Cotton (Airdry)	1.47–1.5
Cryolite AlF_33NaF	2.9
Cupric Hydroxid	3.368
“ Oxid (Black)	6.32–6.43
“ Sulphate	3.516
“ Sulphate ($5H_2O$)	2.284
“ Sulphide	3.8–4.16
Cuprous Oxid (Red)	5.75–6.09
Cymene b. p. 175.°–176.°	0.862 (20.°)
Dextrin	1.0384
Diamond	3.49–3.52
Dolomite	2.9

Specific Gravity of Various Materials — Continued

Earth:	
Gravel, dry	1.4
Humus	1.3–1.8
Lean	1.34
Loam	1.6–1.9
Ethane	1.036
Ether (Diethyl)	0.7183 (17.°)
Ethyl Acetate	.8920–.9028
Ethyl Alcohol	.7937 $^{15}_{4}$
Ethylene	.9784
Eucalyptol	.9267 (20.°)
Eugenol	.0630 (18.°)
Ferric Chloride	2.804 (10.8)
“ Hydroxid	3.4–3.9
“ Oxid	5.12–5.24
Ferrous Carbonate	3.70–3.87
“ Sulphate	1.86–1.90
“ Sulphide	4.75–5.04
Flax (airdry)	1.5
Fish Oil	0.920–0.928
Formaldehyde (–20.°)	.8153
Formic Acid	1.219–25°
“ “	1.244–0°
Fumaric Acid	1.625
Furfural	1.1594 $^{20}_{4}$
Gasoline (b. p. 70°.–90.°)	.66–.69
Gas Carbon	1.88
Glass:	
Window	2.4–2.6
Mirror	2.45–2.72
Crystal	2.95
Flint	3.0–5.9
Glue	1.27
Gneiss	2.4–2.7
Granite	2.51–3.05
Graphite (Natural)	2.17–2.32
“ (Artificial)	2.10–2.25
Gum Arabic	1.31–1.45
Guttapercha	.981
Gypsum	2.32
Hemp (Air-dry)	1.5
Hornblende	3.0
Hydriodic Acid	4.3737A
Hydrobromic Acid	1.278A
Hydrochloric Acid	1.195 (8°)
Hydrocyanic Acid	.697 (18.°)
Hydrofluoric Acid	.9879 (15.°)
Hydrogen	.06949
Hydrogen-peroxid	1.4584 (0.°)
Hydrogen-sulphide	.9–1.1895
Hydroquinone	1.326
India Rubber	.93
Indigo	1.35
Iodic Acid	4.629 (0.°)
Iodine	4.948 (17.°)
Iodoform	4.09
Iron (pure)	7.85–7.88
“ (gray pig)	7.03–7.13
“ (white pig)	7.58–7.73
“ (cast)	7.217
“ (wrought)	7.86
“ Disulphide	4.86–5.18
“ Sesquioxid	5.12
Ivory	1.82–1.92
Japan Wax (m. p. 53.5°–54.5°)	.992
Kaolin	2.2
Lactic Acid	1.2485
Lard (m. p. 41.5–42.C.)	.92–.94
Lava	2.00–3.00
Lead (milled sheet)	11.42
“ (wire)	11.28
“ Acetate. $3H_2O$	2.50
“ Carbonate	6.43
“ “ , Basic	6.323–6.492
“ Chloride	5.8
“ Chromate	6.123 (15.°)
“ Hydroxid ($3PbOH_2O$)	7.592
“ Iodide	6.12
“ Nitrate	4.5
“ Oxid (PbO)	9.2–9.5
“ “ (Pb_3O_4)	9.096 (15.°)°
“ Sulphate	6.23
“ Sulphocyanate	3.82
“ Tungstate	8.235
Leather	.86–1.02
Lime (unslacked)	1.3–1.4
“ (slacked)	2.3–3.2
Limestone	1.86–2.84
Linoleum	1.15–1.3
Linseed Oil (raw)	.93 –.934
“ “ (boiled)	.934–.940
Litharge (natural)	7.83–7.98
“ (artificial)	9.3–9.4
Lithium Carbonate	2.111
“ Chloride	1.998–2.074
Malachite	3.85
Manganese Chloride ($MnCl_2.4H_2O$)	1.913
Manganese Nitrate	1.82
“ Oxid (MnO)	5.09–5.18
“ “ (MnO_2)	5.026
“ “ (Mn_2O_3)	4.325–4.82
“ Sulphate ($MnSO_47H_2O$)	2.092
Marble:	
African	2.8
British	2.71

SPECIFIC GRAVITY OF VARIOUS MATERIALS — Continued

Marble:	
Carrara	2.72
Egyptian, Green	2.67
Florentine	2.52
French	2.65
Marl	1.6–2.5
Masonry:	
Ashlar Granite	2.37
“ Limestone	2.32–2.70
“ Millstone	2.01–2.51
“ Sandstone	2.61
Rubble (dry)	2.21
“ (mortar)	2.42
Meerschaum	.99–1.28
Mercuric Chloride	5.32–5.46
“ Oxid	11.0–11.29
Mercuric Sulphide:	
(HgS black)	7.55–7.70
(HgS red)	8.06–8.12
Mercurous Chloride:	
(Calomel)	6.482–7.18
Methyl Alcohol	.7984 (15.°)
Methyl Ethyl Ether	.7252 (0.°)
Mica	2.65–3.2
Milk (cow's)	1.028–1.035
Milk Sugar	1.525 (20.°)
Molybdic Acid:	
$H_2MoO_4H_2O$	3.124 (15°)
Morphine	1.317–1.326
Mortar (hardened)	1.65
Mutton Suet (m.p.47.° C.)	.92
Napthalene	1.1517 (15.° C.)
Naphthol α	1.224 (4.° C.)
“ β	1.217(4.° C.)
Neatsfoot Oil	.914 (39.°F.)
Nickel (rolled)	8.67
“ (cast)	8.28
Nicotine	1.011 $\frac{20}{4}$
Nitraniline m.	1.43
“ p.	1.424
Oats	.43
Ochre	3.50
Oleic Acid	.8908 (12.° C.)
Oolitic Stones	1.89–2.6
Opal	2.20
Oxalic Acid	1.653 (18.°C.)
Ozone	1.658 (A.)
Palmitic Acid	.8465 (7.6° C.)
Palm Oil (m. p. 30.°C.)	.905
Paper	.70–1.15
Paraffine:	
m. p. 38.–52.°C.	.87–.88
m. p. 52.–56.°C.	.88–.93

Pearls	2.72
Peat	1.2–1.5
Petroleum Ether:	
b. p. 40.–70.°C.	.65–.66
Phenol	1.0597 (33.°C.)
Phosphorus (yellow)	1.8232
“ (red)	2.11
Phthalic Acid	1.585–1.593
“ “ anhydride	1.527 (4.° C.)
Picric Acid	1.813
Pinene	.8587 (20.° C.)
Pitch	1.07–1.10
Plaster of Paris	2.96
Platinum	21.52
Porcelain:	
Berlin	2.29
Meissen	2.49
Sèvres	2.24
China	2.38
Portland Cement	1.25–1.51
Potash	2.10
Potassium	.875 (13°)
“ Bromide	2.756 $\frac{20}{4}$
“ Carbonate	2.29
“ “ $(2H_2O)$	2.043
“ Chlorate	2.344 (17.°)
“ Chloride	1.994 $\frac{15}{4}$
“ Chromate	2.721 (4°)
“ Cyanide	1.52 (16°)
“ Dichromate	2.692 (4°)
“ Ferricyanide	1.8109 (17°)
“ Ferrocyanide	1.8533 (17°)
“ Hydroxid	2.044
“ Iodide	3.043 (24.3°)
“ Nitrate	2.1 (4.°)
“ Permanganate	2.70
“ Sulphate	2.6633 $\frac{20}{4}$
“ “ , Acid	2.245
“ Sulphide K_2S	2.13
“ Sulphocyanate	1.906
“ Tartrate	1.975
Potatoes	1.10
Pumice nat.)	.37–.90
“ (artif.)	2.2–2.5
Pyridin	.9855 (15.°)
Pyrogallol	1.463 (40.°)
Realgar As_2S_2	3.4–3.6
Red Lead	9.07
Rosin	1.07
Ruby	3.95–4.02
Salt (table)	2.15–2.17
Sand (dry)	1.4–1.65
“ (moist)	1.9–2.05
Sandstone	2.2–2.5

SPECIFIC GRAVITY OF VARIOUS MATERIALS — Continued

Sapphire	3.95–4.02
Serpentine	2.4–2.7
Silicon (cryst.)	2.49 (10.°)
" (graphitic)	2.0–2.5
" (amorphous)	2.00
Silk (raw)	1.56
Silver Chloride	5.561
" Cyanide	3.95
" Nitrate	4.352 (19.°)
Slate	2.65–2.7
Snow (loose)	.125
Sodium Acetate	1.4
" Bicarbonate	2.19–2.22
" Bromide	2.95–3.08
" Carbonate (anhyd.)	2.43–2.51
" Carbonate 10 H_2O	1.446 (17.°)
" Chloride	2.1741 ($\frac{20}{4}$)
" Chromate	2.71 (16.°)
" Dichromate	2.52 (16.°)
" Hydroxid	2.13
" Nitrate	2.267 $\frac{20}{4}$
" Nitrite	$2.157^{25°}$
" Oxid	2.805
" Peroxid	2.805
" Phosphate $Na_2HPO_4 12H_2O$	1.5235 (16.°)
" Potassium Tartrate	1.77
" Sulphate (anhyd.)	2.671 $\frac{20}{4}$
" " $10H_2O$	1.492 (20.°)
" Sulphide Na_2S	2.471
" Sulphite $7H_2O$	1.561
" " acid	1.48
" Tartrate	1.794
" Tetraborate (Borax)	$1.694.^{17°}$
" Thiosulphate $5H_2O$	1.729 (17.°)
" Tungstate	3.259 (17.5°)
Spathic Iron Ore	3.7–3.9
Stannous Chloride $2H_2O$	2.71 (15.5°)
Starch	1.53–1.56
Stearic Acid	.8428 $\frac{80}{4}$
Stearin	.9245 (65.°)
Steel	7.6–7.8
Strontium Chlorate	3.152
Strontium Nitrate	2.24–2.98
Sugar (cane)	1.588 (20.) °
Sulphur nat.	2.07
" amorph. soft	1.9556 (0.°)
" plastic Sγ	1.92
" monoclinic Sβ	1.958
" rhombic Sα	2.05–2.07 (0°)
Sulphur Dioxid	2.2639
Sulphuric Acid H_2SO_4	1.8342 $\frac{18}{4}$
Syenite	2.6–2.8
Talc	2.7
Tartaric Acid	1.666–1.764
Terpineol	.9357 (20.°)
Thymol (3:2:1)	.9941 (0.°)
Titanium Oxid TiO_2	3.75–4.25
Toluene	.866 $\frac{20}{4}$
Toluidine	.998–1.046
Tungsten Oxid WO_2: (brown)	12.11
Tungsten Oxid WO_3: (yellow)	7.16
Urea	1.323
Uric Acid	1.855–1.893
Verdigris	1.9
Wax, Bees:	
Yellow m.p. 62.–62.5. °C	.96–.965
White m. p. 63.–63.5°C.	.96–.969
Wax, Japan: (m. p. 53.5°–54.5°)	.992
Wheat	.7–.8
Wood (see table on page 351).	
Wool (sheep) air-dry	1.32
Xylene o	.8932 (0.°)
" m	.866 $\frac{20}{4}$
" p	.8801 (0.°)
Zinc Acetate	1.84
" Blende ZnS	4.03–4.07
" Carbonate	4.42–4.45
" Chloride	2.91 $\frac{25}{4}$
" Oxid	5.78
" Sulphate anhyd.	3.6235 (15.°)
" " $7H_2O$	1.964
" Sulphide	3.98

(All temperatures, unless otherwise noted, are given in Centigrade degrees.)

Specific Gravity of the Elements

Aluminium	2.60
Antimony	6.62
Argon	1.379 (Air–I)
Arsenic	5.73
Barium	3.75
Bismuth	9.80
Boron	2.50
Bromine	3.15 (Air–I)
Cadmium	8.64
Caesium	1.88
Calcium	8.64
Carbon	2.17 3.53
Cerium	6.68
Chlorine	2.49 (Air–I)
Chromium	6.50
Cobalt	8.60
Columbium (Niobium)	7.20
Copper	8.933
Erbium	4.77
Fluorine	1.26 (Air–I)
Gadolinium	1.31
Gallium	5.95
Germanium	5.469
Glucinum (Beryllium)	1.93
Gold	19.32
Helium	.1363 (Air–I)
Hydrogen	.0696 (Air–I)
Indium	7.12
Iodine	4.943
Iridium	22.42
Iron	7.86
Krypton	2.818 (Air–I)
Lanthanum	6.1545
Lead	11.37
Lithium	.59
Magnesium	1.74
Manganese	7.39
Mercury	13.55
Molybdenum	8.60
Neodymium	6.956
Neon	.674 (Air–I)
Nickel	8.90
Nitrogen	.96737
Osmium	22.48
Oxygen	1.10535(Air–I)
Palladium	11.40
Phosphorus:	
(White)	1.83
(Red)	2.20
Platinum	21.50
Potassium	.87
Praseodymium	6.4754
Radium	
Rhodium	12.10
Rubidium	1.52
Ruthenium	12.26
Samarium	7.7–7.8
Scandium	
Selenium	4.8
Silicon:	
(Cryst.)	2.39
(Graphitic)	2.00
(Amorph.)	2.35
Silver	10.50
Sodium	.978
Strontium	2.54
Sulphur	2.07
Tantalum	10.4
Tellurium	6.25
Terbium	
Thallium	11.85
Thorium	11.00
Thulium	
Tin	7.29
Titanium	3.543
Tungsten:	
(Wolframium)	19.1
Uranium	18.7
Vanadium	5.50
Xenon	4.422 (Air–I)
Ytterbium	
Yttrium	3.80
Zinc	7.25
Zirconium	4.15

Pounds of Oil Required for Grinding 100 Pounds Various Dry Pigments into Average Pastes [1]

Asbestine	32
Barytes (Nat.)	9
Black, Bone	50
Black, Drop	50
Black, Hydro Gas Carbon	88
Black, Lamp	78
Blanc Fixe	25
Blue, Chinese or Prussian	62
Blue, Ultramarine	28
Brown, Mineral	24
Brown, Vandyke	58
China Clay	28
Dutch Pink (Quercitron Lake)	28
Graphite (Plumbago), 90%	48
Green, Pure, Light, Chrome	21
Green, Pure, Dark, Chrome	28

Green, 25% Color, Light Chrome	18	Sienna, Raw Italian	52
Green, 25% Color, Dark Chrome	20	Silex	24
Green Earth (Terra Verte)	32	Umber, Burnt American	36
Green, American, Paris	23	Umber, Raw American	38
Green, English Paris	20	Umber, Burnt Turkey	47
Green, Ultramarine	28	Umber, Raw Turkey	48
Gypsum	22	Vermilion, American (Chrome Red)	18
Lithopone	30–25	Vermilion, English (Mercury)	14
Ochre (American)	28	White Lead (Basic Carbonate)	10
Ochre (French)	28	White Lead (Basic Sulphate)	11
Ochre, Golden (Pure)	30	White, Paris (Whiting)	20
Red, Indian (Pure 98%)	20	Yellow, Lemon, Chrome	28
Red, Tuscan	29	Yellow, Med., Chrome	30
Red, Venetian	23	Yellow, Orange, Chrome	20
Red Iron Oxid, Pure	28	Yellow, Dk. Orange, Chrome	18
Red Lead	10	Zinc Lead	12
Sienna, Raw American	45	Zinc Oxid (American), ordinary	18
Sienna, Burnt Italian	45	Zinc Oxid (White Seal)	20

[1] These figures are approximately correct. For instance, lamp black is given as 78 pounds. There are, however, some lampblacks which require as much as 100 pounds, and others which require as low as 70 pounds, but 78 pounds is the exact amount for commercially pure lampblack. This figure means that 100 pounds of lampblack will require 78 pounds (about 10 gallons) of oil to make a stiff paste.

Specific Gravity of Various Woods

	Air dry	Fresh
Acacia	.58– .85	.75–1.00
Alder	.42– .68	.63–1.01
Apple	.66– .84	.95–1.26
Ash	.57– .94	.70–1.04
Birch	.51– .77	.80–1.09
Box	.91–1.16	1.20–1.26
Cedar	.57 ...	....
Cherry	.76– .84	1.05–1.18
Ebony	1.26 ...	....
Elm	.56– .82	.78–1.18
Fir	.37– .75	.77–1.23
Mahogany	.56–1.06	....
Maple	.53– .81	.83–1.05
Mountain Ash	.69– .89	.87–1.13
Oak	.69–1.03	.93–1.28
Pear	.61– .73	.96–1.07
Pine	.35– .60	.40–1.07
Plum	.68– .90	.87–1.17
Poplar	.39– .59	.61–1.07
Willow	.49– .59	.79 ...

Table Showing the Comparison of the Readings of Thermometers

Celsius, or Centigrade (C). Réaumur (R). Fahrenheit (F).

C	R	F	C	R	F
− 30	− 24.0	− 22.0	23	18.4	73.4
− 25	− 20.0	− 13.0	24	19.2	75.2
− 20	− 16.0	− 4.0	25	20.0	77.0
− 15	− 12.0	+ 5.0	26	20.8	78.8
− 10	− 8.0	14.0	27	21.6	80.6
− 5	− 4.0	23.0	28	22.4	82.4
− 4	− 3.2	24.8	29	23.2	84.2
− 3	− 2.4	26.6	30	24.0	86.0
− 2	− 1.6	28.4	31	24.8	87.8
− 1	− 0.8	30.2	32	25.6	89.6
			33	26.4	91.4
Freezing point of water.			34	27.2	93.2
			35	28.0	95.0
0	0.0	32.0	36	28.8	96.8
1	0.8	33.8	37	29.6	98.6
2	1.6	35.6	38	30.4	100.4
3	2.4	37.4	39	31.2	102.2
4	3.2	39.2	40	32.0	104.0
5	4.0	41.0	41	32.8	105.8
6	4.8	42.8	42	33.6	107.6
7	5.6	44.6	43	34.4	109.4
8	6.4	46.4	44	35.2	111.2
9	7.2	48.2	45	36.0	113.0
10	8.0	50.0	50	40.0	122.0
11	8.8	51.8	55	44.0	131.0
12	9.6	53.6	60	48.0	140.0
13	10.4	55.4	65	52.0	149.0
14	11.2	57.2	70	56.0	158.0
15	12.0	59.0	75	60.0	167.0
16	12.8	60.8	80	64.0	176.0
17	13.6	62.6	85	68.0	185.0
18	14.4	64.4	90	72.0	194.0
19	15.2	66.2	95	76.0	203.0
20	16.0	68.0	100	80.0	212.0
21	16.8	69.8			
22	17.6	71.6	Boiling point of water.		

Readings on one scale can be changed into another by the following formulæ, in which t° indicates degrees of temperature:

Réau. to Fahr.

$$\frac{9}{4}t^\circ\ \mathrm{R} + 32^\circ = t^\circ\ \mathrm{F}$$

Cent. to Fahr.

$$\frac{9}{5}t^\circ\ \mathrm{C} + 32^\circ = t^\circ\ \mathrm{F}$$

Fahr. to Cent.

$$\frac{5}{9}\left(t^\circ\ \mathrm{F} - 32^\circ\right) = t^\circ\ \mathrm{C}$$

Réau. to Cent.

$$\frac{5}{4}t^\circ\ \mathrm{R} = t^\circ\ \mathrm{C}$$

Cent. to Réau.

$$\frac{4}{5}t^\circ\ \mathrm{C} = t^\circ\ \mathrm{R}$$

Fahr. to Réau.

$$\frac{4}{9}\left(t^\circ\ \mathrm{F} - 32\right) = t^\circ\ \mathrm{R}$$

International Atomic Weights. 1913

		o = 16
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58–97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton(radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16.00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium(Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

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