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American Leather Chemists Association

INDEX TO VOLUME V, 1910

In this index (P) indicates a patent, and (A) an abstracted article.

INDEX OF AUTHORS NAMES

In the index of names numbers without titles refer to pages on which the name appears in discussions, etc.

INDEX OF SUBJECTS

ARTICLES FROM OTHER JOURNALS

(Numbers without titles refer to abstracted articles.)

Journal of the

American Leather Chemists Association

Vol. V JANUARY, 1910 No. 1

W. H. TEAS . . . . Editor and Manager

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The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL . . Past Presidents

OFFICERS, 1909-'10

PRESIDENT—H. T. WILSON, Dubois, Pa.

VICE-PRESIDENT—J. H. RUSSELL, San Francisco, Cal.

SECRETARY-TREASURER—H. C. REED, Stamford, Conn.

COUNCIL—G. A. KERR, Lynchburg, Va.
F. H. SMALL, Worcester, Mass.
R. W. GRIFFITH, New York.
W. K. ALSOP, Ridgway, Pa.

ELECTIONS

The following members have been elected to membership in the Association:

ACTIVE

Clarence B. Kinney, 582 Jackson St., Milwaukee, Wis.
Paul A. Eston, rear 208 Summer St., Boston, Mass.

ASSOCIATE

Neale Ransom, Court House, Jersey City, N. J.
V. N. Hamann, Treas., The Roessler & Hasslacher Chemical Co., 100 William St., New York City.
Theodore Zschetsche, Sheboygan, Wis.
Sedgwick Kistler, Lock Haven, Penna.
Henry W. Healy, 47 John St., New York City.
Henry Chappell, 784 Arcade, Cleveland, Ohio.

DEATHS

Mr. Henry Ries, of the Stamford Mfg. Co., died suddenly on December 15, 1909.

CHANGES OF ADDRESS

Karl Schorlemmer to Sebastian-Munster Str. 28, Worms a Rhine, Germany.

J. L. van Gyn to 176 Tower Bridge Road, London, S. E., England.

M. E. Mason to 541 Orleans St., Chicago, Ill

THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

SIXTH ANNUAL MEETING.

The Sixth Annual Meeting of the Association was held in Washington on December 2nd, 3rd and 4th, sessions being held at the Hotel Raleigh.

Among those present were: Messrs.

Wilson
Shields
Alsop
Norris
Carr
Vogel
Eachus
Procter
Veitch
Saxe
Mardick
Smoot, Sr.
Haley
Beardmore
Chappel
Hall
Smoot, Jr.
Reed
Small
Rogers
Hart
White
Morrison
Stockberger
Healey
Gensemer
Prosser
Cover
Heald
Bye
Kerr
Adams
Skiddy
Wilson
Speh
Oberfell
Griffith
Wiley
Levi
Teas
Evans
Wallin
Kullman
Stevens
Sadtler
Randall
Greene
Rooney
Southard

The first session was called to order at 10.30 a. m. on Thursday, December 2nd, by President Wilson, who immediately delivered his annual address.

The report of the Secretary and Treasurer was then presented, and passed to an Auditing Committee.

A preliminary report on the "Ingredients of Tanning Materials" was then made verbally by Mr. Small, and a short discussion followed.

Mr. Alsop then presented the report of the committee on

"Determining the Acidity in Tanning Liquors," and the discussion of this report was postponed in order that the meeting might be addressed by Dr. H. W. Wiley, of the United States Department of Agriculture.

After Dr. Wiley's address, the meeting adjourned until 2 p. m.

SECOND SESSION—THURSDAY P. M.

The meeting was called to order at 2.10 p. m., and Mr. Fred A. Vogel presented a paper on "English Methods of Tanning."

When discussion of this paper was concluded, Mr. C. A. Morrison presented a paper on "Extract Tannage," which was followed by a paper on "The Future of Heavy Leather," presented by Mr. Oma Carr.

The discussion on the report of the committee on the "Determination of Acidity in Tanning Liquors" was then resumed, and incidentally the effect of inorganic salts on leather in process of tanning was discussed.

The matter of the establishment of a research laboratory was also discussed, and a motion to adjourn until Friday morning was then carried.

THIRD SESSION—FRIDAY A. M.

The meeting was called to order at 10.45 a. m., and after announcement as to the time and place of the annual dinner had been made, the meeting was addressed by Mr. S. S. Sadtler on matters connected with chrome tanning.

Mr. Geo. A. Kerr then presented his report of the committee on "The Color Valuation of Tanning Materials."

When discussion of this paper was concluded, Mr. Veitch presented his report of the committee on "Leather Analysis."

The consideration of this paper led to a discussion as to the status of extracts made from waste sulphite pulp mill liquor, and to the question as to the proper definition of tannin.

The meeting then adjourned until 2 p. m.

FOURTH SESSION—FRIDAY P. M.

The meeting was called to order at 2.20 p. m., when Mr. R. W. Griffith presented a paper on "The Principles of Liming."

After the discussion started by this paper had been concluded, Mr. Procter read a paper on "The Bleaching of Leather," and on the conclusion of this discussion, Dr. W. W. Stockberger, of the United States Department of Agriculture, addressed the meeting on "The Production of New Tanning Materials in the United States."

The meeting then adjourned until Saturday morning.

FIFTH SESSION—SATURDAY A. M.

The meeting was called to order at 10.45 a. m., and was immediately addressed by Mr. J. E. Stevens on the subject of "The Development of the Quebracho Industry."

Mr. Small then presented his report of the committee on "Filtration."

After considerable discussion of this report, Mr. White opened up the matter of the "Analysis of Sumac."

The meeting then adjourned until Saturday afternoon.

SIXTH SESSION—SATURDAY P. M.

The sixth and last session was an executive session, and was called to order at 2.15 p. m.

The election of two new members of the Council resulted in Messrs. Alsop and Griffith being named as the new members

The proposed change in the by-laws, which read as follows:

"Any proposal to change or add to existing methods must be presented in writing at an annual meeting and voted upon by a mail vote not earlier than two months prior to the succeeding meeting. No change in any method shall become operative unless approved by a majority of the Council and agreed to by a two-thirds vote of all the Active Members of the Association *voting*. The result of said vote shall be announced by the Secretary at the annual meeting," was reported as having been carried as a result of the mail vote.

The proposed change in the method of extraction of crude materials, which was proposed as an amendment to Section 4, *failed* to pass, and this proposed change read as follows:

"Fresh Materials, Woods, Barks and Also Spent Materials. 500 cc. of extractive solution shall be collected by outside condensation in approximately two hours, and the extraction continued with 500 cc. for fourteen hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give by condensation approximately 500 cc. in one and one-half hours."

The proposed change in the analysis of liquors was adopted by mail vote, and the section now reads as follows:

"To be determined by shaking 200 cc. of solution with an amount of wet chromed hide-powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide-powder shown in the following tables:

Tannin range per 100 cc.	Dry hide-powder per 200 cc.
.35—.45 gram	9—11 grams
.25—.35 gram	6.5—9 grams
.15—.25 gram	4—6.5 grams
.00—.15 gram	0—4 grams

It was announced that the provisional method for sampling tanning materials had been made official by reason of the mail vote, and the provisional method for leather analysis was also made official.

A discussion of the present by-laws with respect to the provisions for adopting changes in the Official Method, and also as to the method of election of officers, then took place.

A motion to make the method of color valuation as suggested by the chairman of that committee, a provisional method, was offered and carried.

A proposed addition to the method for the analysis of crude materials, covering the analysis of sumac and kindred materials, was also offered.

These matters were referred to the Council for their action.

A further discussion on the form of reporting tanning matter in tannin solutions took place.

After some discussion on the subject of a research laboratory, a motion was offered to the effect that the Association place itself on record as in favor of the foundation of an institution of this nature, and that the National Tanners' Association should be assured of our interest in the matter, and of our willingness to co-operate.

It was suggested by Mr. Veitch that it would be wise to drop the second decimal place in analysis reports. The suggestion was referred to the Council.

A report of the Editor of the JOURNAL was read, and after votes of thanks had been passed to President Wilson and to Mr. Wallin for their able efforts in connection with the Convention arrangements, the Convention adjourned *sine die.*

PRESIDENT'S ADDRESS.

By H. T. Wilson.

Gentlemen: We take pleasure in welcoming you to the Sixth Annual Convention of the American Leather Chemists Association.

The past work and achievements of this Association have been fully reviewed and expatiated upon in former addresses given at the annual gatherings, and it is not proposed, in these brief remarks to attempt any lengthy review of the past, but rather to speak of the possible future of the Association as a whole, and of its relation to the tanning trade in general throughout the country.

Six years ago this November past, some seven or eight men had the temerity, we might say, to closet themselves in a small room in this hotel, with the avowed purpose of organizing and laying the foundation of an independent Association, the purposes of which were to be, the standardization of methods of tannin analysis, and research into new methods and their application to tannery practice. The degree to which these purposes have been realized can best be appreciated by reviewing the records of the Association for the past six years.

Probably only those who were present at the ceremony of laying the "Corner Stone" of this organization, fully realize the nerve required to have taken such a step, since the opposition to such a move was very strong, even some of the older leather chemists prophesying the speedy and complete failure of the undertaking. The circumstances leading up to this action of the founders of the Association have been so fully gone over in the past, that they will not even be alluded to in these remarks, but the results of the untiring labor of these few men are best illustrated in the present prosperous condition of the Association, both numerically and financially; which condition could not have existed without the constant effort of those who took upon themselves the burden of generating and maintaining the society which we now have. At the time of its organization, each man present was necessarily elected to hold some official position in the Association, and still to-day, the active management of the affairs lies largely in the hands of the original seven or eight. (This will be alluded to later in these remarks.)

The growth of the Association during the first five years has been somewhat phenomenal, from the point of view of membership, surpassing the best hopes of those who were active in its formation, but during the past year the enrollment has been practically at a standstill, even showing a slight falling off in the associate membership. The enthusiasm which always attends any good undertaking is usually followed by a state of partial quietude, during which the forces arm themselves for a steady and persistent crusade for the realization of the original idea. The workings of this Association are probably no exception to this rule.

Has this Association grown too rapidly during its formative period to assure stability? We say, "No." Will it continue to grow in membership and in efficiency, during the period of apparent relaxation? We say, "Yes;" for the progress from this time on, is to excell in real worth, anything that has gone before. The fulfillment of this prophecy lies in your hands, and it means, in plain English, "hustle."

As we see it, the future success of the Association lies largely in the hands of two bodies of men, namely:—the younger members, and the tanning trade in general. A very large majority of the work which has been done in the past, and which is still being done, has been accomplished by what might be termed the "Old Guard," and the representation at the annual meetings, has been composed largely of this same body of men. This condition cannot continue to exist indefinitely, and unless the younger members begin to take a more active part in the shaping of the affairs of the Association, it will eventually go into decadence. There is no real cause, however, for portraying such a gloomy outlook. The men who have joined the ranks since the organization of the society six years ago, are better fitted to assume its responsibilities, than were those who took it upon themselves to form such an organization, since they have the full benefit of the past labor and experience of the older members. To the younger members, we would say, "get yourselves ready for the time when the affairs of the Association will be in your hands."

It is fast becoming necessary that this matter should receive serious consideration, for it must be remembered that a large majority of the men who have fostered the Association through its formative period, and have carried its burdens up to the present time, have now entered into fields of greater responsibilities, which preclude the possibility of their devoting so much time to the guiding of its affairs, and, moreover, they deserve the right to be relieved of the duties which have held them since the formation of the society. The way to educate the newer members into assuming the future responsibilities of the Assiociation, is to begin now to work some new material into the official positions of the society, and increase this from year to year.

The Association has a very large associate membership composed largely of tanners and extract manufacturers. Very few of these ever attend the conventions, simply because they look upon these gatherings as strictly scientific affairs, which would be very dry and uninteresting to them. This branch of our memberbership is in a position to do a great amount of good for the Association directly, and for themselves indirectly, and with this end in view, the programs from year to year, include more and more of the non-technical side of the leather industry, which is given in addresses by representative men, whose labor lies in the practical, rather than in the theoretical field. It has been wisely suggested that a convention which would be composed of both branches of the Association, would be the ideal one, as separate sessions could be arranged for the discussion of both the theoretical and applied science in the manufacture of leather. We leave these matters for your earnest consideration.

We wish, now, to make a few remarks to those who employ, or are going to employ, leather-trades chemists.

The fact cannot be disputed, that leather chemistry has become a fixture in this country, as it is in Europe to-day. Changes are constantly taking place in the methods of tanning, as a result of the more advanced ideas, and the necessary incorporation of new tanning materials into the process of making leather. A few years hence, and very few at that, the bark stack, which has been the heart of the tannery, will be a memory, and will be seen only in photographs. Something must take its place, and who is better fitted than the technical man, in acting as a guide in making those changes which we all admit must take place?

The world's price of hides is very likely to be higher than it ever was before, in spite of tariff revision. The great cattle ranges of Texas and the great Southwest, are being converted into cotton plantations, and smaller farms, which yield quicker and more remunerative returns. The romantic cow boy is slowly disappearing from these sections. These facts most probably mean a curtailment of the domestic supply of raw material, which deficit must be met by importations from foreign countries, and from the inexhaustible Pampas of our sister Republics to the South. The world must continue to have leather, and more of it each year, as the population and new demands increase, but, owing to the ever increasing cost of all raw materials, ways and means must be found whereby leather, good leather, may be produced at a minimum cost.

The assistance of the chemist to the tanner, in working out such problems as are confronting him to-day, in this country, and which are to be more manifest in the future, has long since been recognized by the tanners of European countries. There, the tanners have, long since, been up against the same proposition which confronts us in this country to-day. The failure of the bark supply has been met by the introduction of other tanning materials, and to-day the bark supply is no longer thought of as an absolute factor in the tanning industry, but the production of leather goes on just the same. These changes were not brought about in a day, nor in a year, nor were they brought about without the aid of the chemist's researches into the unknown fields of new tanning materials, and their proper application to the manufacture of leather, but the present excellent quality of the finished product, speaks well for the researches and changes which have been made.

Probably within the memory of most of us, the mere mention of the words "Tanning Extract," was sufficient to bring a very serious look upon the face of the average American tanner. He did not want any such material; bark was good enough for him; it was cheap, and he had plenty of it. There was no apparent concern for the future. To-day, however, if the tank car of tanning extract does not arrive on schedule time, the telegraph company is pretty sure of a fee for a rush message to the extract manufacturer, or dealer. This condition shows the trend of the times.

With the aid of the Government in forestry control, and the more sane methods of individual concerns, the domestic supply of a certain class of tanning material should last indefinitely. However, foreign materials are being imported more and more each year, and it is impossible to prophesy what the future tannages of this country may be. Vegetable tannage is undergoing rapid changes, and mineral tannage is advancing to a more satisfactory state of perfection, so it is not out of the way to prophesy that a combination of the two may be the ultimate result,—at least for certain classes of leather. These problems must be worked out through the co-operation of the tanner and the tannery chemist, it cannot be done hap-hazard.

Of course, a chemist makes mistakes just the same as anyone does. Theories are not always subtantiated by the practical results, but this is only an incentive for further investigation into the causes of the failure of these theories to work out in practice. We beg to disagree with a certain prominent man, and a chemist at that, who, in writing for one of the trade papers, made the statement that he would as soon think of turning a bull loose in a china closet, as to turn a chemist loose in a tannery. This is, to say the least, placing very poor value upon the balance and judgment of the average tannery chemist. It has been our experience that the majority of works chemists exhibit a very conservative state of mind, for they realize only too well, the losses which may be entailed by the misapplication or the failure of the idea which they wish to work out to a conclusion. Is it necessary for a chemist to be an expert in the manipulation of a beamster's knife, in order to be able to judge whether a skin has been properly fleshed, or not? Must a chemist serve an apprenticeship in all of the mechanical details of a tannery, so that he may rightly judge of and make suggestions in regard to the stock in process? We think not. Is it necessary for an art critic to be a great master, that he may be a judge of the perfection of a painting? We have known those who could not paint a stroke, and yet could distinguish the finest shades of color, and point out the defects in the finished work. We do not fail to realize the value of a knowledge of the mechanical side of work in question, but we cannot condemn the average chemist's endeavors, because he had not the opportunity to be a so-called "born tanner."

The thought has been given out that our Association has to deal only with the standardization of methods of analysis, precluding any investigation into the methods of manufacture. This idea was all right at the time at which it was given, but it is limiting the field for to-day. The majority of the methods of analysis are sufficiently perfect for all practical purposes, unless we can find something radically different, and until that time, further changing from year to year, seems unnecessary. It appears to us that our field should be broadened so as to include the investigation into the methods of manufacture. If the natural evolution of the chemist is not into the practical control of the business in which he is engaged, then his field is certainly very limited and unsatisfactory. The management of the great steel industries of the country is, in a large measure, in the hands of men who have had a technical training, and some day the same will be true of all of the great industries of the country, which naturally includes that of leather manufacture.

It is probably not realized by all, that the manufacture of leather stands in third place among the vast enterprises of this country, and when we take into consideration the diversified uses to which leather is put, and the enormous industries which are engaged in converting the raw material into finished products, we can gain some idea of the magnitude of the business to which we are devoting our time and energy, that it may be brought to its highest standard of perfection.

The trend of the times is toward centralization of all great industries in the commercial and shipping centers of the world. As the older tanneries move out of what, at one time, was the "tall timber," others will be constructed along more modern and scientific lines, at the great centers of supply and demand. When this time comes, the services of the technical man will be more than ever necessary, and more in demand.

Now is the time for you to get into line and give your full and hearty support to the organization whose object is, to enable you to manufacture your leather better, and at less cost. Encourage your chemists in attending the annual meetings of the Association, and get yourself sufficiently interested to come and take part in the proceedings. Some of the active members of the Association have not attended the yearly sessions for many years, simply because their employers have not seen fit to advance the necessary funds for the trip, which, in reality, would bring them ample returns, since the services of the chemist would be more efficient were he at liberty to mingle with his colleagues, and exchange ideas with them.

What we need in this country probably as much as any other one thing connected with the tanning industry, is a thoroughly equipped and independent tanning school, which shall be the counterpart of those in Europe. This, we trust, will be the natural development, but it can never be made possible without the sanction and support of the tanners, and others in the leather industry, throughout the country. As it is to-day, the works chemist has his time so completely taken up by the necessary work of the day, that it is impossible for him to even think of delving into the unsolved problems of tanning chemistry. This is, or should be, the work of those who are in a position to devote their entire time and attention to research into the many problems which we are now striving to work out in a practical way. In the future, many of the methods which are being pursued at the present time, will seem as ridiculous to us, as many of the past practices appear to us to-day. We feel vexed at ourselves sometimes, because we have not previously thought of certain points which are suggested to us by others. This is perfectly natural. One man cannot think of, and apply all of the ideas which are evolved in the pursuance of any great business. It requires the interchange of ideas of many men to bring perfection to the object sought. In the business in which we are all deeply engaged, we cannot imagine any better combination of forces than the practical man in the business, and his technical assistant. The former may have ideas which the latter may work out to a practical application, and the latter may devise new ways and means of more economical and successful operation, which had never occurred to the former. Since, as said before, the works chemist cannot devote a large part of his time to the investigation of new problems, both he and his employer would be greatly benefited by the researches of capable men, who might have the time and opportunity to pursue any new line of thought to a practical conclusion. The field of investigation is sufficiently broad.

Before closing these remarks, we wish to speak of one special factor in our Association, which is probably accomplishing more in bringing our work before the public, than any other one thing, and that is the JOURNAL. Two years after the organization of the society, the Council, after much thought and debate, decided that such an organization as we have, should and could support a monthly publication. This step was almost as bold as that of two years previous, when the Association itself was formed, and was not taken without a degree of fear and trembling. The success of the JOURNAL, however, under the management of its able editor, is sufficient proof of the wisdom of the undertaking. Now that success has been attained, it must necessarily be maintained in order to uphold the dignity of the JOURNAL, and the Association. As stated before in these remarks, a very large majority of the membership of the Association is composed of men whose time is almost completely taken up by the daily routine. One cannot sit down and write a scientific discourse on a subject which he has not had the time to fully investigate, but is it necessary that our JOURNAL should be strictly technical? In an organization composed of as many members as the one which we have, there should be many who have the gift of writing on topics of general interest, both to ourselves, and to the practical men. We often see such articles in the trade papers of the country, why should they not appear in the JOURNAL? Since we are not fortunate enough to have a number of leather trade schools, from which to draw a constant supply of technical material, it appears to us that a moderate amount of non-technical matter would be no detriment to the standing of the JOURNAL, and we are even inclined to think that its circulation might be increased thereby. It has been suggested to us that it might be advisable to inaugurate a department of notes and queries. A chemist who is working daily in a laboratory, is constantly encountering small difficulties, and making new observations. Although these items might be small, and probably of no great value, they would still open up a field of more intimate interchange of ideas in regard to the working details of the various laboratories throughout the trade.

We must all make a more determined effort to do our share in keeping the JOURNAL up to its high standard. To some, the task of writing is easy; to others it is a very difficult one, but, nevertheless, a large majority of the membership should be able to bring forward some topic of interest, or some matter of research, during the period of a year. If this were done it would very greatly lighten the burden of those who are responsible for the monthly appearance of the JOURNAL.

In closing these remarks, we would say that our efforts toward an international unification of the methods of tannin analysis have not been without reward. Properly conducted, the present scheme is sufficiently accurate for control work and commercial purposes. Until further research reveals more accurate and rapid methods of procedure, we may devote more time to the investigation and perfecting of those materials which enter into the manufacture of leather, their methods of application, and a study of the ultimate results.

The continued success of our Association hinges upon the loyal support of the entire active and associate membership, and that of the tanning and allied trades in general.

The final success of any undertaking is simply a matter of individual patience and endeavor. "Genius is only infinite patience," so hang onto your patience.

ADDRESS OF DR. H. W. WILEY.

Mr. Chairman and Members of the Convention: I suppose I wear out about as much leather as any man here and have a practical interest in it. I have noticed in the last few years that I have to send my shoes to be half-soled more frequently than I did in earlier life. That would be an indication that the leather was not as good as it used to be if I did not remember at the same time that I have increased very much in weight in these last years and I have tried not to be less on my feet; so from that indication I think it can be explained that perhaps the sole leather is as good as it used to be. As we grow older we always incline, I think, to believe things are not like they used to be. The candy does not taste as sweet as it did 40 or 50 years ago, and pies are not so attractive. I don't go so often in unsuspected moments to the sugar bowl as I did in former years, and there are a lot of things that have changed. Leather perhaps is one of the things that have changed. We all remember the old Latin adage with regard to the change of the times and that men change with them; and if the change is a progressive one, if it means better leather and cheaper leather, more enduring, why we ought not to decry change. At the present time the United States is receiving hides from foreign countries free of duty, and that ought to increase our leather supply, make it more abundant and presumably lower in price to the consumer. I think that was one of the chief objects in putting hides on the free list,—to benefit the consuming public. Let us hope that advantage will not be taken of the lower priced hides by the manufacturers and others, as was the case in the increased tax put upon lemons of half a cent a pound, and as soon as the bill was signed the Southern Pacific Railway increased the tariff on lemons from Southern California half a cent a pound, so that the only beneficiary of the duty on lemons is the Southern Pacific Railway Company. Now I hope that the manufacturing interests of this country will not pursue a similar course respecting free hides. If shoes are not cheaper than they were last year we are going to repeal that clause next Congress and put the duty back on hides so that we can get some income out of them if we cannot get cheaper shoes. (Laughter.) Of course that is not a chemical question; I suppose that is more of a political opinion.

I have been interested in the work of your Association for many years, not as a practical chemist but because the hide being an agricultural product is naturally a question of solicitude for all persons who are interested in our agricultural interests. The revenue which is derived from the hide is quite an item in the income of the farmer who grows the cattle. Apparently the free hides have not decreased the price of cattle, as I read in the morning paper that prices yesterday in Chicago were the highest ever known; that large herds sold for $9.50 a hundred pounds, and in one instance a particularly fine steer for $10.00 a hundred pounds; so that at least the admission of hides free of duty has not had any apparent influence on the price of cattle on the hoof. If that is the case the farmer has suffered no injury from the change in the tariff, and of course if anybody gets the benefit of the free hides it will be either the consumer or the manufacturer.

The technical questions which you have before you are of a very complex nature. There is no such accuracy possible in the ordinary analyses of a substance like leather which can be attained for instance in a mineral analysis or a metal analysis or in fact of many organic substances which are capable of analytical study with the greatest degree of accuracy. The problem in the study of a piece of leather is a very complicated one. First, the definite chemical compounds of leather cannot be very well separated and estimated as such. We must content ourselves with what we might call "mass analysis;" we can tell how much the piece of leather weighs; we can tell how much tannin a raw hide will absorb; we can determine the total amount of nitrogen in a piece of leather and compute from it the gross amount of nitrogenous substance. Or we can separate the nitrogenous element into two or three different classes by appropriate chemical means and determine about how much of the nitrogen is in this particular compound, how much is in that particular compound. But you cannot separate out of the leather the distinctly nitrogenous tissues and get them by themselves as you could perhaps if it were a sugar element you were looking for, or even a tannin element in the leather. And so with some of the other constituents of the leather the problem is a difficult one. The different results which just have been presented to you are familiar to all of us who have ever worked on problems of this kind in a collaborative way. The data are sometimes of a character which tend to throw discredit upon the science itself, or upon the analyst, but that is not the case at all. It is no discredit in working in this way by new methods and in new ways to reach different results. That has been the story of advance in all science. There never has been an absolute concensus of opinion and an agreement of results in scientific study, and never will be until the field of science is all known, and that never will be. As long as there is anything unknown—and there always will be—there will be differences of results and differences of opinion. Now the object of an association like this is not to make machines out of its members at all; the object is not to confine the members to a particular line independent of their own ability to study and discover, but on the other hand one of the great objects of an association like this is to encourage research in those very unknown fields of which I have spoken. Another object is that when a method of determination has been proved by a majority of the workers as one which is reasonably accurate, then another purpose of this convention and of such an association as this is to have all its members so practice that method that given the same particular sample they may reach agreeing results; and that is a matter of training. A man may be an excellent chemist in one line, in the sense of an analyst, and be a total failure if he should attempt a line with which he is not familiar. We all know that, that the skill is acquired only by practice. The theory is the same; the principle of procedure is the same, but the skill is a matter of individual ability and practice. I could illustrate that, for instance, by surgery. The principles of surgery are well known and established; all surgeons are grounded in the same principles; they know the location of the bones and the arteries and the nerves and all of the various tissues; they know the number of wrappers around the abdomen, for instance, and which one is reached first when the knife is used, and which one is second, so that they can cut into the abdomen with a thorough knowledge of what they are going to meet; but a man might be absolutely perfect in anatomy and physiology and in all the theoretical technique of surgery, and if he had never operated on anyone at all or never used the knife, not one of us would like to submit ourselves to his operative skill. We want a man who has practiced on the abdomens of lots of people who have gone before us before we bare our own bosom to the breeze. (Laughter.) Of course somebody has got to be first, and he has got to operate on some one first, but we don't want to be first in that sense. *There* is one occasion in life where a man does not care to stand first. (Laughter.) One great occulist was complimented on his skill in saving the sight in most desperate cases by his operative skill. "It is wonderful," some one said to him, "how you can take an eye which seems to be gone almost and restore its sight." "Well," he said, "I spoiled a bushel of eyes before I ever learned to save one." (Laughter.) Now that was unfortunate for the people who owned that first bushel!

Now it is an unfortunate thing for the analyst, it is unfortunate for his client, if that is the first one he ever made. I do not care how thoroughly he understands the principles of analytical chemistry, if he has never made an analysis of that kind his client is very apt to be led astray even in the simplest forms of manipulation. And so when you come to a complicated subject like this which we have just heard, and which you will see constantly, we realize how difficult the problem is. At the same time it is not impossible of solution. A long experience, now extending over about 35 years, in analytical examination when I used to work myself, and since in examining the works of others, has shown me that it is possible that great bodies of men by the proper method of practice, even in these complex substances, may reach very agreeing results, but it is only by application and experience that they do so. And that is the great value of a comparison of data such as has been illustrated here since I came in, and with which I have been familiar in association with the official agricultural chemists for some thirteen years. I do not know of any kind of collaborative work which promises so much for the industries which are interested therein as just such gatherings as these; and, as a kind of Nestor amongst you, my advice is, don't get discouraged because you do get at the beginning of these problems such very different results in the examination of these matters.

Now I think it is perfectly certain, gentlemen, that practically we are going to have in this country in the near future—I won't say how near—but it is perfectly certain in the near future we are going to have an extension of the Foods and Drugs Acts to all commerce of an interstate nature, and in the States have police control. There is no reason in the world why the buyer to-day should have to depend upon himself to determine whether or not the object he purchases is what it is represented to be. That is the natural state; that is common law. The common law is "*caveat emptor*"—"let the buyer beware." It is based on the principle that the man who buys has common intelligence and has an opportunity of examining the article which he purchases. Now that is true enough of simple articles, which were the sole articles of commerce when the common law came into existence. For instance, the man who buys wheat or corn or buys a horse even, or a cow,—he is supposed to know something of what he is doing. He examines the article he is to buy and he can tell whether the wheat is weevily or not, full of chaff or not; he can tell whether the horse walks lame or not. He has an opportunity to find out. In those cases the common law is good enough: but suppose a man goes in to buy a diamond ring for his sweetheart: What do we who are not experts know about diamonds? Nothing whatever. They can sell us a piece of paste and both we and our girls will be delighted with it,—(laughter)—because we think it is the real article. Now in all such cases as that—what does the ordinary man know about the character of shoe leather when he goes in to buy a pair of shoes, any more than I do about the character of a diamond? I depend solely upon what my merchant tells me with regard to the shoe, and I have known merchants—and you have too—who sometimes romanced a little with regard to what they had to sell you. I have seen newspaper advertisements offering articles for sale which I thought exaggerated a little bit the excellence of the offered articles. And your tailor will tell you he "will have it done Saturday night without fail," when he has no more notion of doing it than he has of praying to God for grace on the following Sunday. (Laughter.)

Now in the matter of leather I have no doubt that there will be—Why, the food law ought not to have "Food" in it at all. I would take that law and strike out "Food" and substitute "Merchandise of all kinds" and apply it to everything entering into interstate commerce. Already the legal effect of the Food Law is filtering into the common law. I am happy to say I am a farmer now and grow cattle. I have 31 steers, and hope to get a good price for their hides next year when I sell them. And I go to the sales of my neighbors who have stock and everything I want to buy. Being a beginning farmer I have to buy everything. I went the other day to a sale to buy a horse, but I took along a man who knew a great deal more about horses than I did. He has been a buyer and user of horses all his life, while I stopped when I was a boy, I am sorry to say; and a great many other people are sorry I stopped too (laughter) ; but I took him along. I was not willing to trust my judgment of swelled joints and other things horses have sometimes. So he says, "We'll go and look over the horses before the sale begins"—there were lots of other things for sale. We went through the stable where the horses were standing and saw one fine looking horse. I said, "There is a fine looking horse I would like to have." He says, "He *is* a fine looking horse." He slapped him on the rump and the horse straightened up and shied a good ways and then he settled down to rest again. He did that several times. I said, "Why did you do that?" He said, "Did you notice the horse was standing on three legs when we came in?" I said, "I have often noticed horses standing on three legs." He said, "So have I; but they don't stand on the same three all the time. A horse that is sound will stand on three legs and rest and then shift after a while and stand on another three. But," he said, "you noticed that horse stood the same way every time. There is something the matter with that left fore foot." I looked at it and could not see there was anything the matter, but he looked at it and said, "That foot is deformed; it was born with a lame foot." He said, "You don't want to buy that horse." They took him out and he did not limp at all. He walked out. But the moral effect of the Food Law had filtered into that community. It was the first time I ever saw it illustrated. The auctioneer took that horse and said, "Gentlemen, here is a fine horse. He's all right and sound; four years old; but he was born with a deformity of his left fore foot which I want to call your attention to before you bid on it."

Now, wasn't that a fine thing to see? That shows what the people of this country are thinking of the moral aspect of representing things exactly as they are. But it is not every auctioneer or every man who had a horse to sell that would do that sort of thing; and it is not every man who has leather to sell who will tell you if it has any defects; and it is not every storekeeper who has a shoe for sale who will tell you whether it is split leather or not. Now I have no objection to split leather shoes, or anybody else, but if you buy a shoe represented as calf-skin and it is a shaved bull hide, why that is quite a different proposition altogether.

Now that is what is coming, and if you are going to put a weighter into leather so as to make it sell heavier, if it has any useful purpose you cannot be ashamed to tell the customer that it is weighted with glucose or talcum or whatever it might be. You know better than I do what you are likely to find there. If that serves some useful purpose, there is no harm in the world in letting it be known, and if it does not serve a useful purpose there is no reason in the world for doing it except—what? That is, to get a bigger price for the leather than you would otherwise; and that is robbery. Already a bill has been introduced into the last Congress called the Merchandise Marks Bill, modeled on the English bill which forbids the mis-branding or adulteration of any article of commerce whatever passing from one State to the other, applying all the penalties of the Pure Food Act to commerce in general. It may be these Acts will come up singly. There is one before Congress, and it has been for several seasons, on fertilizers. There is another one which has been introduced to prevent interstate commerce in adulterated, misbranded asepticides. It may be there will be one introduced with regard to leather.

Now you will see that you are coming to a study which has great and important ramifications with regard to the public good and public morals, and a study which will result in improvements in the tanning and the operations on leather of all kinds and in its manufacture and sale, so that consequently while the business of the manufacturer and producer will increase in the proper way and not through any misrepresentation or adulteration, and the leather chemists are those who will be called upon to decide those questions in the near future, if-you are not called upon to-day.

I am very pleased, Mr. Chairman, to be with you for a short time to-day, and feel honored by the invitation which you have extended to me, and I hope I have said nothing to offend and something to instruct, or at least something to amuse.

THE FUTURE OF HEAVY LEATHER.

By Oma Carr.

Study of the past and gone facts of an industry are, to those engaged in such industry, always interesting and often instructive. The history of an industry is usually an orderly arrangement of the names of men prominently identified with its development, of the broad changes occurring in its methods and products, and of its financial growth. If the industry be old, if its roster of names be properly impressive, and if its progress to wealth be sufficiently spectacular, its history is interesting. But the measure in which such history may be valuable in contributing to present progress and future development, is the measure in which one generation may know the technical accomplishments of the generations gone before.

In industry, as in government, progress is, in its dominant factors, guided by methods of evolution—the gradual conservative, systematic substitution of the new for the old. Industrial changes, in the main, are the results of insistent and persistent effort over wide fields and broad purposes, operating slowly, overcoming prejudices, breaking the restraints of custom—a ceaseless striking of the balance between technical impulsiveness and enlightened conservatism. At the beginning and the end of an industrial decade we find very dissimilar conditions—study of the intervening years discloses exactly the trend of change which has connected the two. In practically every industry which has drawn upon scientific thought for its technical development, the line of change in method will be, to all intents, steadily consistent with the motives which impel such change. Where the basic motive has been cheapening of production it will be found that change of industrial method has gone hand in hand with the intensity of the motive--rarely has an industry whose existence depended upon cheapening of production failed to find means to sustain itself. Where the dominant motive has been enlargement of field—as in electrical applications—the necessary change of method has been accomplished. We stand amazed by the changes wrought by a single decade in transportation, in communication, in manufacture, in agriculture—and study of each through the years of its growth will show the ceaseless substitution of the new for the old, the struggle for higher efficiencies, the battle for greater markets, the fight for greater volumes. Beneath all lies the foundation motive—the profit.

CHANGE OF HEAVY LEATHER METHODS.

The heavy leather industry has, in its change of methods, followed quite consistently the expected course. In all its industrial phases it has shown the expected adherence to the rule. Its growth from the small unit of production to the great corporation and to combinations of corporations, has not been different in any essential factor from the growth of other industries. To pass from the sole leather tannery making a hundred sides a day and making sixty per cent. gains on green salt hides, to the yard soaking four thousand a day and making eighty per cent. gains, spans hardly more than a single decade; and it may be said in passing that the transition in upper leather has been as striking. Quite aside from the debate as to the comparative profitableness of the small and the large producing units, the fact persists that the trend has been towards the large unit, by extension of small units and by outright creation of large units.

Simultaneous with enlargement of the producing unit there has proceeded a marked change of practice. Without going elaborately into the nature of these changes, it is well to draw attention to the fact that hardly a single technical detail of manufacture remains to-day exactly as it was fifteen, or even ten, years ago. Long liming, bacterial bates, light liquors, natural acidification, layaway filling, dusting, hand cleaning, hand oiling, natural draft drying, have all been, in the main, superseded by more direct, more efficient, more controlable and more profitable processess. On the mechanical side, soak and lime reels, fleshing and unhairing machines, rockers, power bleachers, wheel and drum equipment for filling and oiling, mechanical draft for drying, are some of the dominant additions to the handling and process equipment.

TANNING MATERIAL CHANGES.

Tanning materials employed have changed greatly, particularly in recent years. Founded upon the great forests of hemlock and oak in the Northern, Eastern and Southern Appalachians and the Lake region, recent years have witnessed the heavy leather industry come face to face with exhaustion of such supply—tomorrow, as time runs, the actual tanning material basis of American heavy leather will have been shifted from bark to extract, precisely as the tanning material basis of English heavy leather was shifted a half century ago. While it is manifestly impossible to foretell the far future of our tanning material, it is sufficiently certain that bark will continuously, and more rapidly as time passes, be dropped from the tanner's practice.

INDEPENDENCE OF THE FOREST.

It is through the shift in the tanning material basis of heavy leather that we get our most reliable glimpse into its future. With the tanner's independence of bark comes his independence of location—the tie which has bound him to the forest has been broken. Henceforth the growth of the industry may be consistently along lines of least resistance—it is at last possible to manufacture heavy leather wherever assemblage of its materials and distribution of its product may be accomplished most advantageously.

LOCATION OF PRODUCTION.

Manufacture of heavy leather involves assemblage of hides, tanning material, labor, chemicals, water and fuel; and it involves distribution of leather. So far as the tanner is concerned, distribution of leather means its delivery to the manufacturing consumer. At the present time by far the greater volume of leather is distributed to New England shoe centers—in New England the shoe industry has had its greatest development, being founded upon the large leather output of Pennsylvania and the cultivated manufacturing efficiency of the New England people. To the present time Pennsylvania has offered, through its supply of tanning material and a long experience in production, good conditions for assemblage of the materials of production, and it has kept pace, almost, with the rapid increase of demand from New England. Up to the present time the combination, industrially, of Pennsylvania leather and New England manufacturing and merchandising ability, has been sufficient in strength and volume to hold the business of the United States and to open a measurably satisfactory export business. Within a few years, however, there has come a challenge, modest and moderate but insistent and serious, to the dominance of American markets from New England shoe centers—a challenge from the Mississippi. Measuring this challenge by statistical figures it appears worthy not only of consideration, but likewise worthy of study as to its probable bearing upon the future of the industry—whatever the men of the virile West undertake with seriousness one day makes itself a factor in the scheme of things.

A PROPOSITION.

At this point, and leading to the necessary statistical study, I advance this proposition: During the next fifteen years we may assume the hide supply for light and heavy leathers to come from, approximately, the same sources, and through, approximately, the same channels, as at the present time; that the development of shoe manufacture will follow the growth of population, decreased cost of assemblage and distribution, and increase of manufacturing ability near consumption; and that light and heavy leather production will follow, approximately, the location of new shoe production.

This proposition, of course, must be considered broadly. It is incredible, for instance, that any industry will abandon, precipitately, its long-time abode and seek new fields; or, that new centers of manufacture will develop into full strength and capacity without long periods of competitive struggle with older centers. We will see, during a long period (perhaps always) Brocton and St. Louis shoes selling from the same counters in Pennsylvania and Colorado—such has been, and probably will continue to be, the elasticity of our transportation and salesmanship. We may, however, confidently assert that the basic motive of all commerce —the profit—will stimulate, continuously and effectively, that positive business instinct which creates supply for local demand. If there exists, anywhere, a populative group wherein the consumption of a commodity exceeds the production thereof within the geographic or economic bounds of such group, it is certain that there will arise an effort to bring local production to an equipoised volume with consumption. Such an effort may suffer great losses, encounter enormous obstacles, meet numberless defeats—but it will persist, countering each new difficulty with renewed energy, fighting on until it wins. Give to any locality, consuming more than it makes of a great staple article, an even chance on the essentials of producing that article, and it will proceed, with utter certainty, to satisfy its need for that particular thing.

The question now arises: Is there in the United States a populative group consuming a greater volume of boots and shoes than it produces? Along lines of detail, this question may be answered by saying, several. Approaching the answer along broad lines, it is certain that there exists a great populative group, which has recently become also an economic group, wherein the consumption of shoes far exceeds production.

The student of trade currents has of late detected an insistent challenge to the time-long east-and-west movement of business—there has come, in recent years, a clearly visible current north-and-south, not only on the Atlantic seaboard but west of the Alleghenies throughout the Mississippi Valley, where a half-dozen railway systems devote themselves exclusively to such movement. With the industrial development of the Northern Central group of States has come a strong trade current traversing the Mississippi Valley lengthwise. Far seeing transportation experts point out the certainty that this north-and-south current must increase far more, proportionately, than any other current related to the westward and southward trend of population and commercial development.

In the territory east of the Rockies, west of the Alleghenies, and between Lakes and Gulf, the census of 1900 counted in excess of forty millions of people—ten millions more than were found east of the Alleghenies from Maine to Key West. In this Mississippi Valley territory the density of population had risen, in 1900, to 30 per square mile, as against 73 per square mile in the Eastern territory. The railroad mileage in the Mississippi territory was 115,000 miles—in the Eastern territory 51,000 miles; over two to one. The gross area of the Mississippi territory was one and a third million square miles, and of the Eastern territory four hundred thousand square miles—over three to one. In all the essentials of populative expansion the Mississippi territory is self-contained.

SHOE PRODUCTION.

In this Mississippi territory, with forty millions of people, the

LEATHER AND SHOE PRODUCTION.

Eastern Territory.

State	Square miles	Population	R. R. mileage	Density Population	Pounds sole leather used by shoe factories	Pounds sole leather made	Pairs shoes made
Mass.	·8,040	2,805,400	2,111	384.9	135,800,000	1,350,000	107,260,000
N. Y..	47,620	7,268,900	8,126	152.6	24,530,000	21,600,000	23,827,500
N. H..	9,005	411,600	1,175	45.7	25,210,000	....	22,110,000
Penna.	44,985	6,302,100	10,130	140.1	10,980,000	170,000,000	13,334,400
Me....	26,895	694,500	1,917	23.2	13,020,000	8,700,000	9,261,600
N. J...	7,525	1.883,700	2,237	252.7	4,550,000	....	6,274,000
Va....	40,125	1,854,200	4,051	46.2	2,550,000	10,130,000	2,711,000
Other.	243,468	9,989,000	21,445	41.0	2,729,000	33,660,000	2,577,300
Total .	427,663	31,209,400	51,192	73.0	219,369,000	245,440,000	187,355,800
Mississippi Territory.							
Ohio..	40,760	4,157,500	8,878	102.0	17,610,000	....	18,263,500
Mo....	68,735	3.106,700	6,881	45.2	25,160,000	....	16,439,800
Ills....	56,000	4,812,500	10,989	86.1	9,760,000	1,854,000	6,143,400
Wis...	54,450	2,069,000	6,460	38.0	5,450,000	19,600,000	4,407,600
Minn..	79,205	1,751,400	6,770	22.1	4,120,000	....	2,639,600
Mich..	57,430	2,421,000	8,028	42.2	3,230,000	24,300,000	2,012,500
Ky....	40,000	2,147,200	3,084	53.7	1,940,000	7,070,000	1,799,800
Other.	967,175	19,938,900	71,228	20.6	3,270,000	4,317,000	1,995,400
Total	1,363,765	40,404,200	114,318	29.6	70,540,000	57,141,000	53,701,600

census of 1905 shows the production of shoes at about 54,000,000 pairs; in the Eastern territory, with thirty millions of people, 187,000,000 pairs. The rate of shoe production in Eastern territory is 6¼ pairs per capita, in the Mississippi territory 1⅓ pairs per capita—a producing rate, related to population, nearly five times greater in the Eastern territory.

Going a little into detail, we find Massachusetts making 107,260,000 pairs of shoes in 1905—45 per cent. of all the shoes made in the United States, and twice as many as in all the shoe factories of the Mississippi territory put together. While of all the shoes made in the United States, three-quarters, or 75 per cent., are made in the Eastern territory.

LEATHER PRODUCTION.

In the manufacture of heavy leather we find almost exactly the same statistical position. Of the 302,000,000 pounds of sole leather reported in the 1905 census as the product of the United States, over one-half, or 56 per cent., was made inside the boundaries of the State of Pennsylvania, while the Eastern territory, including West Virginia, made 81 per cent., or 245,000,000 pounds.

Obviously, with the Eastern territory making 81 per cent. of the leather, it is not surprising to find New England manufacturing ability responsible for 75 per cent. of the total shoe production.

WESTERN SHOE PRODUCTION.

In the face, however, of the tremendously strong position of Eastern leather and shoe production, the past decade has witnessed a striking development of shoe manufacture in the Northern Central States; and as throwing light upon the future increase of such production in the Mississippi territory, we may examine the statistical story with profit.

From 1880 to 1890 there was enormous increase in the capital employed in the shoe industry, this increase being practically universal and amounting to 122 per cent. in the United States—the capital employed in 1890 being almost 2½ times that employed in 1880. From 1890 to 1905, however, the growth was more temperate and more in accord with increase of population—

from 1890 to 1905 the capital employed increased from $95,000,000 to $122,000,000, an increase of about 28 per cent. on the capital of 1890.

In 1890 the States in the Eastern group employed $76,000,000 of capital, and in 1905, $88,000,000; an increase of $12,000,000 or 16 per cent. on the capital of 1890. During the same period the Mississippi group increased shoe capital from $17,000,000 to $32,000,000—$15,000,000, or 86 per cent. on the 1890 capital. Of the combined capital of Eastern and Mississippi territories, the latter had 18 per cent. in 1890 and 27 per cent. in 1905.

In the Mississippi territory the growth of shoe production was by far the greatest in Ohio, Missouri, Illinois, Wisconsin and Minnesota, in the order given. In 1890 these five States had shoe factory capital of $15,000,000, and in 1905 $28,000,000; or shoe factory capital nearly doubled in 15 years. During the same period the New England and Middle Atlantic States raised their shoe factory capital from $75,000,000 to $87,000,000, or 16 per cent.

As bearing upon the point of manufacturing and merchandising ability, such returns as are available indicate that, in the average, the Mississippi territory factories return about the same profit upon investment as the factories of the Eastern territory. Under the census of 1905 the States of New Hampshire, Massachusetts, New York and Pennsylvania show a ratio of cost to product value of 109.74, while the same ratio for Ohio, Missouri, Illinois and Wisconsin, shows 109.75—identical figures, and of comparative value despite the uniform ability of manufacturers both East and West to handle their census returns with discretion.

As our study is directed primarily towards the future of heavy leather, little direct reference is made to the statistical position of upper leathers; and such reference is unnecessary when it is understood that the development of upper leather production in the Mississippi territory has kept steady pace with the rise of Mississippi shoe production. Manufacture of upper leather has not localized in quite the degree noticeable with heavy leather, owing to its greater independence of tanning material supply—it has been, for years, free to follow manufacturing ability.

FREIGHT RATES.

Let us examine the freight rate conditions on hides, leather and shoes. From the files of the Interstate Commerce Commission I have prepared tabulations of rates from centers of production to typical points of consumption, trusting that the averages so secured may be indicative of governing conditions; and I think such averages may be useful in the intended purpose.

We find the freight rates on green hides from Chicago to Mississippi territory tanneries is 15 cents, to Eastern tanneries 32 cents; from New York to Mississippi tanneries 29 cents, to Eastern tanneries 20 cents; from New Orleans to Mississippi territory 36 cents, to Eastern tanneries 41 cents; from Galveston to Mississippi territory 59 cents, to Eastern tanneries 83 cents. These results are hardly surprising, as they give statistical proof to a well-known fact, viz.: that Mississippi tanneries secure their green hides at less freight cost than Eastern tanneries, but that imported hides cost more for freight at Mississippi tanneries than at Eastern tanneries. The figures do show, however, that on hides of packer take-off the freight cost to Mississippi tanneries is less than half the freight cost to Eastern tanneries, while the advantage of Eastern tanneries on imported green hides is about 10 cents per hundred. The general conclusion from the results is that the Mississippi territory has some considerable advantage in hide freights to its tanneries.

In the leather rates we find that from Eastern points of production to New York the average is 22 cents, to Boston 25 cents, as against 20 cents from Mississippi points of production to Chicago, and, presumably, St. Louis. If we are to assume (which is the statistical fact), that Eastern and Mississippi territories are each self-contained as to balance of leather production and consumption, then the rate differences found applying to leather are net differences—that is, the Eastern factories pay for freight two to five cents more per hundred on their incoming leather than the factories in Mississippi territory.

In the rates on shoes we find New York and Boston on practically the same basis into both Eastern and Mississippi territories. However, from New York into Eastern territory the average rate is 66 cents, while from Chicago into Mississippi territory the average is 85 cents, a difference against the Mississippi factories of 19 cents, or approximately ⅔ cent per pair. On the other hand, the rate is much against Eastern factories shipping into Mississippi territory—$1.19, as against 85 cents from Chicago, or in excess of one cent per pair. The general conclusion from the data is that the Mississippi factories have, in their own territory, a protection against Eastern competition exceeding one cent per pair.

FREIGHT RATES.—HIDES.—CARLOADS.

Eastern Territory.

	From							
	Chicago		New York		N. Orleans		Galveston	
To	Dry	Green	Dry	Green	Dry	Green	Dry	Green
Lock Haven, Pa.	32	27	18	15	50	40	102	97
Binghamton, N. Y.	28	24	18	15	50	40	101	75
Worcester, Mass.	39	33	18	17	55	45	112	84
Island Falls, Me.	55	46	38	41	71	58	128	107
Richwood, W. Va.	32	27	21	26	50	40	102	71
Buena Vista, Va.	32	27	24	22	50	40	105	87
Asheville, N. C.	41	31	48	35	72	50	85	74
Buford, Ga.	81	62	48	35	36	26	76	65
Philadelphia, Pa.	33	28	12	10	50	40	106	98
Newark, N. J.	35	30	8	7	50	40	108	81
Buffalo, N. Y.	21	18	19	16	58	39	95	70
Average, Eastern Ty.	39	32	24	20	54	41	102	83

Western Territory.

Grand Rapids, Mich.	16	13	34	29	67	54	88	81
Milwaukee, Wis.	10	3	35	30	46	28	74	53
Columbus, Ind.	16	13	34	29	81	58	84	60
Columbus, Ohio	18	15	27	23	58	47	88	64
Chattanooga, Tenn.	37	31	40	30	38	24	78	63
Louisville, Ky.	18	13	35	50	37	22	70	49
St. Louis, Mo.	16	17	41	35	37	22	67	46
Average, Western Ty.	19	15	35	29	52	36	78	59

FREIGHT RATES.—LEATHER.—CARLOADS.

Eastern Territory.

From	To Chicago	To New York	To Boston
Lock Haven, Pa.	32	18	21.5
Binghamton, N. Y.	25	18	15
Worcester, Mass.	35	18	12
Richwood, W. Va.	23	21	30
Buena Vista, Va.	29	25	30
Asheville, N. C.	52	42	43
Buford, Ga.	62	41	46
Philadelphia, Pa.	33	12	18
Newark, N. J.	35	8	15
Buffalo, N. Y.	21	19	21.5
Average, Eastern Ty.	35	22	25

Western Territory.

From	To Chicago	To New York	To Boston
Grand Rapids, Mich.	14	33.5	37.5
Milwaukee, Wis.	10	35	39
Columbus, Ind.	16	33.5	37.5
Chattanooga, Tenn.	47	38	43
Louisville, Ky.	18	35	39
St. Louis, Mo.	18.5	41	45
Average, Western Ty.	20.5	36	40

FREIGHT RATES.—SHOES.—ANY QUANTITY.

Eastern Territory.

To	From Boston	From New York	From Chicago	From St. Louis
New York, N. Y.	25		75	87.5
Buffalo, N. Y.	44	39	45	56.5
Pittsburg, Pa.	50	45	45	56.5
Washington, D. C.	45	37	72	84.5
Lynchburg, Va.	50	54	72	84.5
Charlotte, N. C.	108	103	135	133
Atlanta, Ga.	117	117	133	121
Average, Eastern Ty.	63	66	82	89

Western Territory.

To	From Boston	From New York	From Chicago	From St. Louis
Columbus, Ohio	59	59	41	46
New Orleans, La.	118	118	110	90
Knoxville, Tenn.	100	100	111	109
St. Louis, Mo.	88	88	43	
Galveston, Tex.	235	235	167	147
Denver, Colo.	273	273	205	185
Omaha, Neb.	148	148	80	60
Milwaukee, Wis.	75	75	25	49
Grand Rapids, Mich.	72	72	33	46
Indianapolis, Ind.	70	70	31.5	38
Chicago, Ills.	75	75		43
Average, Western Ty.	119	119	84.6	81.3

POPULATION.

In 1900 the center of population of the United States was a little south of Indianapolis—it has crept steadily, almost consistently westward since the foundation of the Republic and in 1940 will be well into the heart of the Mississippi Valley. Population is based, as to distribution, upon prospect of livelihood—the profit is the eternal goad upon gainful man. If the increment of population be no greater proportionately during the next twenty years than it has been during the thirty years ending in 1900, the population of the Republic in 1930 will reach close to 110,000,000, or an increase of 36 to 38 millions in two decades. Statistical prophecy puts the major part of this increment in the Mississippi territory, where agricultural stability is growing magnificently towards the millenium of farm conditions, and where the opportunity for commercial growth is measured largely by the increase of agricultural wealth.

Parallel with the growth of population there is proceeding that settling of productive ability which marks the line between the new and the old in manufacturing—not a slowing down, but a more efficient, direct and powerful use of advantages which characterizes the older manufacturing community. It is a surely safe prophecy that the dominant manufacturing spirit of the Mississippi territory during the coming two decades will be in no sense or degree behind or beneath the corresponding spirit in the Eastern territory—the wastes of inexperience, the losses of haste, the defeats of competition, will all be handled at minimum disadvantage to the rate of progress.

CENTRALIZATION.

An important factor in the future development of the Mississippi shoe and leather industry has not, up to this point, been touched upon. It is a bold prophet who will undertake to forecast the part to be played in the future of industry and commerce by centralized capital, and no such effort will be made here. There must, however, be account taken of present tendencies of the capital employed in shoe and leather production and distribution. During the past decade the control of hides has been consistently centralizing in the packing industry, until at the present time it is commonly accepted that such control is practically certain, and likely to be continued well into the future. Dominance of the meat business will be held by the American packers, certainly for a goodly period into the future, with the probability that such dominance will be fortified by insistent and effective control of South American meat and hide output.

Within a few years the entrance of packing capital into the leather and shoe industries has been of material and increasing volume, until there has arisen a tendency to view the outlook, from the standpoint of independent producers, with a measure of hysteria. How well founded such apprehension may be is debatable, but it appears unlikely that, once having undertaken its present program, packing capital will retire from the shoe and leather businesses.

What stands in the way of the packer-tanner-shoe-maker conducting his program along lines which are in accord with industrial methods of the present? What stands in the way, now of the strictly modern high-power producing unit? If it is possible to tan four thousand sides daily in a single tannery, why is it not likewise possible to tan twenty thousand hides in a single tannery? Viewed strictly from the results in other industries which have amplified the producing unit, it must be admitted that the obstacles ahead of similar enlargement in the heavy leather business are not such that capital will shrink from the risks. And, what more feasible, in view of modern conditions, than that behind such enlarged units of leather production there shall be put similarly enlarged units for shoe production, for harness, belting, light and split manufacture? The production of both heavy and light leather may now be undertaken wherever conditions are favorable for the economic assemblage of all the materials involved; and it is difficult to resist the prophecy that the future holds a very great growth of such production at points where assemblage of materials is coincident with a growth of shoe production induced by favorable factors of population, distribution and manufacturing ability.

So viewed, we see the Mississippi territory holding out a promise not paralleled elsewhere in the United States—a present population of forty millions reached by an adequate and rapidly enlarging transportation system, ideal for the assemblage of materials involved, and already setting into a measure of manufacturing and merchandising ability abundantly fitted to conduct the conquest of its market. Put with these factors the fact that the manufacture of leather is now free of the tie of the forest, the fact that the producing unit is limited only by the needs of the time, the fact that fearless and powerful capital will presently dominate the business, and we have the basis for a prophecy that the future great things in heavy leather will come on the water shed of the Mississippi.

THE PRODUCTION OF NEW TANNING MATERIALS IN THE UNITED STATES.[1]

By W. W. Stockberger.

The cultivation of useful plants probably originated when man felt the necessity of replacing the depleted supply of natural growth and of increasing the quantity available for his use. There is little doubt that certain food plants were first domesticated and that as civilization advanced and the need of man and his desire for additional means of solace and comfort increased, to these there were added plants yielding the fiber for textile fabrics, the dyes with which they were colored, drugs prized for their curative or narcotic properties, and the numerous other products for which human ingenuity has devised a use.

In the list of cultivated plants which now reaches far into the thousands there are some that have been domesticated for centuries, others that came into use at various periods of our recorded history, and still others that are being introduced to cultivation with each succeeding year. In studying the conditions existing at the time when many of these plants were introduced the operation of certain economic principles becomes apparent which I shall endeavor to illustrate briefly. I shall take for one example *Hevea brasiliensis,* one of the plants which produces the crude rubber of commerce. In the earlier stages of the collection of this product it was the custom to rely solely upon plants growing in their native wilderness. The milky juice of this plant

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[1] Published by permission of the Secretary of Agriculture.

was collected by methods that were at once crude and wasteful, as well as eventually destructive to the life of the tree. So long as virgin areas remained which could be drawn upon at will, little or no attention was paid to the conservation of the natural supply. But as the uses for rubber developed and the world's market demanded year by year an increasing supply, it became evident that in a few years there would be a general shortage of this valuable commodity. Attention was then directed to the cultivation of this plant, not only in its native region but in some of the tropical countries of the eastern hemisphere. So successfully has this plant been domesticated that it is probable that in a few years our entire supply will be derived from cultivated sources. Another example is afforded by the camphor tree, *Cinnamomum camphora,* indigenous in Japan and Formosa. In the early stages of the camphor industry mature trees were felled in the native forests and the wood subjected to crude and wasteful methods of distillation. In time it came to be recognized that the natural supply was becoming exhausted and a law was promulgated in Japan requiring that a new tree should be set out for every one cut down. In this manner the tree was there introduced to cultivation. During recent years the demand for camphor has enormously increased, owing to its extended use in the arts, and the cultivation of this tree has been begun in regions where it is not native. In our own land experiment has shown that camphor can be obtained from leaves and twigs removed as prunings without destroying the life of the tree, and in Florida an extensive tract of land is being set with camphor trees by the Satsuma Company for the commercial production of camphor along the new cultural lines indicated.

A third example is afforded by a class of plants which forms the source of supply for certain crude drugs. Among these the most striking for the purpose of my illustration is *Hydrastis canadensis,* or golden seal, the source of the important alkaloid hydrastine. While for many years golden seal has fluctuated widely in price, according to the relative amounts existing in the markets, the continued high prices of the last few years seem entirely due to the fact that the plant is becoming rapidly exterminated. As a consequence of the diminishing wild supply and the continued high prices, cultivation of the plant has been begun at several points in the Eastern States.

One of the principles which these examples illustrate I have formulated for reference later as follows: An economic plant will be brought under successful cultivation only when the natural supply becomes exhausted or difficult to obtain and when the returns from its cultivation offer a fair remuneration to the cultivator for his investment and labor.

Before attempting to introduce to commercial cultivation a plant which occurs only in a wild state or which may be domesticated only in a region remote and widely diverse from the one in which the introduction is to be made, a careful study should be given to the economic, geographic, climatic and agricultural conditions which will affect the new enterprise. It is to a consideration of these conditions with reference to "The Production of New Tanning Materials in the United States as an Agricultural Industry," that I now wish to direct your attention.

The annual Federal reports on the statistics of forest products furnish much valuable information on the production and consumption of tanning materials in the United States. From these it appears that there is a strong tendency toward the diminished use of barks, while the use of extracts has increased very rapidly. The reported consumption of tanbark in 1908 was 7.5 per cent. less than in 1907, which in turn was 11.4 per cent. less than the consumption in 1906. On the other hand the quantity of extract used in 1908 was 7.5 per cent. greater than in 1907, when the quantity consumed was 10.8 per cent. greater than in 1906. In view of the apparent growing scarcity of native bark, the use of which is being rapidly supplanted by extracts, the following excerpt from the last of the reports referred to is of much interest:

> "Of the extracts used in 1908, chestnut and quebracho were the most important, together forming 74 per cent. of the total quantity reported for that year. The quantity of chestnut extract used in 1908 was nearly 12,000,000 pounds more than that used in 1907, the increase amounting to 8.9 per cent., while in the same period the quantity of quebracho showed a decrease of about 2,150,000 pounds, or 1.5 per cent. There was a decrease of about 9,000,000 pounds, or 29.6 per

> cent. in the quantity of oak extract reported, and a slight increase in that of hemlock. The increase in the case of 'all other' kinds was most apparent, amounting in quantity to 26,125,000 pounds, or 196.4 per cent., and in value to $789,969, or 166.9 per cent., and was due largely to the greatly increased use of myrabolam and mangrove extracts."

The reported cost of tanbark and tanning extracts consumed in the United States for each of the past five years is approximately $21,000,000. During the same time the total value of imports has risen from $534,552 in 1904, to $3,580,959 in 1908. The following table compiled from data supplied by the Bureau of Statistics, U. S. Department of Agriculture, presents in detail the course of importations of tanning materials for the years mentioned.

From the facts represented by these figures the inference may be drawn that certain conditions now exist that should stimulate interest in a search for new tanning materials. The time is not far distant when our once plentiful supply of hemlock and oak bark will be exhausted. The increase of 12,000,000 pounds in the quantity of chestnut extract used in 1908 indicates that this source is being drawn upon heavily. Also the heavy increase in importations, which in 1908 were valued at more than six times as much as those in 1904, apparently indicates either that our native materials are rapidly diminishing or that the cost of producing them has so advanced that it is cheaper to depend upon foreign sources of supply. A timely subject, therefore, for the consideration of Americans is whether there are not now undeveloped sources of native tanning materials which can be utilized or whether some of the profitable tannin plants of other lands may not be introduced to cultivation in this country.

The prospect of producing tannin-bearing plants on an agricultural basis is one of growing promise. The introduction and increased use of extracts and the wider employment of a mixed tannage should make it much easier for new materials to gain a footing if they prove to be at all satisfactory. The increase in our knowledge of the chemistry of leather making and of the wider adaptations of which various tanning extracts are capable, due to the indefatigable industry of our leather chemists, en-

IMPORTATIONS OF TANNING MATERIALS INTO THE UNITED STATES, 1904-1908.

	Year ending June 30,									
	1904		1905		1906		1907		1908	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Hemlock bark ...	Cords	Dollars	Cords	Dollars	Cords	Dollars	Cords	Dollars	Cords	Dollars
	14,111	63,460	13,511	64,181	7,467	35,860	6,744	30,757	8,868	43,890
Mangrove bark...	Tons	Dollars	Tons	Dollars	Tons	Dollars	Tons	Dollars	Tons	Dollars
	(*b*)	(*b*)	(*b*)	(*b*)	(*a*)	(*a*)	20,693	426,431	15,192	310,745
Quebracho extract	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars
	(*b*)	(*b*)	(*b*)	(*b*)	(*b*)	(*b*)	79,033,584	2,319,785	79,186,787	2,260,364
Quebracho wood .	Tons	Dollars	Tons	Dollars	Tons	Dollars	Tons	Dollars	Tons	Dollars
	(*a*)	(*a*)	(*a*)	(*a*)	(*a*)	(*a*)	66,810	840,779	48,871	612,971
Sumac, ground ..	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars	Pounds	Dollars
	18,604,644	276,891	15,583,334	225,036	15,131,539	237,309	12,487,103	267,239	8,576,091	227,611
Other tanning materials		Dollars		Dollars		Dollars		Dollars		Dollars
		194,201		923,949		1,419,962		84,406		125,378
Total		534,552		1,213,166		1,693,131		3,969,397		3,580,959

(*a*)—Included in "Other tanning materials." (*b*)—Not stated.

courages the belief that a use will be found for every plant that can be shown to yield tannin in commercial quantities.

The geographical location of any region or section has a distinct bearing upon its agricultural possibilities. The prospects are much more encouraging for a section located where transportation is cheap and where there is direct access to the markets which may absorb the bulk of the products of the land. When other conditions are equal the advantage will lie with the section which has the best railway facilities or which enjoys the advantages of water transportation. So long as the freight rate by rail from the middle West to New York is as great as that on the same class of material brought to New York by water from points on the eastern coast of Africa, the latter are at no disadvantage on account of the greater distance from the market. On the other hand the hemlock bark of Oregon can not be brought to the eastern markets on a parity with the local product on account of the dis-parity in freight rate due to the distance the former must be carried. This condition would limit the marketing of almost any tanning material produced on the Pacific Coast largely to local needs. The most advantageous location for the production of tanning materials would seem to be near large centers of consumption. The states in which these are located may be learned from the statement of the quantity of bark and extract used in 1908. The largest consumption of tan bark was reported from Pennsylvania, Wisconsin, West Virginia, New York and Virginia, in the order named; and of extract from Pennsylvania, Massachusetts, New York, Michigan and Wisconsin, also ranking in the order named. Of the total cost of tanbark and tannin extract 33.3 per cent. was reported from Pennsylvania alone. It does not follow from this, however, that Pennsylvania is the most favorable location for the cultivation of tannin plants as further considerations will show.

Although the distribution of tannin bearing plants is very wide and is apparently independent of climate, yet due consideration must be given to the fact that a large number of the plants yielding high percentages of tannin are native of the warmer regions. Among these may be mentioned quebracho, catechu, gambier, wattle, myrabolams, divi-divi, canaigre, ratanhia, mo-nesia, mallet and churco barks. Many other plants also, which have a high tannin content and seem promising subjects for introduction to cultivation in this country, will survive only a slight degree of cold. It is not intended to convey the impression that tannin bearing plants can not be grown in the more northern portions of the United States for such is not the case, but the balance of evidence at present, subject to revision through experiment, indicates that favorable results may be best anticipated in the warmer southern sections.

The general agricultural conditions in the various sections present a weighty factor that must be reckoned with. The price of land, the cost of labor and the value of the staple crops now being produced will quickly determine the fate of a new introduction. The present tendency toward intensive agriculture under which very large returns are frequently derived from a small area, robs the holder of fertile and highly productive lands of any interest in low priced crops. Should the cultivation of tannin bearing plants in the United States be undertaken on a scale commensurate to supply the demand in this country, it is apparent that a large area of relatively good land favorably located as to transportation facilities would be required. It is also evident that a crop of this kind must be at least as profitable as those now produced in order to receive any consideration from the prospective grower. At present there are no actual data available which throw much light on the subject of probable returns to be anticipated from the cultivation of tannin plants in this country and the same can be secured only through experiments carried out on a commercial scale.

A consideration of the several factors mentioned leads to the conclusion that certain localities in the Southern States offer the best conditions under which to make practical tests of the possibility of cultivating tannin plants on a commercial basis since there considerable areas of relatively cheap land are to be had, the cost of labor is not prohibitive and the distance is not great from the centers of consumption. There also large areas may be obtained which could be devoted to the cultivation of one or more tannin bearing plants on a large scale with a corresponding saving in certain items of the cost of production and marketing.

Aside from the attempt made a number of years ago to cultivate the canaigre practically no work has been done on the cultivation of tannin plants in the United States. The presence of tannin has been demonstrated in many of our native plants and at one time or another a number of these have been utilized in tanning but the supply has been derived from uncultivated material. Preliminary experiments are now under way which it is hoped will yield the data necessary for planning larger experiments on a commercial scale. A survey of the native plants with respect to their availability for cultivation as tannin producers is now in progress and importations are being made from abroad of those tannin plants which seem adapted for cultivation in this country. A discussion of some of the more promising of these will serve to indicate the direction in which work is being carried out.

SUMAC.

The bulk of the sumac used in this country is obtained from abroad, largely from the Mediterranean region, and was imported in 1908 to the extent of 8,576,091 pounds. The cause of the preference in favor of the imported product is generally understood to be due to the presence of undesirable coloring matter in the American sumac. Although the native wild supply is held by some to be more than sufficient to satisfy the present demand it is believed that by cultivation the quality can be much improved and a wider market secured. Two species of sumac, *Rhus glabra* and *Rhus copallina,* occur in the region where the American material is gathered and are not distinguished by many collectors. The former known locally as smooth or white sumac contains from 15 to 25 per cent. tannin and the latter called black sumac has yielded on analysis as high as 38 per cent. Leaves of the latter also from certain localities produce a much whiter colored leather than the ordinary product. If the requisite areas of tillable land can be had in localities where the soil and climatic conditions are suitable for maintaining the high tannin content and good color value of the black sumac, proper cultivation and handling may develop a product that will be of high value. The plant is easily cultivated and when two years old may be readily harvested by an inexpensive method that has been used abroad which consists in mowing over the branches as is done with grass in making hay, and after the leaves are carefully dried removing them from the branches by thrashing. The average yield of Sicilian sumac is only about 2,500 pounds per acre but as this plant does not require a rich soil it may be made to yield a relatively fair return in certain sections where it would not have to compete with other crops of high value.

THE PECAN.

Although the pecan at present promises only a very small supply of material suitable for use in tanning yet it is not devoid of interest. The bark of the tree has yielded 12 per cent. of tannin which appears to produce a soft, light colored leather. The shells also which are to be obtained in some quantity at the centers where the nuts are cracked contain about 9 per cent. tannin which gives a reddish cast to leather. As the shells are at present a waste product they could probably be obtained at a low figure and utilized in certain cases where mixed tannage is employed.

PURSHIA TRIDENTATA.

This is a shrub belonging to the natural order Rosaceae and occurs on dry hills from Montana and Washington to New Mexico and California. In many places it occurs as a small growth scatteringly distributed on hill sides but it is very abundant and of large size in south-central Utah. It has been found to contain 12 per cent. tannin but the distance of the source of supply from the centers of consumption makes its utilization doubtful.

ALGAROBILLA.

The shrub *Caesalpinia brevifolia,* the pods of which are known as algarobilla, is a native of Chile where it attains a height of about six feet. The pods have been found to contain as much as 67 per cent. tannin which much resembles that of divi-divi and myrabolams. The yield has been estimated at six to eight pounds per plant when 1,000 plants were set to the acre. The Chilean product is said to have been sold in European markets[1] at 15 to 25 francs per 100 pounds, which would indicate a gross return

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[1] Albert, F., La Algarobilla, 1901.

of at least $180 per acre. Since this plant requires an arid soil and does not withstand frost, it probably cannot be grown in the United States except along the Mexican border.

DIVI-DIVI.

The pods of *Caesalpinia coriaria,* known locally as divi-divi, libi-divi or cascalote, contain from 30 to 50 per cent. tannin. The plant occurs wild in Mexico and Central America and is cultivated in Jamaica, Curaçoa and in Mombo, East Africa. Since its range extends only to about 30° from the equator it can be grown only in the extreme southern part of the United States if at all. The natives of Mexico claim that trees will begin to bear fruit when between 7 and 10 years of age and that a large tree will produce from 100 to 200 pounds of pods. Seeds of this tree have been planted in Florida and in time it is hoped that some exact information may be obtained as to its possibilities.

ELEPHANT-ROOT.

The elephant-root, *Elephantorrhiza burchelli,* is a somewhat shrubby leguminous plant, native in South Africa. It grows best there along water-courses but occurs on the drier uplands also. The large, club-footed roots attain a length of several feet, and, when air dry, have been found to contain from 12 to 22 per cent. tannin. Used as a tanning material these roots produce a soft and light-red-tinted leather, somewhat lighter colored than that tanned with wattle bark. The plant will bear some frost and its availability will be tested in suitable localities.

EUCALYPTUS.

During the past few years a great impetus has been given to the planting of Eucalyptus trees as a future source of timber supply. These trees should also be considered as one of the possible new sources of tannin in this country. While the tannin content of all the species and varieties that are adapted for planting in favorable locations in the United States has not been determined, the figures that are available show that the bark of nine contain tannin in amounts varying from 8 to 40 per cent., and that the leaves of eleven species yield tannin in quantities ranging from 6 to 18 per cent. The bark of *Eucalyptus* *occidentalis,* which is exported from Australia under the name of mallet bark, is the richest in tannin, containing according to Dekker 40 to 50 per cent. The leaves are said to have been used in tanning with very good results. The leaves of a species growing in Florida, *Eucalyptus robusta,* have yielded 17 per cent. tannin and offer a promising subject for experiment. Since the trees of these species send up sprouts very readily after the seedling trees are cut off, it should be possible to obtain at least an annual crop of leaves, either by cutting over the young growth, as was suggested in the case of sumac, or by planting the trees close together in rows and pruning as a hedge. This method would materially diminish the long period without financial return between planting and maturity of the trees when they are intended for lumber production. A few trees have been planted experimentally in the South from which it is hoped data may be secured as to the probable yield of leaf per acre that may be produced under the method of pruning just mentioned.

It is only just to say that these analyses and color tests were made by Mr. Alsop, and are interesting from the standpoint of practical tests.

Examples enough have been mentioned to show the nature of this work and the direction it is taking. Believing that the time is at hand when we may well attempt to introduce to cultivation tannin bearing plants we are at once confronted with the necessity of obtaining exact and definite information concerning all those that seem to offer a prospect of being adapted to our economic and agricultural conditions. For the most part this work is prospective entirely and before we can hope to proceed far a series of extended and I regret to say laborious experiments on a commercial scale are absolutely necessary. To this end the interest and close co-operation of the tanner, the chemist, the farmer and the agricultural scientist are necessary. If the tanner on the one hand withholds his support until he is assured that these new materials have been tested, proved to be satisfactory and are readily available in hundred ton lots, and the farmer on the other hand declines to become interested until he can be assured of the yield per acre and the f. o. b. price of his crop at his railway siding, nothing will be accomplished. But if the tanner is willing to give some time and expense to testing small quantities of new products and if the farmer will assist in determining the possibilities of their commercial production, some definite results may be accomplished. Meanwhile such experimental work will be carried on as time and means may permit. Your earnest co-operation will greatly further its progress.

EXTRACT TANNAGE.

By C. M. Morrison.

After being urged by quite a few members of this Association to say something along the line of extract tannage of sole and heavy leather, I shall try to deal briefly on the subject.

Tanners as a rule are not speech makers or ready writers, and I am no exception to the rule, however, I am ready to give such information as I possess in regards to the uses of extracts in the manufacture of heavy leather. With the one aim "To help make this meeting of the American Leather Chemist Association a success," and by making this meeting a success, we are doing the tanner lasting good as well as giving the leather chemist a boost, which they so much deserve.

The live, wide-awake tanner knows how to make the most of opportunities as they come before him from time to time and may be able to develop ideas which may be termed original. But some tanners are very close-fisted in regard to imparting these ideas and experiences which often have been expensive in time and money. This policy is, however, somewhat narrow-minded as it pays far more better for practical tanners to work together for mutual advantages and to exchange visits and to go over such points as may be of interest to each. One giving the other the benefit of his experience rather than stand aloof and act as strangers to each other. Quite often it happens that the practical man in charge does not control the situation when it comes to swapping these ideas and visits: but the employer holds the key to the situation and refuses to listen when approached on the subject of giving up something which has cost him good hard money, and to such I will say it is high time they should learn that fools oftimes possess information which might be worth thousands to them, even the very thing they are looking for and same could be easily obtained by a friendly visit and a hearty handshake.

I do not think there is one present who does not vividly remember how tanners five or six years ago kept their doors locked and barred against visitors. It will also be remembered at this time the drum or quick tannage wave had struck the country with full force and tanners were, in most instance, working their brains overtime to perfect his system and to get ahead of his neighbor and about this date the extract tannage was brought before the shoe manufacturer more conspicuously than ever before through the lively discussions which were being carried on in the trade papers at that time, and it created quite a lot of prejudice against extract leather among leather buyers, although there were great quantities of extract leather being made and sold at that time and had been for several years. But shoe manufacturers and leather buyers as a rule are a shrewd set of business men and for a short time they proceeded to make capital by shouting "Extract Leather" and some buyers even went so far as to countermand their orders when they learned the tanner was using extract, and at the same time they had been using this tannage right along with satisfactory results, and countermanded their orders for no other purpose than that they were prejudiced against the name "Extract." To-day these same manufacturers use this same leather and ask no questions.

Tanners have often burned their fingers by adapting risky new processes and there was quite a lot of inferior leather made about this time. But it seems as though many lessons are not thoroughly impressed upon the memory unless a heavy price is paid as a penalty for pioneering along untried paths. While thousands of dollars have been sunk in the effort to make better leather at a lower cost, it is but fair to state that such courageous investigations have been of great benefit to both employers and employees and it cannot be denied that after all it is the live up-to-date tanner, who was not afraid to venture, who has made a success in the tanning of heavy leather with extracts.

BEAM SHOP.

The method of preparing the hide in the beam shop for extract tannage does not differ a great deal, if any, from that of the bark tannage: by this I do not mean that tanners follow one set rule. Of course it is understood that the modern beam shop is a parlor by the side of the beam shop of twenty-five years ago as to cleanliness. We want our limes cleaned out every two or three weeks, our soaks must be cleaned every time they are filled with fresh hides.

There are a great many different methods of soaking and liming, for instance, some tanners first run their hides in a slush wheel from ten to fifteen minutes with a good flow of water to free the hides of all salt and manure possible and to loosen up any dry spots there may be in hide from folding up. The users of this method claim they cut their time in half by using the slush or wash wheel. After going through the slush wheel they hang over stick in still soak for a day. Or some tanners toggle or pin hides together from the wheel and finish the soaking by reeling through soaks, eliminating the dragging of hides from soaks by hand to be toggled up before going into limes.

Another method of soaking which is very popular is to hang hides over sticks and suspend in still soak vat, changing the water quite often. Users of this method claim they do not break up and destroy hide substance. Both of these methods are good and are very popular and are being used in some of the largest tanneries in the country.

Soaking is more important than is generally imagined outside of the tannery, and a great many times, inside of the tannery. Much depends on the kind of water used and it is not easy to advise how often the water should be changed. With spring or well water of low temperature you can soak with more safety and regularity than when river water is used, which is less easy to manage. Water is often responsible for damaged hides and great vigilance is necessary when the water supply is not absolutely under the control of the tanner.

Then comes the liming process, which has had many changes in the last few years. There has been introduced many different chemicals and depilatories, but to-day so far as I am able to observe, lime with the aid of sulphide of sodium is yet king in loosening the hair and swelling the hide. In most all the large tanneries in the country there has been quite a lot of experimenting with sulphide of sodium and there are a few tanners in this country who use sulphide exclusively for swelling and dehairing but the method is not a popular one.

While we have seen some very nice leather made from hides treated altogether with the sulphide process, the majority have a very poor color, dark and spotted, rough grain and spongy; but used in connection with lime, I claim it is a great help. I do not mean by this that sulphide of sodium has no future, I think it is here to stay, provided the cost of same does not become prohibitive and will find a big field in connection with extract tannage.

Now after soaking and liming comes the unhairing, fleshing, fine hairing, bating, washing and so on, putting the hide in a nice clean condition to go into the tan liquors. Some tanners prefer to green flesh, that is to flesh from the soaks before going into the limes: while some prefer to flesh out of the limes. Generally each tanner has his own pet ideas as regard to fleshing, either is good so long as the results show up in the end and it remains for each tanner to work out his own salvation as regards this and many other details.

At this point I wish to repeat what has truly been said thousands of times by old time or bark tanners "the beam shop is the nursery of the tannery," and without the proper treatment and preparation here no tannage will be a success and this saying especially holds good in extract tannage.

Now, with a nice clean, well preserved and properly prepared hide we are ready for the tanning process. There are so many different ways and methods in tanning with extracts, it would be a very difficult proposition to undertake to even describe a portion of them. Generally every tanner has his own ideas as to how certain things should be done. While there are numberless ways in doing things in the tannery we are all working on the one general principle and to the same end. So I shall proceed to describe and outline what to my mind are the two best methods of tanning with extracts exclusively.

For an all vat tannage I prefer a rocker system, suspending the hides in rockers by tacking onto sticks, or hanging over the sticks: of the two methods for hanging hides or sides as the case may be, in rockers, the tacking of sides onto the sticks is decidedly the best plan. It is true this method has some bad features, for instance, you get some nail holes along the back where the side is tacked to stick, but by this method you eliminate all possible chance of getting wrinkled and pipey grain and stick marks, which are so easy to get when the sides are hung over the stick, and the bellies especially are much easier to get a good nice smooth finish on when it comes to rolling: however, it is not practical to tack whole hides on the sticks without very deep vats.

One of the greatest obstacles tanners have had to deal with in tanning with extracts exclusively has been to get a good nice uniform color on their leather. In the past it would not have been a difficult job to walk through the dry loft of any extract tanner in this country and in ten minutes pick out as many different colors of leather. Now I am sure there are but few tanners here that will not agree with me on this one point. Now admitting that this be true, there must be a cause for this and considering that in the next five years 75 per cent. of the sole leather will be tanned with absolutely all extracts, it is high time tanners get their heads together, with the aid of the leather chemist and solve the problem. Now I shall try and dissect this cause. First, the hides from the beam shop have not been properly prepared: some hides have been allowed to go into tan liquors with an excess of lime in the grain. I do not mean that the hides should be bated down low, in fact I do not believe in excessive bating for sole leather, only bate enough to free the grain of lime, so when they go into the tan liquors they will take on an even color.

I wish to say in this respect with regard to bating: I think if we have a good soft water that we can bate our hides for sole leather sufficiently in water without the aid of any acids. Of course it takes a little more time, but my experience has been I have got better results.

To tan with extract it is almost necessary that the tanner have a general knowledge of chemistry: I shall try in a simple manner to explain why. Take a test-tube or a glass bottle full of sour tan liquor, add a few drops of lime water, the liquor becomes cloudy which disappears on shaking: keep adding lime and after a while the cloudiness remains permanent or in other words you have dirty liquor. Let the glass stand and a sediment (tannate of lime) will appear at the bottom. This same action on a larger scale is going on in the coloring vats every day when the new hides are worked in. When a green pack is put in the tail rocker the acidity of the liquor acts on the limey grain of the hide and a sort of thin scum emerges. This explains why it is absolutely necessary that from time to time this old liquor should be thrown away and a fresh sour be run down to take its place so that the lime in the hide will be rapidly neutralized, leaving the grain clean and in nice even color for the sweet tan liquors.

Now, it can easily be seen and understood why it is necessary for green hides in the coloring rockers, to have plenty of room, so that the lime when drawn out of the grain has an opportunity to drop to the bottom of the vat. On the contrary if the young sides are crowded and pressed close together the tannate of lime is unable to escape and this explains why dirty and cloudy grain result when the young packs do not get the room they should have and I wish to say here that ninety-nine out of every hundred tanners make this vital mistake of crowding their vats too full, especially their tail rockers or coloring vats. By coloring on this plan—plenty of room for the green stock—such labor as sticking, shifting and changing the position of the sides are avoided. All this labor is required when sides are jammed close together, otherwise there would be bad touch spots or stains.

What I have referred to has been the pressure or force system, where the tan liquors are forced through the sides or hides in a section of several vats and the liquors are allowed to slowly circulate through the entire section. Consequently when the liquor reaches the tail vat the tan is about exhausted and practically worthless. In this connection the leather trades chemist is an absolute necessity as such liquors should be analyzed from time to time, so the tanner may know the value of such liquors in tannin as well as the acidity of same.

Now to those who disagree with me in regard to allowing the young packs plenty of room, I would respectfully ask you to take a few sides and hang them clear of each other in the dirtiest slop liquor you have, then crowd a pack in the cleanest slop or coloring liquor you have and note which comes out the best color. I trust you will not get the impression from the above that the color gotten in the tail rocker or coloring liquors will be easily carried through the remaining tanning process, far from it. In the days of bark and a last layer liquor of 20 to 24 degrees this rule held good, but to-day when our slop liquor contains from one-half to one per cent. tannin and we finish up the tanning process in thirty to sixty days with a 42 degree twaddle extract containing 35 per cent. tannin, do you wonder that the color can be changed in almost any stage of the process and I assure you that some of us have spent some sleepless hours over this one thing.

Then what is the remedy? I shall say the proper blending and dissolving of our extract. I think I am safe in saying that there is not a tanner of any great importance in this country to-day who is not using less than two to six or eight different kinds, grades and qualities of extracts. Now each of these extracts when put to the test will show up a different color. Therefore, it is absolutely necessary if we want to carry a uniform color on our stock at all times that we be everlastingly on the alert, and see to it that the proper portions of each extract be added each day and I feel that I cannot too firmly impress on your memories the great importance of the proper blending and dissolution of extract liquors and the keeping of them in solution.

Here I think the rocker fills a threefold purpose, viz.—keeping the liquors in solution, hastening the tanning and aiding in getting a uniform color by constantly washing the hides or sides through the liquors, thereby preventing any sediment from forming on the sides which stains or creates what tanners call touch spots. The last but in nowise the least cause I want to call your attention to, is the difference in the quality of extract as it comes from the manufacturer. Some makers are continually striving to improve their product and keep it up to the standard, while others seem to think the tanner will continue to buy gold bricks: consequently he continues to send his extract along, each car throwing a different color. It is true all tanners buy extracts on a ten unit base, but in doing so he expects a good color peculiar to the kind of extract he is buying, and not a tank of Indigo Blue.

It is useless to say extract makers can get repeating orders when they fail to deliver the goods they sell. There have been cases and if I think rightly, quite a few of them, where extract has been sold to contain a large per cent. bark, the goods would come along and pretty soon the tanner would get suspicious and start a little secret investigation of his own and in a short time he would find that his nearly all bark extract actually contained about 40 per cent. bark and 60 per cent. chestnut wood: and in most cases the tanner quit buying bark extract and made his own bark liquors by blending chestnut wood and quebracho together.

I want to say in this connection,—you had some discussion on it this morning; I don't say this to cast any reflection on the chemist at all;—it is impossible for the chemist to tell you how much bark has been used to make up this extract. Is that true or not?

This is one point he is helpless on and it behooves every reputable extract maker to be honest in his representations when selling his goods if he expects to live in peace with the customer. There is not a tanner here who does not vividly remember sometime in his career what happened when he sent out a batch of leather to a customer that did not quite come up to his standard. Why the leather was returned at once, no questions asked, not even for shipping directions and the possibility was that all his troubles were caused by a tank of bad colored extract.

I have now, to some extent described to you the rocker process of tanning with extract exclusively. The next process in order which I think is especially adapted to extract tannage is to partly tan in rockers as described and finish up in drums or wheels. The wheel if used properly in the later stages of tanning gives a finish that we can get in no other way. But I shall not attempt to go into the drum tannage other than to say that the tanner who has not tried the drum to his sorrow is scarce and far apart. I cannot recall at this time anything that has given the tanner more trouble than the drum and extract salesman combined. However, if we predict rightly both the drum and salesman are here to stay and will be used very extensively in the future growth of extract tannage.

One of the greatest mistakes American tanners are making, especially those who are using extracts exclusively, is the using of too many different kinds and makes of extracts. I do not think it policy for business reason to confine ourselves to one extract alone. If we should, I think it would also be to our detriment in various ways. But for illustration, say I am using three or four makes of chestnut, about the same of quebracho in connection with hemlock, cutch, myrabolams, spruce and a number of other kinds. The result would be: pretty soon I would have a yard of liquors that would require the combined effort of all the chemists of this Association to tell me what I really did have—and I am thinking then they would fall short in their task. And there is no doubt in my mind but that a few of us have taken a ride in this boat, to our sorrow.

Now the question naturally arises, how far can we go in mixing these different extracts to get the tannage we desire. This, I think, each and every tanner must work out for himself as it would be very hard to find two tanneries working under the same conditions and a prescription that worked happily for one would give the other a bad case of "the blues." So you can see, that should I attempt to prescribe, I would soon get myself in a hole with one or the other of these tanners and possibly both.

Now then the best thing for each tanner to do is to find a combination of extracts which suits his individual needs, whether it be exclusively chestnut wood, quebracho, or something else, and the fewer different extracts he uses the more easily he will be able to keep the situation in hand and at the end of the year I feel sure he will find a greater reward on the right side of the ledger than if he should have used a combination of a dozen or more different extracts.

Of course the new tanning agents which spring up from time to time must be tried out, but should be done in a conservative way, thereby avoiding worry and trouble which we so often bring on ourselves by being guided by the smooth talker instead of consulting our own common sense.

For the past seven or eight years tanners have been putting forth all their energy to shorten the time required to turn out their stock thereby saving a large interest account. The higher prices of hides and other materials that go into the manufacture of leather has compelled most of the tanners to borrow large sums of money to keep their plants going. With bark and a weak liquor it was impossible to shorten the time to any extent. However, extract came to their assistance and they were enabled by its use to divide the time required to tan heavy hides by three and at the same time make a piece of leather equally as good, if not better, than his longtime tannage.

But this shortening of the time has gone too far in quite a few cases and at the present time we hear quite a few talking longer time in the tanning process. This is taking the wrong road, especially in an exclusively all extract tannage. The quicker we can convert hides and extract into leather, the more profitable we will find the business and the reason for this is very simple. Extract when received in the tannery is in a cleaner condition than it ever is any more and it continues to become dirtier with use, and this explains why it is necessary that we must continue to filter old dirty liquors. Tanners who use no bark must go to the expense of buying materials for filters. All of this can be avoided if we exhaust our liquors while they are fresh, before they become foul and filthy.

No doubt most every one in this room has seen and handled sole leather that was tanned with extracts in three or four days, and while I do not know of anyone who is tanning leather successfully in this short time I predict that in the next five years seventy-five per cent. of all our sole leather will be tanned in 12 to 30 days.

Now in connection with this paper I have made some effort to gather the early history of the manufacture of extracts in this country but have been unsuccessful to some extent. However, what I shall give you I think is about correct and I feel sure it will be interesting to some of you at least, but should I make any misstatements, I wish it distinctly understood I do not do so intentionally.

Hemlock extract was the first to be made in this country and was first produced about 1863 and was very crudely made. C. A. Miller & Co., in which John H. Heald & Co., who were tanners in Baltimore were interested, built an extract factory for the manufacture of hemlock extract, at Elmira, N. Y.

About 1864, N. Spencer Thomas built another plant for the same purpose at Painted Post, N. Y., and about the same date there was a similar works built at Mullet Lake, Mich. In 1867, said Spencer Thomas built another factory at Trout Run, Pa. Mr. L. J. Backer, founder of the Smethport Extract Company being manager of the plant at Trout Run, Pa.

These plants were equipped with an open evaporating pan with the heat applied direct to the bottom of it. When the extract was thick enough, it was dipped out and run into barrels. The first factory to install a vacuum pan was the Painted Post, N. Y. factory. In this connection and by the kindness of one of the oldest hemlock manufacturers now living I wish to quote what he has to say of this early extract, as follows: "My father was superintendent of a tannery in Buffalo, N. Y., and I can remember as a boy of seeing casks of hemlock extracts in the tannery. It was thick black stuff and the heads had to be taken out of the barrels in order to get the extract out. With the cold liquors used in those days it was absolutely impossible to get the extract into solution and of course it was properly damned and condemned. Prejudice against extracts continued with this firm down through my time and they never would consent to trying it again, always remembering their first experience."

In 1869 the foundation of the present plant at Lynchburg, Va., was built for the manufacture of chestnut oak bark extract. Our understanding being that this was sort of an experiment, the plant was small having a capacity of about fifteen barrels per day.

In 1877, Mr. L. J. Backer and others formed the Smethport Extract Company at Smethport, Pa., and built what was at that time the largest plant in existence, having a capacity of twenty thousand barrels hemlock extract per year.

About 1870 the scarcity of tanning material in Europe lead to the manufacture of extract from chestnut wood, the value of which as a tanning agent had been known for years.

Between 1880 and 1885 the higher price of bark in this country lead to the erection of a few plants for the manufacture of chestnut wood extract and about the first of these were one at Huntingdon, Pa., and afterward moved to Grapeville, Pa.. also one at Huntingdon, W. Va. I think I have these two confused. I have one at Huntingdon, W. Va., and one at Huntingdon, Pa., and I think possibly it is the same plant, (Mr. Haley: It is.) and soon after this others were built. However, it was not for several years after this, I think about 1895, that chestnut wood extract came into use on its own account. Previous to this it had been used sparingly with bark liquors.

These first factories for the manufacture of chestnut wood extract were well equipped, their facilities being practically the same as used to-day but some were not a success financially.

It is said that ninety per cent. of the early manufacturers troubles were the lack of proper preparation of the bark and wood and the application of too much heat in the leaching process. However, these early pioneers broke the ice and paved the way for the large and successful manufacturer of extracts of to-day, there being no less than nineteen factories for the manufacture of chestnut wood extracts alone and most all have large capacity.

Quebracho extract was first imported into this country on a small scale from Germany about 1892. However, business of any importance did not begin until 1897. In that year the New York and Boston Dye Wood Company began the manufacture of this extract in Brooklyn, N. Y., and since that date its use has increased very rapidly and the figures I shall quote later on will show how it has increased in popularity.

In order to put before you more plainly how extracts have increased in use in this country in the last few years, I shall here quote a few statistics taken from the United States records for the last three years.

In 1905 the Department of Manufactures reported

10,830,000	lbs. hemlock extract.
107,195,500	lbs. oak bark extract.
62,262,200	lbs. quebracho extract.
1,000,328	cords hemlock bark.
422,269	cords oak bark.

In 1908 the report was,

810,231 cords hemlock bark.
307,817 cords oak bark.
40,808,723 lbs. hemlock extract.
146,818,963 lbs. chestnut extract.
143,174,614 lbs. quebracho extract.

It will be seen from the above figures that in 1908 we used 29,978,723 pounds hemlock extract, 39,623,463 pounds of chestnut extract and 80,912,414 pounds quebracho extract more than in 1905.

It will also be seen that we used 190,097 cords hemlock bark and 114,452 cords oak bark less than we did in 1905.

The above figures are not a true and accurate report of all the bark and extracts made and used in this country for 1905 and 1908, as the Census Department find it impossible to get reports from small operators. However, the figures here given bear me out in saying that extract tannage for sole and heavy leather is "*The* tannage" of to-day.

The total reported cost of tan bark and tanning extracts consumed in 1908 by the active tanneries in the United States was $21,361,719. Practically the same amount was expended for tanning materials of this character in 1906 and 1907 but the quantity of bark consumed in 1908 was less by 87,001 cords than in 1907, while the quantity of extract was greater by 27,201,552 pounds.

The total cost of bark used on 1908 was only $245,155 greater than the total cost of extracts consumed, while in 1907 the corresponding excess was $1,906,201 and in 1906, $4,060,749. Of the extracts used in 1908, chestnut and quebracho were the most important, together forming 74 per cent. reported for that year. The quantity of chestnut extract used in 1908 was nearly 12,000,000 pounds more than that used in 1907, while for the same period the quantity of quebracho shows a decrease of about 2,150,000 pounds.

Chestnut extract blended with a small per cent. of quebracho has grown to be a great favorite in the heavy leather tannage.

In conclusion I want to say if the 90 million of this country were to request bark tanned soles for their shoes, 89 million of us would certainly be compelled to go unshod. Also all enterprising tanners are realizing more clearly than ever that the leather trades chemist is not a luxury, but an absolute necessity and a valuable annexation to the tannery force, and the tanner with the aid of the chemist is looking forward to great accomplishments in the near future.

REMINISCENCES OF QUEBRACHO DEVELOPMENT.

By J. E. Stevens.

If, in giving you a few reminiscences on quebracho development during recent years, I may seem to be less technical and somewhat more personal than is usual at a convention of this character,—I shall have to put the blame on your Mr. Kerr who was good enough to say in his invitation to me to address you that something about quebracho development along popular—rather than dryly scientific or technical lines, would answer every purpose—especially on the last day of the convention, and a half holiday at that.

111 years ago, in 1798—out in the suburbs of New York City, at Greenwich Village, now West 10th St., downtown, William Partridge hitched a horse to a small windlass-grinder for producing cut dyewoods, and to the best of my knowledge, was thereby the pioneer manufacturer in the dyeing and tanning extract industry of this country.

It was almost a full century after Partridge started his horse in the manufacturing business, that his direct—though distant, successors, the Company with which I am associated, cut the first quebracho log and made the first quebracho extract produced in the United States. This was in April, 1897, and at that time none of us dreamed that before a decade had passed quebracho, which had come to our attention more or less by accident,—would be of such interest and importance to American tanners as to change our entire organization and compel us to make a large investment nearly 8000 miles away in the Argentine Republic. For several years prior to this—to be sure—small quantities of quebracho extract had been brought to this country from Germany and put out at high prices in a half-hearted way at some few points, in the trade,—but it is safe to say that prior to 1897 the scant interest shown by American tanners in this new material gave little inkling of the development that was to come.

I say that quebracho came to our notice by accident, for prior to '97 our business had consisted almost exclusively of the manufacture of cut dyewoods and dyewood extracts, and we had no intention of going into other fields when a broker in our line came to us, saying that he had for sale a consignment of some 50 tons of a new tanning wood from the Argentine which he understood was being used to some extent in Germany. He produced samples of this new material which seemed to us like scrap iron, but which,—on being subjected to chemical analysis—proved so interesting that we were promptly led to buy the first 50 tons of quebracho wood which ever came to this country. It was then that our troubles began and from that day to this quebracho has made demands upon us entirely new and unusual to our previous experiences in the dyewood industry. Although some of the dark red looking logs which came to us in our original purchase were only two to three feet in diameter and a dozen feet long, they weighed from one to three tons apiece, and how best to handle them—much less to reduce them to pulp and convert them into extract—were questions that faced us at the start, and took several years of study and experiment for solution.

Quebracho wood has a specific gravity of about 1.40, weighs between 80 and 90 pounds to the cubic foot, and is, accordingly, almost half again as heavy as water. From the very start, therefore, we were obliged to disabuse ourselves of any visions we might have cherished of quebracho logs floating gracefully down Argentine rivers to ports of shipment, since the matter of transporting and handling wood of this iron-like character was one of the most important problems that had to be contended with in the business.

Quebracho is one of the heaviest and hardest woods known,—its very name meaning "axe breaker"—and the ordinary cutting machinery used in the manufacture of wood extracts stands poor chance when it comes in contact with these cast iron trees—centuries old—that grow in the Gran Chaco forests of Central Argentine. Our saws lost their teeth and our cutting machines their knives on even the smaller of these tough logs, and how to reduce the larger pieces to a size which could be handled gave us prolonged concern. In desperation, however, we finally bored holes in the worst offenders, put in a charge of powder, lighted a fuse and ran. While some of these blasting attempts injured, and came close to being fatal, for some of our men, yet the wood was at length reduced to workable proportions for our cutters and finally leached out into liquid extract standing at approximately 51° twaddle. Our first sample barrels were sent to nearby tanners in April, 1897, and thus the manufacture of quebracho in this country began.

Peculiarly enough—quebracho seemed to awake instant response among those to whom we made our first shipments and much to our surprise our 50 tons of logs were soon used up. The interest inspired by this small shipment encouraged us to arrange for further supplies, and in the summer of 1897 a full cargo of quebracho wood by sailing vessel was secured, while plans for new and heavier machinery, with which we hoped to overcome the difficulties had with the original shipment, were made. Before our first direct vessel had completed her 90 day passage to New York from Buenos Aires, with a full cargo of some 700 tons of logs, I had started for the Argentine to investigate the source of supply so that if quebracho extract—some day—became really popular we might be intelligently informed as to conditions governing the raw material on its home ground.

On my way down via Europe, I stopped in Germany and found tanners there using quebracho quite freely but chiefly in the form of shredded wood which they dusted over their hides, laying them away dry in the vats and running liquor in later on. Some of these tanners had their own sawing and shredding machines, with a supply of quebracho logs in their yards, but in most instances they bought the shredded wood in sacks from some neighboring manufacturer who had charged them prices which none of our tanners here would have considered. Some of the German extract makers were at this time turning out quebracho in extract form but I gained the impression during my limited stay there that the ground wood was more generally popular in the tannery than the concentrated extract.

After a voyage of three weeks from the English Channel, I reached the Argentine on New Year's day, '98;—to find it still suffering from the effects of the Baring panic of five years before. Buenos Aires, however, was a thriving city of a million people, a good deal of the size and shape of Philadelphia, and I was much impressed in finding such a modern and splendid city in a part of the world that was at that time unfamiliar to most of us. Few of us, I think, realize, that the Argentine Republic is of about the same area as the entire eastern half of the United States, bounded by the Mississippi River on the West, and yet that vast country to-day contains only some 5,000,000 people, fully one quarter of whom are concentrated in the one city of Buenos Aires. After becoming acquainted in the capitol, I spent several months 400 to 800 miles North, and found there a rude wilderness of forests, plains, rivers and locusts, which latter were so thick at that time that they actually stopped the train on which I was traveling, and swarmed through the cars like flies.

The quebracho districts of the Argentine cover a wide and comparatively level area in the northern central, and semi-tropical portions of the Republic and some of them are so vast that exploring expeditions have gone into these forests never to return. Much of the territory consists of rich alluvial lands running back from the Parana River, and the saying with regard to the soil is that you merely have to "stick your cane in the ground to see it sprout." In fact, nature in one of her prodigal moods—seems to have spread over the surface of this whole district, a blanket of so-called black earth of the darkest color and richest quality to a depth of less than two feet, and it is in this thin stratum of top soil that the quebracho trees spread their roots almost horizontally (to avoid the underlying beds of sand and clay), and from it that they draw the 18 to 25 per cent. of tannic acid comfortably tucked away in their solid hearts. Quebracho trees are largely predominant in this locality, remind one of the live oaks seen in some of our Southern States, and flourish amid the thickest sort of high underbrush. They are of extremely slow growth, sometimes increasing only a few inches in diameter in a generation and the trees now being used for extract purposes run all the way from 200 to 1000 years old. Consequently, experiments in cultivating quebracho trees from the seed are not likely to become popular, as no one would live long enough to see a seedling grow much larger than a clothes pole.

Most of the 15,000 odd miles of railway, to-day existing in the vast area of the Argentine, are laid on quebracho sleepers, and the story goes that it was a pile of sawdust near a saw mill making these ties that was originally responsible for the discovery that quebracho wood was a good tanner as well as a long-lived sleeper. Back in the early 80's some wide-awake scientist, so they say, saw a yellow looking brook running out of a sawdust pile after a downpour of rain, wondered what caused the color, tasted the water, and immediately found the astringent qualities of tannic acid. This sawdust pile and the rain water constituted the first extract factory in embryo and it was a short step from this to making experiments with the sawdust for tanning. Thus, to-day the wood is of quite as much value to the leather man as it is to the track layer—notwithstanding the fact that quebracho sleepers sell for about $1.25 apiece, and are indispensable to Argentine railway construction. Unlike our own ties, which are laid in stone ballast to let the air in and keep them dry, quebracho sleepers are completely buried in the earth to protect them from the air and keep them moist, in which condition they will last no one seems to know how long. At one of our recent expositions quebracho ties laid over 50 years ago were shown in good condition. Holes must be bored for the track spikes as otherwise they could not be driven but once that the spike is in place, the tannic acid in the wood acts on the iron of the spike so that it becomes an almost permanent fixture. If *tanners* do not want quebracho, therefore, the Argentine *railways* do, but with the demand that has sprung up in the leather trade of Europe and America for this material to-day,—the Argentine roads do not find it so easy to obtain the large quantities of ties necessary for their extensions at as fair prices as they did a dozen years ago.

The export to Europe from the Argentine of quebracho wood for tanning purposes had already begun to assume importance in 1897-98 and some 180,000 tons were shipped out of the country, mostly to Germany and Italy during those years. There were, at that time, two or three small extract plants located in the forest districts working irregularly and under comparatively crude methods, but neither the United States nor Europe had as yet been quickened to the use of quebracho extract, and reports indicate that only about 1200 tons of extract left the Argentine during the above mentioned period. It is interesting to note, however, that in the decade following, the number of extract plants has increased to about ten,—big and little, not including the large plant our own Company have just completed in the heart of the extensive area of quebracho forests which we found it necessary to acquire some years ago to assure us of an independent supply of raw material.

The plants more recently built in the Argentine are quite different from the earlier structures, and in the main are solidly constructed and costly. Not only the expense of transportation to the forest districts from Europe and America of the machinery necessary for these plants is heavy, but they are located at points so remote from civilization that important settlements must be built around each factory. Railway or river connection with the outside world to the South is essential and the enterprise, therefore, is apt to include the building of branches from the main trunk line or from the river to the factory site. Furthermore, the necessity of supplying these communities with provisions, constitutes a serious question and the actual cattle necessary to provide meat for the many hundred men working in or around an Argentine quebracho factory means that the ranching business is a most important adjunct to local extract manufacture. The store, buildings, dwellings, sawmills and other equipment necessary to the enterprise, in fact, require such an important cash investment that the business of making quebracho extract is practically confined to the hands of the few who were first on the ground, who have survived the floods, droughts, and other difficulties which surround pioneer work of this character and who are not fearful of burying their money in the backwoods of a foreign country miles from anywhere.

And speaking of dry seasons and wet—it seems as if the quebracho districts of the Argentine were either in the throes of one or the other of these natural phenomena all the time, and they often seriously reflect on the production of both quebracho wood and extract. The droughts deprive the bullocks used in operating the forests of grass and water and they either die off or must be driven away to outside pastures, thereby stopping the movement of logs from the forests to the factory or the railway. During the past ten months, for instance, an unusually severe drought has spread over the Argentine generally and not only has caused the death of several millions of sheep and cattle in the central districts of the Republic but has left its mark in the quebracho country, making the wood both scarce and high. Prior to this long drought there occurred a series of rains and floods in 1905, which turned the forests into seas of mud and water, making operations difficult over a long period for quite a different reason. And as all of this country is so very flat that the water won't run off when the rains cease, it becomes at such times a matter of patience in waiting for the sun to dry up the landscape sufficiently to permit of a resumption of work. So in the Argentine it is generally one thing or the other, and few of the American consumers of quebracho extract realize the amount of patience and resource, in addition to capital, necessary to produce in quantity this remarkable tanning extract, which has almost revolutionized the heavy leather industry of the country in one short decade.

In the twelve years that have passed since we cut our first quebracho log—steamers carrying 4000 to 6000 tons of wood or extract to America or Europe have supplanted sailing vessels, carrying a meagre 1000 tons, and starting as we did with one small sailing vessel cargo of wood in '97 our Company is now running practically two direct steamers a month from the River Plate to New York, bringing full cargoes of our own each trip. In addition—the imports of Argentine-made extract have increased from 1,000 to 50,000 tons annually, and what the leather trade of this country would to-day do without this material is hard to say. This is shown by the fact that during 1907, according to the report from the Census Bureau, about $5,000,000 worth of quebracho extract was used in this country out of a total extract consumption of approximately $9,000,000. The quantity of bark used during this same year is put down at about $11,000,000 so that quebracho constitutes fully a quarter of the entire money value of bark and extracts used in 1907. Figures for 1908, on account of the relapse of business following the panic, are not of comparative value.

So much then for the general sequence of events in a short resumé of quebracho production, and now for a few words as to developments in its application in the American tannery.

In the early attempts to introduce quebracho it must be said that those who sold it, including ourselves, were not acquainted with the peculiarities of this unusual material. In like manner the tanners found in attempting to adapt quebracho to their old and established processes it was like playing with fire. At the very start the barkometer played them false, for a quebracho liquor of a given density in barkometer degrees turned out to be half again as strong in tannin as a oak, hemlock, or other liquor of the same density. Consequently, the early days of quebracho usage resounded with the woes of tanners who found their leather shriveling up from the use of this new extract with a difficult name. It was not long before there came to be as many different opinions about the merits and defects of quebracho as there were users, and it was not at all difficult to find two tanners on opposite sides of the street flatly contradicting each other as to the results produced by this new tannage. One said it made his leather hard and brittle with no fibre,—another said it left his stock soft and spongy, while another reported that it plumped his hides but made no weight, and another that it flattened his leather out and failed to penetrate below the surface.

Not being tanners ourselves we for a long time could only look on, hold our breath and say in a general way that it could not be the fault of the extract but of the manner in which it was handled. Claims for leather damaged by quebracho were not infrequent and several important consumers who had taken considerable quantities of this extract at the outset actually threw it out of their tanneries, bag and baggage, only to come back to it months later when their neighbors, who had more successfully studied its peculiarities, made a success of its use.

Quebracho difficulties seemed to be largely that it was too strong, too penetrating, *too sweet* and too rapid in action for most of the old guard, whose fathers and forefathers were wedded to the slower-going bark tannages in which the acid forming bacteria were born, grew old and passed away into ferment before the hides were metamorphosed into leather. The constant presence of natural acids in their vats tended to keep their hides plump no matter what happened. No exact knowledge of the period that a hide should remain in one layaway before it went to a stronger one seems to have been common and reports go to show that much of the time in the old slow process the hides were actually doing nothing. Quebracho, on the other hand, contained little or no acid forming matters, did not ferment, and worked so rapidly that for its successful employment an entire revision of old systems became necessary. This opened up an entirely new vista to the old tanning industry, for quebracho actually *demanded* that the time of tannage be reduced and demonstrated that under proper manipulation it could aid enterprising tanners in greatly increasing their output without the addition of equivalent equipment, thereby releasing important amounts of capital tied up in hides and leather, formerly undergoing the longer process.

After working in the dark for two years or more following our advent into the quebracho business, we found that if we were to talk quebracho intelligently we must ourselves investigate its actual workings in leather manufacture. We, therefore, devoted some $25,000 to equipping and operating a small tannery, with a capacity of 50 hides a week, in one of our spare factory buildings;—and I mention the amount involved only to show that our experiments were not trivial but were conducted along the broadest and most practical lines. A complete chemical laboratory outfit formed part of our equipment and for three years we maintained in this small plant a straight quebracho tannage on heavy leather, including harness, belting and sole. In our experiments we not only had the counsel of practical tanners but also of practical chemists, who had for years made a thorough study of tannery liquors and tannery conditions, with a view to eliminating waste of time and waste of material. Our idea was to prove that a satisfactory piece of a heavy leather could be produced with nothing but quebracho extract in a minimum time and at minimum cost, and I believe our records will show that we fairly demonstrated this fact. Drum tannage at that time was in bad odor so that in our experimental work we used vats only. Not to go into lengthy details, we found that if our hides were properly prepared in the beamhouse and properly plumped in liquors made sour by artificial means, they would hold their plumpness in the yard and become properly tanned, *if* the quebracho were fed to them as fast as they needed it. Our experiments worked along the lines of determining exactly the proper make-up for each of the several liquors used at various stages of our process, and the proper periods that hides should remain in each liquor before going to a stronger. Uniformity was our keynote and we worked with hides of uniform weights and with liquors uniform in their make-up which stood at uniform temperatures in hot weather and cold. Our weakest liquor stood at about 7° barkometer and our strongest at about 30. Between these two points the hides had feedings from eight liquors at regular advancing strengths, and were shifted twice a week during the four weeks they remained in our yard. During the latter part of our experiments they were not even hung in the weaker liquors but thrown in flat after coming out of the color. Old fashioned tanners did, indeed, marvel at our short three and four day layaway—if in fact, anything as short as three days could decently be called a layaway,—but from light Texas hides we regularly produced solid, well filled leather with excellent gains which sold at market prices. This leather was both plump and of good texture, and our loss in tannin between what the hides theoretically required and that which we actually gave them, from all causes, was reduced to a minimum. Our liquors were sweet all the way up the line and the leather did not fall back in process as often happens when quebracho is improperly used, largely because we did not starve our hides but *fed the tan to them as they needed it,* and in the quantities they needed it. This, I believe, is one of the secrets of quebracho tannage not readily appreciated.

In the old-time, slow process bark tannage, the loss in tannin between the theoretical and the actual, due to fermentation alone, was enormous and in several important tanneries we found that in addition to what was left in the spent bark actually twice as much tannin was being put into the liquors as ever came out in leather. This meant that fully half of the bark piles used were thrown away, not so much by poor leaching but in the fearfully expensive process of securing sour liquors by natural fermentation. And yet in those days tanners looked coldly at tanning chemistry because the low cost of bark had not made a revision of old methods necessary.

But bark grew scarcer and prices advanced. Extract qualities improved and experiments like our own and like those which were begun elsewhere gradually cleared up difficulties in connection with the use of quebracho so that it was not long before consumers who had previously thrown it out of their yards reconsidered and again became users. In fact, our small tannery had not been in operation for over three years before the demand for extract was so great that the supply from both Argentine and local sources was not sufficient to meet it. As our entire output became needed by our customers, we were forced to conclude our tanning operations sooner than intended, but not before we had learned much as to the proper manipulation of quebracho liquors and as to the kind of extract which tended to produce best working results.

It is interesting to recall that almost the last hides which we ran through our process were tanned into belting butts in a 25 day period, making about 70 per cent. gain in the rough. These butts were finished by a prominent belting manufacturer and were first tested for breaking strength against the best grade of oak butts then on the market. The quebracho tanned butts, in a series of tests at Columbia University, showed between 10 and 15 per cent. more strength than the bark tanned butts. At our suggestion these butts were later on made into half the length of a heavy three-ply belt, a second half of which at our request was made of best grade of oak tanned butts obtainable. Then in order to test the two leathers for stretch and general wearing qualities, we bought his belt, marked off with copper rivets a 10′ line on each section, and ran it on our heaviest cutting machines for a period of a year. In this position it was given the heaviest kind of work, as in the process of cutting up the heavy quebracho logs several hundred horse power are alternately thrown on and taken off the belts operating our machines. At the end of the year the belt was taken off and measured in order to see how the stretch in the portion made of quebracho leather compared with the stretch of that made of oak tanned stock. The 10′ section on the quebracho portion of the belt had stretched to 10′ 2″ while that of the bark tanned portion had increased to 10′ 4½″,—showing that the quebracho leather in this long, hard run had stood the stretch test better than the oak to the extent of 2½″ in every 10′.

It was experiments like these that demonstrated what quebracho could do if properly handled, and, as bark has grown scarcer and dearer, the interest in quebracho has increased until the leather industry of this country could not at present do without it. The figures of exports of both quebracho wood and extract from the Argentine for a series of years as given by local trade journals illustrate this fact more than anything that can be said about it.

	Wood, tons	Extract, tons
1892	29,700	....
1893	49,400	....
1894	54,500	....
1895–96	115,369	646
1896–97	114,627	1092
1897–98	184,800	1197
1898–99	146,601	2037

After a lapse of five years note the increased amounts.

1904	289,839	15342
1905	317,520	32855
1906	271,670	58955
1907	301,621	57194
1908	291,423	68626

To keep pace with this rapid development has required revision of organization and constant increase of capital investment on the part of those engaged in the business of producing quebracho extract. The smaller Argentine producers who started with insufficient capital and with insufficient knowledge of conditions, surrounding the marketing of their output in this country and abroad, were badly crippled by the panic of 1907, with the result that the quebracho business of to-day has largely gravitated into the hands of a few important companies, who have the lands and the capital, and the organization necessary to conduct a business complicated with building of towns and railways, or ranching on a large scale and of undertaking all that is meant by pioneer development in a wilderness of forest.

To be personal—we ourselves are to-day the only American firm in the Argentine engaged in Quebracho production and it has become necessary for us to maintain two large and separate organizations,—one here and one there, for the prosecution of this business. Besides a head office in Buenos Aires, where we are in touch with the large English banks and shipping firms, we operate stations and stores at various points in our forest districts to the North, including an important post at our new extract plant recently completed and now the centre of a settlement of going on 2,000 people, whom we have been obliged to house and whose many needs we have to supply. These needs in clude the hotel, the store, the bakery, the school, the small hospital, the butcher shop, from which the meat of nearly 4,000 head of cattle per annum is distributed, and the police station,—from which latter our mounted men make their daily trips around our boundaries and preserve order. Before all this was done, however, it was necessary for us to carry in a branch railway some fifteen miles from the main line, in itself something of a task, particularly from the bridge-builders point of view, as some of the small streams to be crossed, while but a few yards wide in dry weather, expanded into majestic rivers a mile or two wide in seasons of flood. Now, however, we have our own brick railway station and telegraph office, and one mixed train a day reaches our growing town from the South, later to leave on the return trip—picking up at the various sidings along the line flat cars loaded with quebracho logs, on its slow journey down to the river ports 200 miles away.

Similar developments are going on elsewhere under other auspices and while at the time of my visit to the Argentine twelve years ago most of this forest country was a vast wilderness,—much of it now resounds with the sound of the Collins axe and the hammer of the track layer.

How long will the supply of quebracho last? It is hard to tell.

Vast quantities of it exist in the Northern parts of Argentine and Paraguay, but more and more is being used in this country and Europe every year. Once the primeval trees are cut off they are not quickly replaced by new growths, and if they were—the quebracho tree grows too slowly for us or our children to wait for. These great forests with their thousands of tons of wood to the square mile will last many years yet and before quebracho gives out, at the present rate of the world's progress, leather may be tanned by other than vegetable or mineral agents, or may be superseded by some other material altogether. In the meantime, however, those of us who are closest to the business of quebracho production are more than occupied in the endeavor to keep pace with the increasing demand accompanying its unprecedented development.

ABSTRACTS.

Theory of Leather Formation (concluded). W. Fahrion. *Zeit. Angew. Chem*, 1909, [22], No. 45, pp. 2187-94.—

Mineral Tannage.—In studying the chemistry of the double bath chrome process, the action of chromic acid upon hide powder was investigated. This was absorbed, but the product was not leather, for it completely dissolved on boiling 10 hours with water. Hide powder impregnated with chromic acid and left stand 5 days in the air seemed to form some leather, giving a water resistance of 27.5. The author admits that the first action of the chromic acid may be an adsorption by the fiber, but holds that gradually a salt is formed, the hide acting as base. Parallel experiments with 1 gm. of each material showed that paper and cotton absorbed no chromic acid, while silk took up 14.2, wool 33.0 and hide-powder 33.3 mgs., the amount absorbed increasing with the basic character of the fiber. Neutral chromate is not permanently absorbed, as Stiasny has also shown. Further experiments showed that following the salt formation an oxidation of the hide takes place. Portions of 1 gm. each of hide-powder were exposed to the action of chromic acid for different periods and the free chromic acid remaining titrated with alkali (phenolphthalein indicator); the whole was then acidulated and the peroxide titrated in the usual way iodimetrically.

	CrO_3 used up as acid	CrO_3 used up as peroxide
9 hours	3.2	2.7 mgs.
15 hours	9.2	8.4
15 hours (partly in direct sunlight)	16.4	13.4
30 hours	13.2	10.6
3 days	22.4	14.3
5 days	29.1	21.0

In the double bath process, the action of the chromic acid on the hide does not proceed far, being interrupted by the reducing bath. The tanning process is essentially the same in either process, hence only the single bath will be further discussed. Chromium sulphate is the real tanning agent. This is dissociated by water, the tannage being accelerated by alkali, showing that free chromic base is essential. On impregnating cotton, silk, wool and hide-powder with pure chromium sulphate (Merck) and igniting the products, the ashes were increased by 0.24, 1.11, 0.37 and 7.52% respectively. Parallel experiments with Cr, Fe‴ and Al sulphates gave ashes of 9.23, 2.71 and 1.02%. Only the chrome product showed complete penetration of the reagent. According to the physical theory, the ferric salt should have been the most active from its higher colloidal character. Green chromium sulphate is shown to be a complex salt by its precipitating only about 1/3 its SO_3 with $BaCl_2$; moreover, on drying at 110° it becomes totally insoluble in cold water. Hide itself by catalysis probably produces and precipitates this dehydrated complex salt. To approximate practical conditions, tanning experiments were made with a solution of 10 gms. chrome alum and 1 gm. soda in 150 cc. water acting upon 5 gms. of hide-powder for 6 days. The ratio of Cr to SO_4 in the product was 52:146, nearly that for neutral sulphate; leather had not been formed, however, for the product had a water resistance of only 2.4. On first deacidifying the product with borax, as is done in practice, the residue was found to have a resistance of 93.3, the ratio $Cr:SO_4$ being 52:58, or even lower than in $Cr(OH)SO_4$. This shows that basic salt is essential. The author finally concludes that in the single bath process, the end product is a condensation of the hide molecule with basic chromic oxide. Alum tanning is considered to be fully analogous, the tannage being less perfect because of the lesser inclination of Al salts to hydrolysis and formation of complex anhydrides.

Conclusion.—Leather is animal fiber which after treatment with water and drying, remains soft and flexible and then on boiling with water yields no glue. Tanning is essentially a chemical process; physical processes, such as colloidal adsorption, are essential to bring the reagents in contact, but leather does not result until chemical action ensues. This involves an oxidation with water formation, the tanning agent directly or after a transformation supplying the oxygen, the hide furnishing the hydrogen. The final result is a complex condensation product. In "pseudo-tannage," the chemical nature of the hide is unchanged, as in tanning with phlobaphenes for example. By the action of water, the precipitated pseudo-tans are withdrawn and the hide yields glue.

Adsorption in Solutions. J. PAESSLER. *Collegium,* 1909, Nos. 383-4, pp. 379-82, 385-9.—Following Freundlich, the author outlines the theoretical conceptions employed in the study of these phenomena. Adsorption means a change of concentration (only solutions are discussed here) brought about by contact with another substance. In an ordinary solution at rest in a vessel, the concentration is the same throughout, except in the outer boundary layer, which differs in properties from the rest of the solution, and therefore has probably a different concentration. This layer, however, is extremely thin (10^{-6} mm.) and ordinarily this local change in concentration is negligible, not being evident. By introducing, however, such a material as powdered charcoal, the boundary surface becomes enormously multiplied, and the change in concentration may be made evident by separating the charcoal (by centrifuge) which retains the surface layer, and examining the residual liquor which in almost all cases becomes less concentrated. Other adsorbents besides charcoal which have been studied are infusorial earth, clay, meerschaum, wool, cotton, silk, alumina, hide-powder, etc.

The amount of adsorbed substance contained in the surface layer is computed directly from the loss of concentration in the residual solution. To determine the concentration in the surface layer, this layer may be assumed as proportional to the amount of adsorbent taken. Then if x represents the amount of adsorbed substance and m the amount of adsorbent (charcoal), then $\frac{x}{m}$ represents the concentration. If values $\frac{x}{m}$ be plotted as ordinates to the corresponding concentrations c of the residual solution as abscissae, a curve is obtained ; for low values of c, $\frac{x}{m}$ increases fastest, but with higher values it increases more slowly. This is expressed by the equation $\frac{x}{m} = ac^{\frac{1}{n}}$, where a and $\frac{1}{n}$ are constants dependent upon the natures of the adsorbent, solvent and dissolved substance. Expressed logarithmically, the above equation transforms into $\log\frac{x}{m} = \log a + \frac{1}{n}\log c$, the equation of a right line.

This may be utilized in graphically adjusting the errors of observed values. The equation for $\frac{x}{m}$ is identical in form for that representing changes in surface tension of solutions of various concentrations, a proof that adsorption may be regarded as a phenomenon pertaining to surface. This is also confirmed by the fact that during adsorption all chemical substances behave alike in rapidly reaching the end concentration c. If this is long delayed, chemical decomposition is suspected and has been detected in all cases. Exceptions to this appear only in the case of colloids which have unfortunately been little studied.

The adsorbing power of different materials naturally varies greatly, being dependent upon the character of the surface. Different substances are in general differently adsorbed by various adsorbents, but the same relative ratios are preserved. Adsorption is lowered with increasing temperature. The adsorption of dye-stuffs by fibre has been found to obey the general law. Hide-powder also takes up various substances, especially acids, according to the same law. The author has found similar results in the adsorption of tannin by hide-powder.

$c\left(\frac{\text{gms. tannin}}{\text{liter}}\right)$	$\frac{x}{m}\left(\frac{\text{mgs. tannin}}{\text{gms. hide powder}}\right)$	
	found	calculated
6.59	684	689
4.26	574	583
1.39	388	394
0.81	333	322
0.52	281	281

Study of Tanning Extracts (continued). U. J. THUAU. *Le Cuir*, 1909, [2], No. 18, p. 426.—An Austrian chemist, Dr. Pollak, (patent of Redlich and Pollak) discovered that quebracho extract could be made totally soluble without use of sulphites, small amounts of alkali being substituted The process, as carried out at the Wilsdorf factory, consists in allowing the hot diffusion liquors to cool and deposit, and then separately heating the sediment for 6 to 7 hours with about 1% of alkali reckoned on the original liquor. A clear liquor of a rich red color is obtained. Of this about 50 liters are added to 1000 liters of the original decanted liquor, producing immediately a precipitate. This settles after several hours, leaving a very clear liquor, and the sediment may be treated with alkali and used anew for clarifying fresh liquor. The clarified solution is concentrated as desired, even to the solid state, and remains totally soluble in the cold. The surplus of the dark red alkaline solution of the sediment is utilized by mixing with acid liquors prepared from sumac, bark, woods, etc., with addition of acetic acid, if necessary, to completely neutralize the alkali. The sediment from this mixture contains no useful tans and the liquor may be concentrated as desired. The author has found the products of this manufacture to produce good leather of high rendement.

Color Reaction for Gelatine. R. E. LIESEGANG. *Collegium*, No. 386, p. 402.—Ordinarily a mixture of cupric chloride and excess of tripotass. phosphate give a whitish-green precipitate of cupric phosphate; in the presence of gelatine, a violet color ensues. To a mixture of 14 cc. 40% phosphate and 1 cc. 10% cupric chloride, 20 gms. of 10% coagulated gelatine were added. The next day the jelly and the fluid were colored strongly violet, with decrease of the precipitate. If gelatine is used in aqueous solution, it is precipitated by the dehydrating action of the phosphate; the color reaction is the same.

Sulphite Cellulose Liquors in Tan Extracts. ANON. *Ledertechn. Rundschau*, 1909, No. 46, pp. 361-2.—The recent paper of Proctor and Hirst (reprint this JOURNAL, 1909, [4], p. 146,) is harshly criticised as throwing discredit upon "pinewood extract" in general without a broad investigation of the entire subject. The writer attributes the defects in leather made from the extract examined by the English chemists to the presence of lime. A properly manufactured lime-free extract is declared to be suitable for producing good leather when combined with other materials, especially untreated quebracho; the difficult soluble tans in this are dissolved and the quebracho red is toned down to a desirable leather yellow. Pine bark itself is alone a poor tanning material; if its reds were removed, it would also show as poor results by the Löwenthal method as those cited by Procter and Hirst for the pine wood extract.

Leather in Air Ships. FERD. KOHL. *Collegium,* 1909, No. 380, p. 353.—For aeroplanes and the outer envelopes of dirigible balloons, thin chrome leather is incomparably stronger and more durable than cotton or silk, and does not absorb moisture. The writer believes it feasible to prepare a chrome leather which will serve for the balloon itself, dispensing with the outer casing, and calls the attention of the inventive leather technologist to this promising field.

Adulteration of Shellac with Rosin. *Le Cuir,* 1909, [2], No. 19, p. 452.—This may be detected by dissolving 200 gms. of the lac in 400 gms. 95% alcohol, adding 30 gms. spirits turpentine, 30 gms. raw linseed oil; a little of the mixture is placed on a wad of cotton and then rubbed over a smooth board of hard wood. With pure lac, the rubbing may be continued without resistance until dry, but if rosin is present, when the alcohol has evaporated, the varnish becomes more and more resistant, sticky and gummy, only drying after a time.

Chrome Goatskins. FERDINAND KOHN. *Ledertechn. Rundschau,* 1909, No. 39, pp. 305-7.—At the start a careful sorting is essential so that all the hides of a given lot are uniform. Dried hides after soaking a day are further watered in the wheel and finally in water containing a little caustic soda. Salted hides do not require the milling. An old lime sharpened with arsenic is first used 3 to 4 days, followed by 5 to 6 days in a fresh white lime. After dehairing a fore-bate of dog-dung is necessary for hard, good hides, then follows the bran bate. A good substitute is erodin bate (Popp & Becker). The de-liming is important and often does not receive sufficient care; phenolphthalein afterward applied to the hide should not redden. The hides are next milled 3 hours in a pickle of 10 k. NaCl, 2 k. HCl in 150 l. H_2O. For the stock tanning solution, 20 k. chrome alum, 3 to 5 k. potass. chromate, 5 k. glycerin, 2 k. 40% formaldehyde are dissolved in 50 l. water. The drum liquor is first made up to 1 to 1.5° B. and later gradually brought up to 3 to 4°. The reduction of the chromate with antichlor is carried out in a separate drum. This combined single and double-bath process gives increased fullness of chromic oxide in the leather. Finally the leather is milled for 1 hour with 1 to 2 gms. calcined soda to 100 k. in sufficient water. The total time of tannage is 4 to 6 hours. The regular double bath system may also be used; in this case the hides are apt afterwards to show an irregular color and if they are to be dyed bright, must be lightened by milling in luke-warm water containing sufficient HCl. After splitting, the acid is removed from the leather by milling with borax solution at 28 to 30° C.; this is important and should be controlled by a litmus test. If acid be left in the leather, it precipitates the dyes later and acts on the fat emulsion as well. Specific directions follow for the dyeing with Cassella's colors.

PATENTS.

Leather-Staking Machine. U. S. Patent No. 941,851. A. C. BRILL, Oberursel, Germany.

Evaporating Apparatus. U. S. Patent No. 942,407. C. ORDWAY, New York.

Dressing for Leather. French Patent No. 402,292. A compound of gum lac and an alkali, which is then mixed with a soap and dye. The product is a solid soluble powder.

Increasing the Hardness of Leather, Etc. French Patent No. 402,460. L. KRAJEWSKI. The leather is impregnated with finely powdered inert material (such as carborundum), and is then heated with a binding agent.

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W. H. TEAS . . . . Editor and Manager

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The American Leather Chemists Association

G. A. Kerr, W. H. Teas, H. C. Reed, J. H. Yocum, F. H. Small . . Past Presidents

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President—H. T. Wilson, Lock Haven, Pa.

Vice-President—J. H. Russell, San Francisco, Cal.

Secretary-Treasurer—H. C. Reed, Stamford, Conn.

Council—G. A. Kerr, Lynchburg, Va.
F. H. Small, Worcester, Mass.
R. W. Griffith, New York.
W. K. Alsop, Ridgway, Pa.

ELECTIONS

The following have been elected to membership in the Association:—

ACTIVE

C. A. Reisig, 2 Colliston Road, Brookline, Mass.

ASSOCIATE

J. S. Robeson, Au Sable Forks, New York.
Willis R. Fisher, 95 South St., Boston, Mass.

CHANGES OF ADDRESS

G. Wackenreuter to 145 West Kinzie St., Chicago, Ill.
A. Sandig to 12 West Kenzie St., Chicago, Ill.
C. Propach to 146 West Kenzie St., Chicago, Ill.
W. P. Maxwell to 323 West Church St., Lock Haven, Pa.
Dr. August M. Kilp to 8 West Long Av., DuBois, Pa.
W. F. Wilson to c/o J. H. Heald & Co., Lynchburg, Va.
P. F. Reilly to Orthodox St. & Delaware River, Philadelphia, Pa.
Charles S. Forsyth to 586 Astor St., Milwaukee, Wis.
Thomas A. Faust to 323 Academy St., Newark, N. J.
Dr. Lous E. Levi to 192 Twenty-second St., Milwaukee, Wis.

COUNCIL PROCEEDINGS.

COUNCIL MEETING, JANUARY 3, 1910.

Present; Messrs. Wilson, Reed, Alsop, Griffith, Small.

Voted to refer the proposal to change from basic lead acetate to normal lead acetate in precipitating tannin in sugar determinations in leather analysis, to Committee on Leather Analysis.

The Provisional Method of Sampling proposed at the annual meeting was discussed, no action being taken as this is provided for by the By-laws.

The proposal to make certain changes in the Method of Leather Analysis was discussed and referred to the Committee on Leather Analysis. It was voted to approve the change suggested by Mr. Alsop in the official method for acidity, namely, to substitute the so-called gelatine-hematine method for the present method. Under the by-laws the change does not become operative unless so voted by the Association.

Voted that a committee of three be appointed to revise the by-laws with especial reference to Section 6 and Section 23. The President reserved the appointment of the committee to a future date. The change in Section 6 of the by-laws is to enable members not present at a meeting to vote for officers by proxy. The change desired in Section 23 is to permit provisional methods to official methods which is not allowable under the present by-law.

It was voted that the Council sanction the method proposed by Mr. Reed for the analysis of sumac and kindred materials as a provisional method. The provisional method for the analysis of sumac and kindred materials proposed by Mr. White came in for discussion. Both proposals are to be voted upon by the Association prior to the next meeting.

The matter of holding a joint meeting of the Association with the National Tanners' Association was discussed, the Secretary having been instructed by the Association to correspond with the Secretary of the National Tanners' Association for the accomplishment of this purpose.

It was voted that the Secretary be instructed to correspond with the members of the Association to find out whether there is any sentiment for or against reporting of analyses to the first place in the decimal.

It was voted to accept the annual report of the Editor.

It was voted that the Council follow the instructions of the Association and refuse to accept the resignation of the President.

The question of the conflict between the use of 12 to 13 grams of dry hide per 200 cc. of solution and of the non-tannin giving a precipitate with gelatine-salt when the official method is followed, was referred to the Committe on Hide Powder for investigation.

It was voted that the front cover of the JOURNAL be not given over to advertising purposes.

It was voted that the Secretary be instructed to obtain as exact an estimate as may be possible as to the amount of money which the Editor of the JOURNAL can be allowed for the preparation of Abstracts for the coming year and to report the same to the Editor and that it is the sense of the Council that the Abstracts should cover the field as completely as possible with the funds available.

It was voted that Mr. Small's resignation as Chairman of a Committee to co-operate with a Committee of the I. A. L. T. C. on the preservation, cure and disinfection of Hides, be accepted and that Mr. Wallin be appointed Chairman of said Committee and that Mr. Small be instructed to turn over to Mr. Wallin all the data in his possession and further, that Mr. Wallin be requested to report back his findings to the Council with recommendations.

The following Committees were appointed:—:

Leather Analysis.—Mr. Veitch, Chairman, with power to select his Committee.

Detection of Ingredients in Tanning Materials.—Mr. Dean, Chairman, with power to select his Committee.

Color Valuation of Tanning Materials.—No Committee appointed. (Council thought it best to allow the new provisional method to work itself out.)

Determination of Acidity of Tan Liquors.—Last year's Committee retained with Mr. Alsop as Chairman, and the question of the preservation of liquors and the proposed alterations in the methods of sampling them, referred. It was suggested that further work be done on the question of an indicator. The measurement of the plumping effect of liquors was also referred to this Committee.

Oils and Fats.—Mr. Alsop, Chairman, with power to select his Committee.

Natural and Artificial Acids.—Mr. Griffith, Chairman, with power to select his Committee.

Chrome Methods.—Mr. Sadtler, Chairman, with power to select his Committee.

Chroming of Hide Powder.—Mr. Oberfell, Chairman, with power to select his Committee.

Rapid Cooling of Tan Solutions.—Mr. Maxwell, Chairman, with power to select his Committee.

Filtration (Asbestos-Kaolin Method).—Mr. Maxwell, Chairman, with power to select his Committee.

Acidity of Hide Powder.—Mr. Fox, Chairman, with power to select his Committee. The question of fixing a definite acidity for hide powder and a smaller limitation of the amount of dry hide used was referred to this Committee. Also the investigation of the effect of the dilution of the solution and the amount of hide powder on the resulting non-tannin, referred.

It was voted that the Council extend to its Vice-President, Mr. Russell, through Mr. Griffith, its cordial good wishes.

ENGLISH METHODS OF TANNING.

By F. A. Vogel.

In taking up the subject of English methods of tanning, I wish to confine myself more closely to the sole leather methods, because this is probably the most important and most advanced state of the leather industry in England. But that is not the only reason I wish to confine myself to sole leather; the other reason is because that was the one line that I followed at the time I attended Herrold's Institute in London, and Dr. Parker was very kind to me at the time and helped me a great deal in getting on to the English system of tanning.

I am not much of an orator, and I will confine myself to reading to you what my experience was and what I learned while there.

Of course we all know that the English sole leather bend has for years been considered the standard of manufacturing perfection as far as sole leather is concerned. It is worked out admirably, lays out absolutely flat, has good color, (the better tannages at least) and of fine plumpness and firmness. In fact the entire product of the little island is the outcome of highly specialized conditions brought about and extenuated by peculiar local circumstances.

In introducing my subject, I desire to trace the historical development of the English sole leather industry, and from which, by the way, I desire to draw a little comparison with our own later on. In years gone by England tanned for the English with raw materials, using their own oak bark and exported no leather. Their methods were primitive and their leather was good, but it took them a long time to tan. Still the leather was plump and wore well; however, the gains were poor.

Along in the early 80's, however, the English bark supply, which was oak began to diminish at a very rapid rate, and our British cousins began to look for substitutes. This need of suitable substitutes is no doubt a trying one and one felt by many of us here to-day.

They found first of all, valonia, the nearest material to oak that they could use. Then followed myrabolams, hemlock extract from Canada, continental chestnut and oak extracts, colonial tanning materials and extracts, such as mimosa, mangrove, divi. divi. algarobilla, mallet bark, and last but not least, quebracho. In order to put this condition more forcibly before you, gentlemen, I wish to ask you a question. Supposing that hemlock bark would suddenly jump to $15.00 per cord, a fact which would eliminate it from the tannery material list provided other materials had no such corresponding advance, what would we do? This is exactly what happened in England, oak bark was no more obtainable and other materials were necessary. How did they meet the situation? Mind you, it was far more difficult for them because the old-fashioned oak bend was already perfection, as to plumpness, color and wear. They had Dr. Proctor and Dr. Parker, both experts and men who willingly gave advice and counsel when needed, Dr. Proctor highly scientific, Dr. Parker intensely practical, and an extract expert of no mean ability. Between these two gentlemen, the English sole leather industry attained that point of perfection in a mixed tannage which places it in a class by itself.

From the straight oak bark tannage they evolved a system of mixed tannage that is very complex. They use valonia and hemlock, oak extract and chestnut extract for weight, myrabolams for plumping and algarobilla for color and mangrove for penetration. Before going into the details of manufacture, I just wish to draw a parallel between the evolution which took place in England some years ago, and the evolution which is now going on in sole leather tanning in this country. Where is our old fashioned hemlock side? Our good old solid leather made with 70 per cent., 75 per cent. gain. It is gone, and in its place we have an indifferent side of mixed tanned leather, produced by the judgment of individuals, indifferent as to wearing quality, color and nicety of appearance, many poorly rolled and poorly trimmed. Still we are in the running because it supplies a need, it is cheap, well weighted and cuts to advantage. By this I mean it yields a good percentage of No. 1 soles and shoe manufacturers both in this country and in England like it because it is workable. We have worked out our problem individually without aid of certain few individuals directly, but if we honestly ask ourselves, we must admit we have profited immensely by the experience of our English cousins. Despite this fact, our memories are not that bad that they will not recall the fact that quantities of poor leather were thrown on the market due to extract tannage when first tried. How many of us introduced oak extract and quebracho into our liquors at random and with what disastrous results as to plumpness, color and grain.

If we seriously think of the similarity in the changes which took place in England, I think more of you will readily agree with me that the historical development of the use of varying tanning materials, both in England and in this country, have a close resemblance. Before I take up the question of extract and foreign materials as used in England I wish to briefly enumerate the British process as taught me by my friend Dr. Parker.

The process in use in England is, or was, really two-fold. One was the old West of England, the old valonia tannage and the other is the present mixed Warrington or North of England tannage. The first tannage is now pratically extinct, Evans of Bristol being one of the last to drop it. This tannage made an exceptionally fine piece of leather. The raw material used was the best, plumpest, of South American and Liebig or Continental hides, and the process of tanning consumed almost a year. This method was in use up to 1906 and I can say exists in a small way to-day. It was the tannage that the old fashioned oak bark man adopted after he lost the bark.

Briefly, the method of tanning was this, after thoroughly softening the dry hides, they are soaked like the salted, namely four days, handled each day and every time they come up they are laid out perfectly flat. I must not forget to tell you that all hides for sole leather in England are worked whole. The hide is laid out flat every time it comes up in order to make this nice even, smooth, leather for which the English are known. After the fourth day's soak the hide goes into the lime. These limes are absolutely cold and very strong but clean and fresh. The first lime in which the hide remains is the old lime of the pack removed to the unhairers. In this they remain one night. They are then hauled out again perfectly flattened out and allowed to remain in this manner until evening. That is one way of getting this perfectly flat, even bend that they ultimately get. They start not only in the soaks and lime yards, but they keep it up right through the tannery. Then they are again carefully put in the pit which has been made fresh with a lime which equals 10 pounds of fresh lime per hide. In this they remain four to five days without being disturbed. It is very important that the hides are allowed to settle into the pit without any folds or creases. After the 4th or 5th day they are handled out, 2 pounds lime per hide added and again put away for about one week. The hide is now thoroughly limed and ready to be unhaired. The entire liming consumes from ten to twelve days.

After unhairing and fleshing which was done during my stay in England, 1905, largely by hand, the ordinary beam knives being used for unhairing and the spring flesher used for fleshing. I will say this, though, that down in the Evans yard in Bristol I saw a very ingenious fleshing machine, invented by some man in England whose name I do not recall. It had a circular knife like the belt in a splitting machine, only it had teeth in it like saws, and this knife worked back and forth, and as the hide was fed through the rolls this knife would gradually work off the flesh in passing over with a forward and sideways motion simultaneously, so that when the flesh came off it was more like a network. You could lift it right up; it was all in one piece; it was not chopped or broken. But the difficulty with that machine was that when it got to the butt or heavy part of the hide, it would very badly break into the thickness of the hide and thereby destroy the plumpness. The sides are then folded along the back bone and cropped in a manner that yields whole shoulders and straight cuts in the flanks. The bellies are cropped so that the soft parts of the flanks are cut off entirely. This makes a trim on these plump hides of about 50 per cent. This brings us to one of the most interesting phases of English tanning development. They tan the butt, the best part of the hide, with extra care and labor. The offal is rushed through as cheaply as possible.

The material used in the butts in this particular tannage is valonia 65 per cent. to 70 per cent. and mimosa and myrabs and gambier 35-30 per cent. The latter materials are used as plumpers and acidifiers because valonia does not plump or sour readily when fresh. It takes a valonia liquor really a month or more to mellow sufficiently to make good full leather. In this aspect it resembles hemlock more than other vegetable tanning material I have had any experience with.

After rounding, the whole bends go to the suspenders where they remain from three to four weeks hung on sticks straight into the vat without fold or bend. Everything in the early stage is done to make the ultimate product firm and level. The first liquor measures 20 B. and contains about .2 per cent. tan and .3 per cent. organic acid. This liquor is built up by the press system to 45-50 B. containing 3 per cent. tan and about 1.50 per cent. acid. The waste liquors from the suspenders are run away and not used again. In the Warrington tannage, however, I have seen vacuum pans installed, which converted this waste liquor into extracts. From the suspender this stock goes to the handlers where it remains four to five weeks. The last liquor is 45 and the head liquor 55. It is the old duster liquor run down to which gambier has been added. The stock here, for the first time is laid out flat in a vat and handled every day. Considerable gambier is added now. It is the first fresh tan given the stock. It is interesting to note that the fresh tan is of such a mellow character as gambier, especially when you think they are making firm sole leather. In some instances I have known as high as 500 pounds of gambier added to an old liquor sufficient to cover 100 hides. The next step is the dusters. Here we have the first attempt at filling the pelt. There are four dusters of one week each. The liquor 60 B., and between each butt there is a dusted mixture of myrabs and oak bark or valonia so that 200 pounds of material is used for 100 butts. The second last step in the process was to me the most interesting, namely the so-called hemlock round. The hemlock round was introduced solely for weight and is another proof of the able paper written by two of Dr. Proctor's students that hemlock is the best weight giving material in the vegetable tans, for it was only after practical experiments that this was introduced and then not in all tanneries. The hemlock round consumes four weeks and four changes of liquor, one at the end of each week. The liquor is made up out of the fresh leaches which yield 35-40° B. To this hemlock extract is added to make it up to 60° B. The first two weeks the stock is handled twice each week and next two weeks only weekly. No dusting material is used, and great care must be exercised that the change in the color of this liquor is not too great, for spotted leather would be the inevitable result if such were the case. One way of overcoming this difficulty is by pumping the old liquors of the hemlock round over the leaches of valonia, mimosa and myrabs and then again adding extract. Out of the hemlock round, the stock goes into the layers.

1. Layer two weeks 60° liquor fresh, 2 cwt. oak bark, 2 cwt. mimo.

2. Layer two weeks 65° liquor 4 cwt. valonia.
3. Layer three weeks 70° 6 cwt. valonia.
4. Layer four weeks 75° 6 cwt. valonia.
5. Layer four weeks 80° 6 cwt. valonia.
6. Layer six weeks 90° 6 cwt. valonia.

From this it is seen that the entire time of tannage consumes 36 weeks. The result is fine plump leather. The difficulties are color and manipulation of liquors. The waste layers are used again in the leaches. The first layer goes to the dusters, the dusters go to the handlers and the handlers to the suspenders. The hemlock round is kept entirely by itself. The material used for dusting is taken to the leach house for leaching. The pelt itself is saturated with tan and analyzes up to 66 per cent. When it comes up the last time, it is allowed to drain 3-4 days. This permits the tan to solidify. After that the butts are rinsed off in a waste liquor, then washed thoroughly by hand.

There are two ways of finishing the leather, either the bloomed or the unbloomed. The method of finishing the bloomed hand scoured butt is as follows. After the butt is washed by hand, it is oiled and hung up until the oil is thoroughly dried in. After that the butts are piled down until they heat. This loosens the bloom and softens the grain, the stock then being in condition for a thorough washing on the grain. This is cleansed and worked down to a certain extent by hand which spreads the loose sediment evenly, filling the grain with the fine dust of the valonia and myrabs. After a second careful oiling it is hung up in the loft to dry which takes about one week. The unbloomed butt is thoroughly washed and then scoured in the Wilson scouring machine which removes the bloom successfully. The loss in weight due to machine scouring is about 4 per cent. Some tanneries try to replace weight scoured out by putting sides into hot sumac liquor about 50° B. for 20 hours or immerse them for the same length of time in treated extracts of about the same strength. The butts are then oiled and hung in a dark cool room until dry. They are then piled down and allowed to sweat until they have a sort of whitish scum. That whitish scum which comes out on leather is due to valonia deposits, so Dr. Parker tells me, and it is hardly explainable; but the fact remains that under heat this little scum comes out in the grain, and it is there. This is again scoured until clean. The slickers this time are not stones but brass. This smooths the grain and does not work out as much tan. The stock is then ready for final oiling and drying. The first rolling is done fairly damp with medium pressure. The butts are now trimmed carefully up the back and dried thoroughly. I mean now all this time the shoulders and bellies were off and the butt was tanned all the way through, split up the back, until the second rolling,—in this particular tannery; in other tanneries they split the butt earlier; but in this case they split it when it was slightly wet, before the second rolling. Then they are rolled finally dry with heavy pressure and delivered to the store. So much for the old fashioned English bend which was gradually abandoned because of large cost of manufacture.

I cannot here go into cost because what information I obtained in that line was confidential, let it suffice that it cost over eight cents per pound on these butts as far back as 1905, not including interest. This put them beyond a competition basis because the Warrington extract tannage was cheaper and quicker.

The North of England or Warrington tannage had reached its greatest development in the Northampton tannery. The Penkieth plant and the North British Tanning Co., Ltd., of Liverpool. In the plant of the North British Tanning Company of Liverpool I saw for the first time a traveling crane in the beamhouse. They had a large travelling crane in the beamhouse and laid their hides away in lime vats which had a crate at the bottom, and when these hides were ready to come out they would hook the crane onto the chains which were fastened to this crate and lift it right out and bring the sides all in, pack by pack, back of the unhairing machine, where they were unhaired. I thought that was quite an ingenious thing to do. Of course the beamhouse construction would have to be adapted for the installation. The beamhouse process here is no different except as to the hides used. Instead of using high-grade foreign hides, they use the green English market hide or the Anglo American hide. This requires less soak of course but the liming is the same. I found one Leidgen machine and one Vaughn drum machine in use in the north tanneries. After unhairing and fleshing they are rounded like previously described. After this the stock is bated lightly in a formic, lactic or acetic acid bate. Here is the first instance we have of trying to hasten the process. They use a mild organic acid to remove part of the lime which the West of England tanneries did with sour liquors. This cuts down the time in the suspenders from the 14-21 days to 4-5 days. The liquor strength is about the same but perhaps a little richer in tan. The barometer strength is 25°-45°. After that the stock goes to the handlers and is handled daily in a 45-60° B. for four weeks. This liquor comes from the leaches and is mixed with the old liquor in the vats. The surplus old liquor goes to the suspenders and from there into the sewer except as stated before that one or two tanneries have vacuum pans for converting of all liquors into extracts. After the handlers the stock goes into the layers which are the dusters at the same time, the materials used for dusting being principally myrabolams. The stock receives three layers, one of two weeks with 65° B., a second of three weeks of 80-85° B. The tanning materials used in this tannage are myrabs, a little valonia and the rest extracts. Possibly mimosa, algarobilla and gambier. The extracts used are principally chestnut, oak-wood and mangrove, some quebracho and mimosa, in fact every conceivable tanning extract known. The method of finishing the butt is the same as the unbloomed butt previously described except that highly clarified extracts and sumac are used hot to replace the weight scoured out. This is tried to far greater degree than in the West of England tannage.

There now remains only the tannage of offal. The shoulders and bellies are hung in the suspenders and then put into a drum where they are drummed first in old liquor and then in cheap extract. The time consumed in tanning bellies is about seven weeks, while the shoulders, especially the better ones, are laid away for an additional period which brings their time up to about ten weeks. This now brings us to tannery cost and estimates. Each day's batch of hides is calculated and a record made of trimmings and butts. The trim is carefully made. The standard or ideal trim can be illustrated in this manner: Take 20 green hides, that is unsalted, weight 1200, green. The beamhouse weight in a good batch of these hides would be approximately 1100 pounds. The English tanner figures that B. H. shrinkage should never exceed green weights by more than 16 per cent. and ought to average 8 per cent., and in the summer it should be a great deal less than that, but it should never average less than 8 per cent. the year round. The trimmed weights on these 1100 pounds should be divided as follows, butt 550 pounds, shoulders 275 pounds and 275 pounds bellies. The estimated yield on the butts is 70 per cent. of the beamhouse weight on a paid green weight basis and when we consider that this is with horns and tail bones on, it is very remarkable.

The estimated yield on the offal is only 50 per cent. On this basis an estimated profit or loss is figured for each lot as the current price for hides and leather plus its manufacturing cost. 70 per cent. beamhouse weight would mean 385 pounds leather which would be divided into the long and the short butt and its extra plump, etc., and figured accordingly. This sheet then goes to the store room and made estimate is compared with the actual yield when the sides reach the store. The cost of the manufacture at the time I was in England was about as follows:—

2.7	Material
.15	Salary
.74	Wages
.30	Maintainance and rent
.10	Depreciation
4.00 d	

This is about the average but I have run across a plant which has made their leather as low as 3.65 d. per pound. This of course is from the North of England or new system of tanning. In the old method it was safe to add a ½ d. to interest charge and at to-day's high price for hides it would probably be ¾ d. additional.

In conclusion I wish to discuss extracts as used in England for sole tannages. Extracts to-day are of more interest to sole tanners than they have ever been before for the reasons previously stated and the English method of handling extract, no doubt, is interesting indeed. When the use of extracts increased in England between 1895 and 1900 tenfold, it was but natural that adulterated extracts should have been made and sold. The results of these poor extracts were discolored leather; flat and empty. The tanners immediately set to investigating and before they knew it they had learned many most interesting things. They learned that chestnut extract from France was better than the Italian, that the oakwood extract from Slavonia was the best of all. They found out that the solid unclarified quebracho was one of the most expensive materials that could be used. They knew this long before we stopped importing tons and tons of the unclarified into the United States. They found that their Colonial descendants were not adverse to adulterating gambier, mimosa, mangrove and mallet bark. In fact, the more diversified the material, the more the tanner learned to be on his guard. After five or six years of patience and fight the atmosphere had considerably cleared and extracts and imported materials came better and they then tackled the two larger problems of even color when using so many different kinds of extracts and to the questions of weight. The color problem they solved by careful blending and gradual introduction of various materials. They did not as it has come to my notice here, run one period six months on chestnut extract, and only a little hemlock, and the next six months on only quebracho and then be really wondering why the color was poor. They always used their lighter colored extract or tanning agents last such as mimosa or quebracho extract. In other words they built up their color. They started with a liquor of a darker shade and gradually, but very carefully, went on until they got to the highest extracts, which they used last.

As regards the weight giving properties of tanning materials, a very able paper was prepared by the two assistants of Dr. Proctor (one here to-day) which illustrated very forcibly that color and weight were not the only desirable qualities in extracts and materials. They found that hemlock bark was the best weight giver, they found that valonia was next and then came the extracts. From this it would naturally follow that this being the case, the two highest weight giving materials in combination would be most desirable. Theoretically, then, hemlock and valonia would make the heaviest leather but such is not the case. I tried it in a small way, got very good color, no plumpness and consequently no weight. If, however, one introduces some myrabs into the mixture, the results are most surprising. This is what the English sole leather tanner knows more thoroughly than we. He knows what to combine to bring results and when you consider that they gain 65-70 per cent. on green weight, horns and tail bones on, it is quite remarkable.

This brings up the question of weights and loaded leather. Dr. Parker, of course, led the fight against American leather loaded with glucose and salts, which attack certainly was resented by us, and we, of course, naturally asked ourselves what are the English doing in this line and of course certain accusations were made. I will tell you frankly that I visited eight of the largest tanneries in the Kingdom and never saw a sugar barrel or $BaCl_2$ or Epsom or glaubers salts. Now they may have fooled me but I did not see it. The only loading of leather I did see was loading with extracts. By manipulations they raised their loading vats and drums to 100° B. and they allowed the hide to absorb this clear clean tan after scrubbing and washing. They use bisulphite extracts to a certain extent but no chemical bleach and the weights they obtain though high are legitimate. This too, must be our view of the loading of leather. Introduce clear tan which certainly makes finer leather and let us study the circumstances which are best to give highest weights so that the tannery can receive the highest benefit.

In conclusion I will say that the English bend represents more labor, more care and more science than our own produce. It will never be copied in this country, nor will it ever be imported in any large quantities. It is too solid and our shoe men at large do not understand the working of this leather nor does it fill a need. The tendency in shoes has been to soften the leather and I do not believe that we need fear an invasion of English sole leather even though there are many good points about this product from which every American sole leather tanner can profit.

COLOR VALUATION OF TANNING MATERIALS.[1]

By G. A. Kerr.

By referring to the discussion following the presentation of last year's report upon the color valuation of tanning materials (JOUR. A. L. C. A., Jan., 1909), and Mr. Reed's paper on the same subject (JOUR. A. L. C. A., Dec., 1908), it will be observed that general opinion favored the necessity for a visual demonstration of color, in order that the tanner could compare the color quality of one shipment of extract or other tanning material with another, and thereby satisfactorily check the color uniformity of different deliveries of material.

From such information as the writer has been able to gather, it is very generally conceded that, notwithstanding the value of sheep and calf skin to the individual as a basis for color testing, they are without value in cases where comparative results by two or more laboratories are demanded, or when a tanner wishes to check the uniformity of color of a series of shipments covering an extended period.

Therefore, in proceeding with investigations this year, these methods, as well as those involving mathematical expression of results, were discarded.

Acting upon the suggestions relative to the use of grain splits from heavy hides by Messrs. Small and Alsop, and a consideration of the results upon woolen cloth submitted by Mr. Reed, an elaborate line of experiments was carried out in the writer's laboratory, with the object of determining their value for a comparative method. Availing ourselves of Mr. Small's experience with the heavy hide grain, one was procured from him, prepared in accordance with his usual treatment, as given on page 7, of the JOURNAL of the A. L. C. A., Jan., 1909.

Numerous trials were made, following the general line of Mr. Small's method of tanning the grain, the results demonstrating that, in some respects, the heavy hide grain was better than sheepskin, the most noticeable difference being the intensity of color, which is a desirable feature, as it affords a better index of ultimate color than the lighter pelt. Like sheep- and calf-skin, how-

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[1] Report of 1909 Committee.

ever, uniformity or concordance of results seems to depend upon the part of the grain used, and pieces tanned in the same liquor, taken respectively from the soft and firm parts, do not give similar results. Our trials would indicate that, by using only the better parts of the hide, fairly concordant results can be obtained by the individual with one particular grain, but that one grain is not comparable with another, so that a new standard would be established with every grain used.

As a comparative method for general use, the heavy hide grain does not seem to possess sufficient advantage over any other pelt or skin to warrant its adoption. If the color depends upon the texture of the hide, it is obvious that no two laboratories are likely to be using hides of identical character at the same time, and, as both buyer and seller usually test the materials in question, there can be only one conclusion as to the utility of pelt or hide methods.

No special collaborative work was sent out to test this method, as we were constantly receiving color tests in the course of business from other laboratories using the split grain, treated in the same manner as Mr. Small's: These tests, along with our own, were never sufficiently comparative to identify the extract tested, although the samples were taken from the same bottle.

Various methods of treating the hide were tried, aside from merely washing with water, with negative results. It was found, however, absolutely necessary to remove all traces of the boro-phenol solution in order to get a representative test. The presence of boro-phenol has a very decided effect upon the color. In the case of chestnut or oak extract, there is a bleaching effect, whereas upon quebracho there is some darkening, due to the development of the coloring matter by the solution. This is a feature worthy of notice by those who use heavy hide grains preserved in boro-phenol. This action is clearly illustrated by the sample which I will show.

Aside from the lack of comparative value, this method is open to the serious objection of taking too much time. Thorough and well finished tests cannot be completed in less than three and a half to four days, even when the shaker or drum is used the first day, and to hasten the tannage by using the shaker entirely is in most laboratories impracticable.

This question of time may not make any difference in some laboratories, but in those acting as referees between buyer and seller, or where a manufacturer is withholding deliveries pending his chemist's analyses, it is a very serious one. There are still further objections to the adoption of the heavy hide grain as a comparative method of color valuation, as it at present stands, but we believe the difficulties cited must be eliminated before its adoption could even be considered. It is not the contention that the use of pelt or hide has no value or place in the tannery laboratory, but that its value is confined to the individual.

After satisfying myself as to the limitations of present pelt methods of color valuation, the investigation of the method employing woolen cloth, as suggested by Mr. Reed, was taken up, and, considering the results now obtainable, it seems rather remarkable that the use of textiles, which was under investigation some years ago, did not result in something definite before this time.

Mr. Reed's method consists of fixing the color upon white woolen cloth, such as broadcloth, by steeping it in a strong cold solution (of about 4 per cent. tannin) of the material to be tested for about 24 hours, then washing out the free coloring matter and drying on a sheet of glass, presumably away from strong sunlight.

In the writer's laboratory, the results obtained in this way were more nearly comparative than those in the usual run of work by either sheep-skin or hide methods, therefore, a more thorough investigation as to its possible merits was instituted.

Many experiments were made to determine the conditions which would best demonstrate the difference in color and shade of various tanning materials, and also show the distinction between samples of similar tanning materials of different manufacture or source. Considerable effort was also made to ascertain the simplest means possible of making the test and eliminating in the greatest degree sources of variation in results.

Preliminary experiment having proved that cold solutions containing 3 per cent. to 4 per cent. tannin precipitated very considerable quantities of matter soluble in weaker solutions, and might, therefore, affect the resulting color, a series of trials was made with solutions ranging in tannin contents from 0.5 per cent. to 3 per cent., and it was found that any solution containing less than the latter did not yield sufficient intensity of color to clearly demark variations in tone, even after more than 24 hours immersion. Confirming our preliminary experiments, it was also noted that variations in laboratory temperature did not affect the solubility of these strong solutions.

During the moderate seasons of the year the question of temperature might not seriously interfere with concordant work, but during winter and mid-summer, the temperature frequently covers a range of variation that would probably interfere with comparative results. That the influence of temperature upon the color value of tanning materials is very great has been fully confirmed by subsequent investigation.

The collaborative work done by the cold method, specimens of which I submit for examination, tends to confirm the foregoing conclusions.

Failing to attain the assurance of comparative results considered necessary, by the cold method, it was determined to experiment with heated solutions, and an extensive series of trials was made with solutions ranging in tannin contents from analytical strength to those containing 3.5 per cent. The variations in time of immersion and the temperature of the bath covered an even more extensive range.

It would necessitate the recitation of much wearisome detail to deal with this series of experiments exhaustively; briefly, it was found that weak solutions of the tannin materials tried required such extended immersion, and the application of such high temperature that the resulting colors were seriously affected, whereas stronger solutions under the same conditions of time and temperature gave too great an intensity of color to be serviceable.

By gradually circumscribing the limits of solution strength, time of immersion and temperature, what now seems the best conditions were eventually ascertained.

They are essentially as follows:—

Immerse a piece of thoroughly wetted cloth, three inches by four in size, in a solution of the material to be tested, containing 3 per cent. tannin, and allow to remain, with frequent agitation, for 45 minutes.

The solution, previous to immersing the cloth, is heated in a water bath to 50° C. and the heat then turned off, the coloring being affected without a continuance of the heat. (Care must be taken that the temperature of the bath is not greater than that of the solution, *i. e.*, 50° C.). The solution, in volume 250 cc. should be contained in a porcelain or glass beaker not less than 3½" in diameter and 4" deep, and the beaker immersed at least 3½" in the water.

The bath should not be exposed to rapid cooling (5° being the usual drop) during the test. At the expiration of the time of immersion, the cloth is removed from the solution and the free coloring matter washed out thoroughly in water heated to 50° C., then well squeezed in the hand and further excess moisture removed by rolling for a minute or two in a clean towel. It is then dried smooth between pieces of blotting paper in a letter press.

Any visual method of demonstrating color value is necessarily empirical, and, to be successfully comparative, must be not only easy to control, but practically under absolute control, and, among the important points to be favorably considered regarding this method, is the simplicity and facility with which this is done. Much work was done before it was learned that, to secure concordant results, it was only necessary to bring the temperature of the solution to a given point and begin the fixation of color at the maximum temperature of the bath and also that a variation of only a few degrees in the temperature of the bath upward would vitiate the results entirely if wanted for comparative purposes.

All methods involving any great length of time like the split hide grain, introduce complications which influence more or less the color obtained. With the cloth method suggested trouble from this source is well nigh eliminated, as a test can be completed in less than three hours. This feature will be best appreciated by commercial laboratories. The most important feature of all is that of concordance and comparison and I do not think I overstate the facts when I say, if a method is desired which will yield identical results in any laboratory, that the cloth method will more nearly do so than any other.

The use of a uniform base upon which the color is fixed is the first and most important step towards securing uniform color tests, and, now that such a base has been found, it seems the final working out of a satisfactory method could soon be accomplished.

To demonstrate just what value could be attached to our investigations, it was decided to submit the method to collaborative trial, and samples of cloth, tanning materials and copies of the method were sent to the members of the committee. Color tests were made of Hemlock, Quebracho (Natural and Decolorized) and Chestnut (Natural and Decolorized) extracts, materials which perhaps present the greatest difficulties in the way of obtaining uniform results upon pelt. I submit the results for your inspection.

It is not claimed that the results now being shown are absolutely uniform, but it is safe to say they are infinitely more so than any like number of pelt color tests would have been. It must be considered these trials were made without previous experience on the part of the various laboratories, and probably represent the greatest degree of variation likely to occur at any time.

The results with the chestnut extract are exceptionally good, in fact, nothing better could well be hoped for with this, the most difficult of all extracts to test satisfactorily. Such slight variations in color tone as exist are doubtless due to some variation in temperature of the bath.

It has been suggested that a possible difficulty of cloth testing would be the wide difference in the color produced thereon and that of leather tanned with the same materials. So far as this method is concerned, however, it is not a question of the color produced on the cloth, but its value in yielding a concordant and comparative index of the color value. The color that will be produced on hide in the tannery is a matter each individual laboratory must determine for itself. No two tanneries will produce identical results with the same materials, and, when the endless variety in the combination of tanning materials employed is considered, the supposed advantages of pelt tests seem doubtful.

That is to say, it is not quite apparent what value as an index of ultimate color a skiver or steer hide grain tanned with chestnut or quebracho extract will have, if that material forms, as it does in most cases, a minor proportion of the tanning material employed. Color tests of eight of the principal tanning materials prove that, with one exception, the color on cloth approximates the color produced on leather as closely as the sheep-skin method, whereas the sensitiveness to shade is incomparably superior to either sheep-skin or split hide grains. As an index of identification of various tanning materials, I submit for your examination specimens of cloth colored with the following:—

Mangrove extract, decolorized.
Hemlock extract, natural.
Chestnut extract, natural.
Chestnut extract, decolorized.
Quebracho extract, natural.
Quebracho extract, decolorized.
Mimosa bark liquor.
Myrabolam extract.
Chestnut oak bark extract.
Black oak bark extract.

Illustrating the sensitiveness to shade or color tone rendered by tanning materials of the same kind, but of different manufacture, I offer for examination tests made from various quebracho and chestnut extracts. Repeated tests of these extracts by three operators yield the same differentiation of shade, and thereby furnish further evidence of the possibility of making the woolen cloth color test a satisfactory comparative method.

Reverting to the comparison of color between that produced on pelt and hide and that on cloth, we find that quebracho extracts do not yield the salmon pink color that they do upon hide. The color obtained is a brilliant yellow, the shade varying in accordance with the character of the extract.

I am not able to suggest a reason for this peculiarity at present, but it seems to be a function of the wool. At first it was thought the cloth possessed some quality of selective color absorption, and this may be the case. We find, however, that cloth exposed to sunlight after coloring assumes the characteristic salmon pink color produced on hide, which makes the theory of selective absorption seem doubtful. The addition of mineral acids to the dye bath also develops the reddish color. The specimens I herewith submit illustrates the reaction very distinctly.

The following comments upon the method by collaborators were received: Messrs. Reed and Wisdom:

"The cold method seems to produce, as might be expected, considerably less intensity of color than does the warm method. This is pronouncedly evident in the case of Hemlock extract, the cold method showing so little color in this instance as to raise the question whether between two Hemlock extracts there would be much variation in the shade. The same comment is true perhaps to a less degree, to all the samples. There is to be said against the warm method that it dulls the color and that it varies in practice from tannery usage, there being more reds in solution in the warm liquors, it is to be expected that there will be decided variation in color and intensity. As the method is entirely empirical it perhaps makes but little difference whether the warm or cold method is employed, provided one or the other is definitely decided upon. I am not so sure the warm method would not present an advantage if carefully observed, in that the cloths are introduced at a definite temperature. The cold method prescribed laboratory temperature which may vary we all know a considerable number of degrees at different seasons and at different places.

"On the whole I think I am inclined to the warm method for the following reasons:—

1. That it gives quicker returns.
2. That it gives greater intensity of color.
3. That it will, I believe, give better comparative results.
4. That I believe comparisons between extracts of the same character will be better shown.
5. That although the warm method differs from tannery practice, yet I believe that the actual colors obtained by it more closely approximate the colors obtained in tannery practice than in the cold method."

MR. F. P. VEITCH: "Nothing more simple could be desired."

MR. W. K. ALSOP: "I should judge that different analysts would get almost identical results on the same samples, if the tests were carried out in the same manner.

"What worth the results would have is another question. They are absolutely no indication of what may be expected on hide and in the case of extracts containing any marked amount of coloring matter, that seems to be taken up by the cloth practically to the exclusion of any color to be expected on skin.

"The method might be of value to check different shipments of extract or to control the color during the manufacture, providing one knew what colors to expect from it."

DISCUSSION.

PRESIDENT WILSON:—This paper which Mr. Kerr has just read should incite considerable discussion because the color valuation question has been very unsatisfactorily settled; in fact it never has been settled, and the methods which we have had heretofore have been open to very serious faults, and I would say to Mr. Kerr that his recommendation that this be made a provisional method will come before the executive session tomorrow afternoon. Mr. Reed has probably had more experience along this line than any one else except Mr. Kerr, and I would like him to open the discussion on the subject.

MR. REED:—Mr. Kerr has covered the ground very well, I am somewhat pleased, I am glad to acknowledge, that he has come to the conclusion that he *has* arrived at. I advocated some such method as this last year in a paper. I thought at that time that I was perhaps a little ahead of the game, so to speak, but at that time I came to the same conclusion that Mr. Kerr has now come to, that in order to get any comparative results between analysts on this matter of color testing, it was absolutely necessary to have a standard basis. We had to have something to start with that was uniform, and that we certainly did not have in pelt.

Now as to the value of this method as compared with the pelt method, the question will be raised I presume by the tanners, and Mr. Alsop has pointed it out in his remarks, that the color that we obtained upon the cloth is not indicative of what a tanner will get on the skin; but granting that, has this method much more value than the pelt method? For example: a purchase is made of a tanning material—a tanning extract; a contract is made, the contract is made with the idea of a certain color given by that extract. Now, with the old pelt method of testing it is never possible in my estimation, to check up from the original shipment other shipments that come along. By this method I believe it is absolutely possible to keep a standard and to check up every shipment that comes along; and there, I believe, is the value of this method as compared with the old method.

Mr. Small:—I haven't anything at all definite to say, because I know absolutely nothing about the use of the cloth method. I have not tried it out, and I do not know what is to be expected from it. From the samples that I have just seen, I should agree with Mr. Alsop's comments as I understood them to be read, that the method would be of value as a supplement to some other method, but I cannot see how it can absolutely replace tests on skins of some kind or other. My personal preference has always been for the use of a skin or a grain of a particular class of hides I was using for the simple reason that the result I get that way is a pretty good picture of the sort of thing that you can expect. Of course that is not absolute. Even granting you get a method which would give you exactly the same results always with a particular extract, it wouldn't give you the color that you could get in your yard necessarily, by any manner of means. It does, however, give a very good picture of what is to be expected from any particular tanning material. Moreover, it requires a very short time of immersion in the tannin bath to set the color sufficiently well so that you can tell whether your extract is very much off or not. You don't have to wait until you get your color skiver finished before you are able to determine whether your extract is up to standard or not. A little experience in watching the setting of the color on a piece of pelt enables me to tell pretty closely what I am going to get from it after it has been in the solution a comparatively short time. If it is possible to get an absolutely definite shade on cloth and comparatively small differences in the color of the extract as shown up definitely and absolutely in cloth, I should say the method had a distinct field of usefulness; but as to the sensitiveness of the cloth to slight changes in the extract, having had no experience and not having had an opportunity to examine these samples carefully, I haven't any opinion to express.

MR. VEITCH:—I am something like Mr. Small; I haven't any opinion to express on the subject although I did a little work with it,—Mr. Rogers and I,—but it seems to me that the method has some value in that if two shipments of extract each give the same color on cloth we might reasonably think they could give the same color on the skin if handled in the same way, and to that extent it seems to me it has value.

Now there is one point I have thought of since Mr. Kerr commenced to read his paper, and that is it seems to me there is some doubt about whether different samples of wool cloth, will give always the same color. It may be there that we will have difficulty in getting the same color on different lots of wool cloth. Wools grown in different sections of the country behave in different ways with dyeing materials, I believe is the opinion of dyers, and it may be we would want to look a little into that before expressing too definite an opinion on the subject. It seems to me though it may have a value.

MR. KERR:—With reference to Mr. Veitch's observations, wool cloth I find comes in bolts of fifty yards, and that will cut up enough samples to standardize all the samples used in twelve months by all the chemists in the country, just the same as we standardize hide-powder now. The wool can be distributed from a central source just the same as the hide-powder is distributed.

MR. VEITCH:—Of course that difficulty can be overcome in that way; but if you get your wool from one section of the country and I get mine from another, it might make a difference.

MR. KERR:—What we are looking for is a comparative method. This pelt method is not a comparative method. You can send a sample of extract to half a dozen chemists and you can get half a dozen color tests on pelt, no matter how well a man may be able to judge the color value of an extract by just simply striking the color on the grain in a commercial laboratory, that is not what is done and it is not what the tanner wants. He wants the finished skiver; he has to have it for a record. Now. unless you do tan the skiver fully and finish it up carefully there is not value to the tanner at all; whereas for an individual, he might immerse it a couple of hours and see whether his extract was colored in a certain way, and then throw it away. But that is not what we are looking for. We are looking for a method that will give the same result in the hands of a number of chemists and something than can be filed away as a record covering the deliveries of an extract over a period of time. I do not think that is possible with pelt. I believe that Dr. Levi has had some experience with color testing on wool.

Dr. Levi:—Not wool; cotton. In 1887, or just about that time, in order to color sheep skins we had to make quite a number of different shades, and in order to simplify the work we tried to get the colors in the laboratory, dyeing them on mordanted cotton at a certain temperature. After certain experiments we had to drop that method as useless, so from that time on we bought simply straight dye-stuff; got a five-gram skein of cotton yarn soaked that in boiling water, rinsed it out thoroughly, and then put it in the dye-bath, with .05 of one gram of the dye-stuff, doing that at a temperature of 90 degrees for one-half hour. We took the temperature of 90 degrees to get as near to the actual condition of leather as was possible in the laboratory on textile fabrics. We found that would work very well, but with mixed colors it would not go. So the next experiment that was made we took the skeins and hung them in the old dye vat. We found also for the same reason, that the variation of temperature in the vat caused the same troubles as in the laboratory with mixed dye-stuffs; so we let that go. Then the only thing to do it seemed to us, was to take sheepskin and dye it. Sheepskins we couldn't use very well, although we were skeepskin manufacturers at the time, on account of the variation of the amount of grease contained in the skin, so we took calf, which has a good deal less grease, and we got a good deal better results, but not exactly what we wanted. So, from step to step we went on, and took up the extract to see if we could not get some method to determine the shade that we would get on leather by the cotton method. Of course you can judge in the laboratory very well comparatively the shade you will get, but take that out to the superintendents or the different foreman and they will be entirely at sea; so we simply used the method of taking three per cent. of our extracts with .05 gram skein of cotton yarn. The yarn is first heated up in water to 212 degrees, rinsed thoroughly and then placed in the dye-bath with three per cent. of the extract if the tannin in the extract runs at 25 per cent.; if it runs 50 per cent., take so much less. We heat it to 90 degrees and dye for one-half hour. After one-half hour rinse off thoroughly and hang up to dry in a dark place. We found excellent results and we can judge fairly well in our own laboratory the color that we get from our extracts on leather.

MR. ALSOP:—I think this cloth method gives more uniform results than any other method undoubtedly, and that it should be valuable in such a way a Mr. Reed suggests, and it could be supplemented of course, by the works chemist by tests on skins. Of course, for checking up different extracts and things like that it certainly gives more uniform results than any test on skins that has been devised or probably will be devised.

MR. SADTLER:—I might venture a few remarks. I don't want to appear presumptuous because I am not a bark tanner, but I am just thinking of the chemistry of this thing, and there seems to be a desire if possible to use some form of skin, or something with the grain of the leather on it, and it seems to me that the greatest disadvantage in the using of skins is the impurities or the material other than the fibre of the skin itself. Now, if it would be possible to treat that skin so as to remove as much as possible of every thing in the nature of oil and probably free acid—because skin almost from the time it is taken off the animal begins to develop some rancidity—it can be found that skins of different nature would show up more uniformly with the different bark extracts. Now, I do not know how fully you have gone into the thing, but here is the idea I have in mind: the skins might be treated—take a certain kind of a skin—a skiver—a goat skin or something like that—and treat it with acetone—say boiling acetone. I never tried that on skins, but unless somebody should say it would not work it would seem to me that might remove the organic acids. It would also remove any oil. If that were put in a large Soxhlet extractor—they come with large ground glass joints now, with a very large extraction chamber, and you could put a very good roll of skin in there, and that might be set going and run all day, or a couple of days if necessary; or a larger one might be devised in which a great deal of leather could be treated. And if that did not remove all acidity it might be preceded by immersion in a weak ammonia solution. Now I do not want to inject myself into this thing, but I just thought that possibly if the skin were treated in a way by analysis to find out what you have got when you are through treating it, that you would have a better starting point for getting color valuations with the animal skins than you would by merely a certain amount of washing or no treatment whatever. I think that something like that might be helpful. Maybe if you were perfectly satisfied with this method going on as a provisional method, some experiments might be started along the other lines as well.

Dr. Levi:—From the remarks of Mr. Sadtler it seems to me like this: For instance you take a sheepskin; take one grown in Ohio and one grown in Louisiana and one grown in Illinois, and one grown in Texas and another in Australia and we treat them with the acetone method, or any other method, and I guarantee you when you make your dye test you get five different shades from the different skins from different sections.

Mr. Sadtler:—Very possibly—I don't know.

Mr. Levi:—That is the objection to the skin or hide method in coloring.

Mr. Veitch:—Why?

Mr. Levi:—I don't know.

Mr. Sadtler:—I thought the difficulties were largely from the oil and things of that kind, but I cannot conceive why the difference of the size of the apertures of the grain could make any great difference in the color absorption. That would hardly seem to make very much difference.

Mr. Kerr:—I believe a great many different methods of purifying the skins have been worked up in the last ten years,—degreasing; and the more complicated the preliminary method the greater the variation in final results.

President Wilson:—I was just going to mention in regard to this method of treating the skins and getting variations from different localities, that it seems to me that these variations on sheepskin or any material we can get are largely due to the pigment in the skin. We could not take a darkey for instance, and treat him with acetone and get a good skiver.

PRESIDENT WILSON:—It occurs to the Chairman that this matter of making the color valuation on the broadcloth is by far the best thing that has ever come up yet. Of course, it is especially valuable to the extract man, and it is also to the tanner, because, as has been remarked before the tannery chemist can take any number of shipments from the same source of supply and he can almost absolutely check up those color valuations. If he wants at the same time to make his absolute color on the kind of skin he is working in his yard, then of course that is doubly valuable.

MR. WALLIN:—As a tanner, it seems to me it is very important that there should be some standardization of color tests. I think the average tanner when he is handed out a color test by an extract manufacturer gives it very little consideration because he knows from his experience that there is not much opportunity to judge different color tests relatively as they come to him on skins. And I think up to a very short time ago there wasn't even a standard solution in which color tests were made. One man would come around with a beautiful color test made with a three degree liquor, and compare with another's made with a 20 degree liquor perhaps. Of course that is very much improved now, but even now the color tests as made with skins are very unsatisfactory, and it seems to me that the fact that you can take one bale of material and divide it up and all of you have the same thing to start with, in itself is a great advantage: and if those colors were intensified somewhat beyond the tests that have been shown here to-day so that the tanner who is accustomed to seeing stronger color and not accustomed to distinguishing between fine, light shades, and could have a more intense color to judge by, it would be a great advantage. I should hope to see this thing further worked on and something along that line adopted. It seems to me it is in line with the color tests Dr. Levi has had to adopt in his own laboratory.

Mr. Saxe:—There it is well known, and in the cotton industry and the woolen industry, that dyers who receive as low a compensation as two dollars a day are able to make remarkable comparisons in connection with their dye-stuffs. I use, because I am compelled to use in a sense, the sheepskin test in offering extracts. I saw at the Heald laboratory some weeks ago the tests made on wool, and it struck me then as compared with the tests I have seen made in textile laboratories that was truly the safe method. The comparative tests made on wool are safe. You take the dyer and when the cloth is handed to him from the scouring department it is supposed to be absolutely clean,—thoroughly scoured—otherwise the dye goes on very uneven. It is very easy to get broadcloth from certain mills which makes a specialty of that, where they are turning out as much as fifty or one hundred pieces all alike. That would standardize according to the ideas of Mr. Veitch. That is, where you can get wool cloth of all one kind. Now if you take those and dye them,—the dyer will use perhaps within one ounce on his whole dye there of coloring matter for his fifty pieces, and the tones are so alike that when they come to match them up to ship the cloth it is difficult for the matcher to find any difference at all. I should say from my experience with pieces of sheepskin and pieces of pelt—splits—that I would rather buy extracts on the method proposed by Mr. Kerr than on the present one. I think Mr. Levi will bear me out on my observations on wool.

THE PRINCIPLES OF LIMING.

By R. W. Griffith.

The importance of beamhouse work has always been recognized in the art of tanning. The process of a hide's transition through the beamhouse is a period of uncertainty, and it is generally conceded that when the hide has reached the tan liquors safely, the battle is half over.

Having regard for the admitted importance of the subject, it is a little surprising to find that very little attention has been paid to it by chemists and perhaps in consequence, the destinies of the lime yard have been presided over by a man who usually has little sympathy with the chemist.

Indeed, it is conceded that the art of liming hides and skins is only developed in practice.

Proctor, in his principles of leather manufacture has little to say of his own researches into the subject, and we find only Eitner and Von Schroeder quoted on original research.

The absence of scientific data is not altogether the fault of the chemist.

Commercial Lime is an inconstant material, varying with the locality from which it is derived. Again, it is practically impossible to standardize hides, and without some definite standard upon which to build, the chemist is considerably handicapped. This may be said in mitigation of the chemist, but certain principles yet remain to be established, and these come within the scope of the chemist.

The use of calcium oxide in the preparation of the hides for tanning dates back to antiquity; nevertheless, its use marks the introduction of the first manufactured chemical into the art and mystery of tanning.

Lime, because of its limited solubility, which permits of its use in extravagant excess, is an ideal material with which to treat hides in their green state, which is perhaps their most sensitive condition, although its presence in later stages of the tanning process causes considerable trouble. Yet, in spite of many objections to its use, and the fact that as a depilatory it has many competitors, lime continues to be the most popular beamhouse material to-day.

Lime is unfortunately a very variable commodity. From the tanners' standpoint, its value is determined by the amount of calcium oxide which is present. In commercial lime this fluctuates between 50 and 99 per cent.—Lime containing less than 50 per cent. calcium oxide should not be used for tannery work. The common features of a poor lime are caused by bad burning of the lime stone and the presence of magnesium and iron oxides.

A good lime will slake easily and crumble into a fine powder. The presence of magnesia makes slaking very slow and difficult, and its presence to any extent is very objectionable on this account.

The methods of using lime are as varied as the foliage of a forest in Autumn.

As we are here considering principles, it is unnecessary to go into the details of the various methods employed. The quantity of lime which should be used is a much discussed point, and in determining the amount it is, of course, necessary to consider the percentage of calcium oxide which the lime contains.

The amount of lime used should be based on the green weight of the hides, rather than upon the volume of the vat.

When one considers that the solubility of lime is something like 13-hundredths of one per cent., and that only the lime in solution is immediately available, it will be recognized that in practice a tremendous excess is employed. But there is reason on the side of practice, because a clear saturated solution of calcium hydroxide will not depilate, and it is necessary to constantly charge the solution as it becomes exhausted, due to absorption by the hide, and hence, the necessity of the presence of a constant excess.

A good lime liquor should be such that when agitated, all the lime particles should be suspended in the liquor, forming a fairly thick milky solution without any great amount of lime paste remaining at the bottom of the vat.

With a good commercial lime, say containing 90 per cent. calcium oxide, it is possible to obtain depilation with one per cent. of such lime based on the hide weight. But in order to obtain results with such a small quantity, conditions would have to be adjusted in such a way as to be hardly practical in the tannery. A good practical lime liquor can be prepared with 5 per cent. of a good lime on the basis of the hide weights.

The lime should be slaked in a tub some hours before it is required for use, in order to ensure complete hydration of the calcium oxide. The amount of water used in a vat should be adjusted so as to just cover the hides when they are immersed in it.

The value of clean limes has been recognized by sole leather tanners for many years, but in the manufacture of upper leather, it is only since the chromium tannages have been commonly adopted that their value has been appreciated in this section of the industry. Previously, it was the common practice in upper leather manufacture, to employ chiefly stale lime liquors.

It is rarely the practice in any tannery to-day to prepare a fresh lime for each pack. It is a good method, however, to use the liquor from one pack to make up a new liquor for a fresh pack, and afterwards to run that liquor away.

In this way a certain "mellowness" is always present, and the "harshness" of a new lime is avoided.

The mellowing of a lime is caused by the solution of hide matter into the liquor, which produces ammonium salts. This effect can be produced artificially by the addition of ammonium sulphate to the lime liquor.

Liming has a remarkable influence upon the character of leather. The shorter the process of liming the firmer and "tighter" the leather. Long liming tends to produce soft loose leather. The two extremes of liming are well illustrated in the production of sole leather on the one hand and glove leather on the other.

The maximum plumping of a hide by lime is reached in eight to nine days, after which the hide commences to deplete.

A well limed hide which has become depleted can be made plump by immersion in cold water.

The plumping effect on a hide is caused by the hydroxyl group of the calcium hydrate.

In the case of an acid plumping, the action is due to the H ion. It is interesting to note in passing that salt effectively prevents the hydrogen ion from plumping hides, whereas it exercises no influence at all upon the hydroxyl group.

Before proceeding further to a consideration of plumping, it would be well to examine first the manner of the absorption of lime by the hide.

We find by an analysis of the limed hide, that it contains considerably more calcium oxide than is contained in a saturated solution of lime.

We cannot explain the presence of this calcium oxide in the hide by inferring that it has become mechanically deposited there, because in the first place the hair of the hide provides an excellent filtering medium for the suspended particles of lime, and the web-like tissue on the flesh is no less an obstacle to the inroads of solid lime.

The most practical explanation, therefore, would appear to be that a process of dialysis is going on where the saturated solution of hydroxide enters the fibres, and by reason of an affinity which the fibre has for the oxide, the latter is deposited and the water of the hydroxide being liberated, passes to the surface, where it becomes charged again with the oxide and repeats the process.

Hide fibre has a strong affinity for all metallic oxides, and as is well known, those oxides of the formula M_2O_3 are capable of completely tanning the fibre.

The amount of calcium oxide held by fibre is, of course, variable, but in practice it is usually present to the extent of about half of one per cent. on the green weight of the hide.

Returning to the consideration of the plumping effect of cold water on a limed hide—the apparent cause of this is that the calcium oxide in the hide tends to return to solution and in so doing increases the volume of hydroxide within the fibres, but decreases the amount of calcium oxide.

It is clear, therefore, that by frequent changes of cold water, it is possible to remove about half of the total oxide of calcium held in the fibres, and still preserve the plumpness of the hide.

Probably the best condition for a sole leather hide to enter the tan liquors would be to have reduced the amount of calcium oxide contained in it to a point where it would represent a water solution of the lime. This would bring the alkalinity of the hide to a point where it would be easily neutralized by the weak acids of the tan liquors, and set up an immediate plumping by these acids.

The immersion of limed hides in warm water causes a depletion, not because of the removal of the lime, as the solubility of lime is known to decrease with the advance of temperature, but because of the physical influence of temperature upon the hide, the tendency of the hide being to go into solution itself.

The time required to remove the hair by means of lime varies considerably and depends largely upon the manipulation of the process. Depilation can be accomplished in twenty-four hours with the aid of warm water, or it may extend to nine days.

The theory of the action of lime as a depilatory is as yet unsettled. Proctor lends his support to the theory that the depilating action of lime is principally a bacteriological one, and Eitner furnishes some evidence in support of this view.

On the other hand, Von Schroeder contends that the action is purely chemical and has published some interesting observations on this point.

The evidence which is submitted in favor of the bacteriological theory appears at first glance to be well founded, but on closer examination it is found to be far from conclusive.

It is claimed that a sterilized hide in a sterilized lime liquor will not depilate.

A process for liming—patented a few years ago, and known as the Pullman Liming Method—apparently supports this claim. This process is very ingenious and consists in treating the hides in a solution of a definite strength of caustic soda, and afterwards in a bath of calcium chloride.

This resulted in the precipitation of calcium hydrate to a greater or less extent. Hides subjected to this process, however, failed to unhair unless they had been previously immersed for several hours in a putrid water soak until the hair slipped.

In fact, the depilation was brought about entirely by this means, so that the real purpose of the subsequent liming operation was to plump the hides and saponify the grease preparatory to tanning.

Examining this evidence in support of the bacteriological theory, the author carried out some experiments with pieces of hides previously sterilized with carbon bisulphide and with phenol, and the liming as carried out in sealed jars.

In both cases there was apparently a reaction between the sterilizing agent in the hide and the lime liquor. The hide treated with carbon bisulphide developed a deposit of sulphur. When the liquors were eventually examined, it was found that the caustic lime in both was much below a normal lime liquor. A normal liquor showed 0.4 caustic lime—the carbon bisulphide hide liquor showed 0.08, and the phenol hide liquor showed 0.18.

The carbon bisulphide hide unhaired in twenty-four days and the phenol hide unhaired in eighteen days, and an experienced bacteriologist was unable to discover the presence of bacteria.

The amount of hide substance dissolved in the carbon bisulphide hide liquor was slightly higher than in a normal lime liquor, whereas the phenol hide liquor was more than twice as high.

From the fact that the alkalinity of the lime liquors was considerably reduced by the sterilizing agents in both cases, it is manifestly unfair to conclude that the absence of bacteria retarded the depilation. Before such a conclusion could be safely reached, it would be necessary to employ sterilizing agents which do not react with lime.

Von Schroeder experimented with fresh salted hides under sterile conditions, but without employing antiseptics, and he was unable to discover that the absence of bacteria influenced the activity of the lime as a depilatory.

If we now turn to an investigation of the chemical theory and take for our premise the principles already referred to in this paper, we have for our first principle the fact that a clear saturated solution of lime water will not depilate, and that the presence of an excess of lime is necessary.

In the second place, we have the established fact that the calcium oxide contained in the fibres after depilation is about three times the amount which the saturated lime solution contains. From this fact it would appear as if a certain degree of alkalinity had to be reached within the fibres before the epidermical structure softened and became loose.

A practical observation of a hide in the unhairing process will show that the action has apparently worked from below the epidermical structure rather than from the hair surface.

In the Pullman liming process the fact that the depilating action is not comparatively rapid, can be explained by the absence of a sufficient deposit of calcium hydrate within the fibres, as the tendency would be to form a deposit of the hydrate on the surface, immediately the hide was introduced from the caustic soda into the calcium chloride, and as we have already endeavored to show, the absorption of the calcium oxide into the fibre is a slow process of dialysis.

The amount of hide substance which is dissolved in the process of liming has created a little uneasiness in the minds of some tanners, and some chemists have undoubtedly exaggerated this loss.

The method by which the amount of dissolved hide substance is determined is based on an estimation of the nitrogenous matter contained in the lime liquor.

It should be remembered that the epidermical structure, which it is desired to remove, is a nitrogenous body, as also is the loose tissue of the flesh side, and to distinguish between leather forming substance and the undesirable hide substances is a practical impossibility.

This admission does not concede the fact that valuable hide substance cannot be lost in the process of liming, but under the conditions in vogue in most modern tanneries, the amount of hide substance lost in the limes is not worth considering.

The estimation of dissolved hide substance, however, furnishes valuable data for comparisons. Some experiments made for the purpose of determining the influence of previous soaking in water upon the amount of hide substance dissolved in the operation of liming showed that a previous soaking of twenty-four hours rendered no more hide substance soluble in the lime than an unsoaked hide.

After soaking forty-eight hours, there was a notable increase in the amount of hide substance dissolved in the subsequent lime, but between this and a seventy-two hour soaking, there was no apparent difference.

After ninety-six hours soaking, there was a rise of nearly one-half per cent. in the amount of hide fibre dissolved over the seventy-two hour soaking. This would show that the soaking of hides preliminary to liming exercises an important influence on the amount of hide substance dissolved in the process of liming.

In conclusion it has been shown that the process of liming is controlled by practical methods, rather than by analytical control, and the problem in practice is to obtain uniformity in the liming operation.

Definite measures of lime, based on definite weights of hide, in definite volumes of liquor, make for successful liming.

The mechanical operation of drawing the hides should be at regular intervals. When the operation of liming is carried out in a methodical manner, it will be found that the pelt weight of the hides after unhairing and fleshing is a very constant factor in hides of the same class, and the weight of hides at this stage provides an excellent criterion of the yield in tanned leather.

It is the common practice in England to weigh all the hides in the white pelt condition, and in this way an excellent indication as to whether the hides are profitable or not is obtained.

The English method of liming for sole leather is somewhat different from that employed in this country. No reels are used and the pack is usually limed in a single vat.

The lime vats are built with a "fender," which has a surface measurement about equal to that of the vat, and the fender is so constructed that it slopes into the vat about 16 inches. A great deal of space is thus occupied by each vat.

The hides are drawn from the vat on to the fender each day and allowed to drain for about an hour, when they are returned.

The average time of liming in England is about six days.

The greatest care is exercised to see that the hides are well spread out and kept flat during the liming operation, and the reason for this is the belief that this care ensures a freedom from "Bagginess" in the finished leather, and allows the leather to be rolled flat.

Resuming our consideration of practical methods, it should be pointed out that a considerable excess of lime in a vat does not facilitate depilation, but on the contrary, retards it, and the common practice of so-called strengthening a lime liquor by the addition of further quantities of fresh lime is a great mistake.

An investigation which the author had occasion to make in a tannery where the beamhouse work was causing trouble, revealed the fact that the lime vats contained two feet of solid lime paste, and the hides which became embedded in this unhaired with considerable difficutly—especially difficult to remove was the undergrowth of fine hair.

Apart from the extravagant and unnecessary use of such quantities of lime, this instance would show that water as a vehicle for the lime is a necessity to proper liming, and it also lends some support to the principles which we have sought to establish in this paper.

We have not, in this paper, considered the influence of sulphides, which it is now the common practice to use in conjunction with lime, but their influence, principally in facilitating depilation does not materially alter the relation of the lime to the hide.

The theory and practice of liming is well worth the study of the chemist, quite apart from its practical importance, and if this brief survey of the situation will tend to stimulate some interest in the subject, the author will feel that he is amply rewarded.

DISCUSSION.

PRESIDENT WILSON:—Mr. Griffith's paper has been extremely interesting, to all of us, and it has opened up a field for discussion which should lead to some very interesting thoughts. I think the general opinion among all of us, of all tanners, has been that the removal of the hair has been due more largely to bacteriological action than anything else, and this theory that Mr. Griffith advances, that it is possibly due to the re-absorption of calcium hydrate, is very interesting. If any of you have any remarks now on the subject, I know Mr. Griffith will be only too glad to answer you.

MR. HEALEY:—I would like to ask you if in removing the hair by means of lime the agitation of that lime would not materially hasten the process. For instance, assume that your hides are hung over sticks in a lime vat and that a paddle wheel or air compressor agitates the lime continually, thereby bringing a new solution in immediate contact with the surface of the hide; would not immediately materially increase the absorption of the lime and cause the hair to be removed?

MR. GRIFFITH:—Yes it would. I think it is a pretty well established fact that the more the lime is agitated the quicker the process of depilation is. But with regard to the mechanical means of agitating, such as blowing air or any mechanical device for stirring up lime, it involves a question of cost, and that usually puts it out of court with the tanner. With regard to the suspension of hides, that is a very good thing, to suspend hides in a liquor, but then you have always to keep it agitated, because as soon as you stop the agitation the particles of lime settle to the bottom, and the basic principle upon which liming is based calls for an even distribution of lime particles throughout the liquor, in every part of the liquor. You are all probably familiar with an agitated lime liquor. The particles of lime are so finely divided that it looks like milk, and these particles are continually in contact with the hide surface, and apparently we have that automatic action going on of dialysis,—the attraction of the fibre for a base of a hydroxide, which is milk of lime in suspension with water, and that going back becomes re-charged again with the lime, and it goes back and forth continually. I don't know how clear I have made that point. I should be very glad to enlarge upon it to the best of my ability if it is not quite clear.

MR. HEALEY:—I brought up that question in that form rather as an academic one than as a practical solution of the trouble, and judging from your previous remarks, it would seem as though our customary practice of leaving a pack of hides in a lime in the form of a pack would cause very uneven liming inasmuch as certain portions would be subjected to the renewal of the saturated solution whereas others would not. And again, if you plunge up the lime very thoroughly as each succeeding hide goes to the bottom, it must necessarily form a deposit upon its surface, of lime, and taking the extreme case would it not be a similar action, although to a less degree, as if deposited in a lime paste at the bottom?

MR. GRIFFITH:—Not altogether, because as I pointed out at the end, water is a vehicle for the penetration of the lime, and if you have a lime paste of course you have a solid mass to the exclusion of water. Water is a very active vehicle in the case, and we know that if you constantly draw lime—the usual practice I think is once a day—in this country probably twice a day—but in England the practice is once a day; and my reference to English methods was only because I thought some of the tanners here would be more interested in English methods because they know what their own methods are better than I do. But it involves a principle, and the idea of removing the hides from the vat, which in England they call "drawing," and returning them, is to permit of the liquor being agitated when the hides are passing, and then they are returned immediately to the milk of lime, so that as each hide settles down there is a different film of lime settles with it between each hide. Now your point as to whether the uniformity of the lime is affected by settling in a pack is a very good one, and it is one that I looked into a few years ago. It was in connection with the early days of chrome tanning of heavy leather, and I felt that the troubles we were up against were right in the lime yard because we were liming our hides just as bark tanners did, and it wasn't that we were unable to get good leather but we were unable to get uniform leather. I went to the lime yard and I started a system there which took up a little time, and it made for uniformity, and the system was this: (Of course you must remember that I am on the English system where we have a fender leading down into the vat). Now this fender is equal in space to the space of the vat, so that it takes up really two vats in surface measurement, and the fender inclines into the vat in that direction (indicating with one hand against the other at an angle of about 45 degrees). The walls of the vat come up here, see? (Indicating). Now the vat starts here. The hides are drawn into this fender and the whole pack is laid on that fender. That is the first operation, to lay the whole pack on that fender. flat, and the liquor is prepared all below. Now instead of making my lime liquor in the vat, I made my lime liquor in a tub alongside the vat, and I had just an ordinary lime-water solution in my vat instead of a lime liquor, and by means of brushes—two men always operate a pack in an English yard—by means of brushes I swabbed the hair surface of the hides with this lime liquor from the top by a brushing application, which could be done very quickly; as a man became expert at it it did not take but thirty minutes to take a whole pack into the liquor, which is comparatively short having regard to the principle which we sought to establish. The extra time we took was fully compensated for by the results we got if the results were successful By doing it that way I was able to get very uniform liming because I distributed my lime in the vat by a thin paste on the hide itself.

and by so doing I ensured a very great uniformity in liming. Now, if I were to be asked to emphasize one point more than another where the American tanner could benefit from English methods in liming, I should say in regard to the taking of the pelt weight after liming. With a little work one can get more information from the limed hide than one can get by any other means. I have weighed pack after pack on the same class of pack—that is English market hide; of course they are trimmed, and where the trimming is all done more or less the same fluctuation between one pack and another is only about a pound or two pounds. It is most remarkable; and we get that weight—that lime weight. It is a very easy matter to calculate the yield in leather.

Mr. Green:—I would like to ask Mr. Griffith if it is not commonly held that the sweat process gives us better gains than the lime process. How does he explain this in view of the fact that the lime removes very little of the hide substance?

Mr. Griffith:—You must remember that when you bring a hide into my solution at all—and the most simple solution is a water solution—you will immediately set up a solvent action on your hide. You must not attribute your solvent action to your lime. This is a mistake tanners enter into because, as I said in the figures I gave, the soaking preparatory to your liming is of vital importance, so that you probably lose as much hide substance in the preliminary soaking to your sweating—in fact it is well known you do lose quite a little. Of course you do not lose the same amount probably all together in the sweating, but then you do not lose any more in liming, because the amount that is dissolved in the lime is largely influenced by the preliminary soaking, and that is a process common to both methods.

Mr. Green:—Then in actual practice would you suggest the use of an acid solution for soaking your hides.

Mr. Griffith:—No, I simply illustrated a simple solution in the case of water. Now an acid solution would have just the same effect, probably. You see, I have illustrated here where I endeavored to get away from the bacteriological influence—the bug influence—and I found that I dissolved considerably more hide substance when I took means to sterilize my liquors and my hide, so that quite apart from the bacteriological theory, or the bug theory, of dissolving hides, there is the solvent theory—the actual solvent effect of any liquid on hide. So that any solution, would, to my mind, have exactly the same influence in relation to the time it is immersed in the solution. Of course the time is the most important factor.

MR. GREEN:—Isn't it true that in an acid solution there would be less hide substance lost than in a neutral solution?

MR. GRIFFITH:—Yes, because most acids have a tendency to retard the solvent action, and there is a slight antiseptic value in all acids.

MR. WALLIN:—I would like to ask Mr. Griffith if he would say what effect the sulphide of sodium has in addition to the lime. Would he consider it desirable or undesirable? Many tanners use it.

MR. GRIFFITH:—It is practically a very common custom throughout the country to use a little sulphide with the lime, but I think there is no tanner in the country to-day who uses sulphide alone. I do not doubt that most tanners have tried it without success, but the influence of the sulphide is largely towards the facilitating of the depilation or to hurry the removal of the hair. It is a peculiar thing that according to Procter—I think Procter mentioned it; or it is Von Schroeder—or—I think Procter mentioned it anyway; I don't know whether he did the work,—but he says that there is not as much hide substance dissolved by caustic soda as there is by lime.

MR. WALLIN:—Then that would indicate that an addition of sulphide of sodium, if it hastened the action of the liming, would be beneficial?

MR. GRIFFITH:—I think so; I think so most certainly, because the use of a little sulphide of sodium enables you to unhair quickly.

MR. WALLIN:—Shorten the time in the solution?

MR. GRIFFITH:—Yes.

MR. VEITCH:—Increases the alkalinity of the solution?

MR. GRIFFITH:—Yes.

Mr. Vogel:—I think the point Mr. Griffith made that the water in the lime is really the solvent in a way answers Mr. Green's question, whether the sweating or the liming process would give more weight. The liming process as practiced in England and by some tanners in this country, being cold and slow, would not hinder your gains as against your sweating process, but I think most tanners in this country, especially in sole leather, have followed the Buffalo system, that is two days liming and then hot water, and it is the hot water in the end that loosens the hair and reduces your gains.

Mr. Green:—Yet it is commonly held that the Buffalo method gives better gains than the old-time lime process which perhaps occupies a week or ten days.

Mr. Vogel:—Because those limes were old and stale and not fresh and cold.

Mr. Mardick:—I would like to know whether the small quantity of sulphide with lime would produce flatness of leather; that is, where you use entire lime if you get your leather more plump than without it. I have noticed that in tanneries with the use of lime while you take out the hair easily yet it is at the expense of plumping. The lime plumps the hide and there is where it unhairs. If you use the sulphide in it you don't get the plumpness; you do with straight lime, isn't that the fact?

Mr. Griffith:—If you are comparing straight sulphide with straight lime I would say generally you are right.

Mr. Mardick:—Just a small quantity of sulphide in the lime.

Mr. Griffith:—That has not been my experience. I think a little sulphide is a very good thing.

Mr. Mardick:—How about the plumping qualities?

Mr. Griffith:—I have not found it to influence the plumpness, where you use sufficient sulphide so as not to alter the strength of your hair—and that should be the guide in using sulphide.

Mr. Mardick:—I would like to hear the experience of some of the others, of the tanners, where they have used sulphide in conjunction with lime, and whether they have obtained flat leather or plump leather.

MR. GRIFFITH:—I think probably Mr. Wallin might say whether he has noticed that particular flatness.

MR. WALLIN:—To the extent that I have used it I have not noticed any flatness. I have not destroyed the hair with it.

MR. GRIFFITH:—I think that is the point.

MR. MORRISON:—My experience has been with the sulphide process and with what experiments I have carried on with sulphide—I use some sulphide right along all the time, a small per cent., and I have tried it in most every conceivable way, even straight sulphide. Now I find I get as good gains on straight sulphide as I do on straight lime, but I cannot get the color. I cannot get a smooth grain, it will not finish up as straight lime will, but I think in connection with lime that sulphide is a great advantage, and I think there is a field open for sulphide if we ever strike the keynote; that is, if we ever strike a happy medium where we can use it. My experience has been right along all the time—and I run quite a lot of it—I could not get a finish; I could not get a color. It would be dark, but I could get as plump a piece of leather, as solid a piece of leather, and firm, but you cannot get the finish on it.

MR. HEALEY:—Did you plump with acid or non-acid process when using sulphide straight?

MR. MORRISON:—Non-acid.

MR. VOGEL:—My experience along those lines is identical with Mr. Morrison's except we have used acid, and in addition to plumpness and poor color and finish we got brittle leather.

MR. MORRISON:—I might add that too, Mr. Chairman. I will make a little correction there; the fibre seems to be as strong as otherwise except the grain is very tender. That accounts for the roughness of the grain, you know; it is a coarse grain.

PRESIDENT WILSON:—Any other tanners here who would like to talk on this matter?

MR. SAXE:—Do the English tanners make any point as to the temperature of their lime; that is the constant temperature?

MR. GRIFFITH:—Yes, they all work on the cold lime system.

MR. SAXE:—How high?

MR. GRIFFITH:—A normal—an atmospheric temperature; and they always slake their lime twenty-four hours before they use it; and that is an important point.

Mr. Green:—Mr. Chairman, can Mr. Griffith suggest any method by which the hides can be preliminarily soaked with the minimum loss of hide substance?

Mr. Griffith:—I am afraid I cannot, because water is a common solvent and I do not know as I can offer you anything better than water just now.

Mr. Morrison:—I do not thoroughly understand Mr. Griffith on the English method of taking weight. Do I understand it is as it comes out of the lime or after it is unhaired—fleshed?

Mr. Griffith:—Yes, after it is unhaired.

Mr. Morrison:—What we called white weight in this country?

Mr. Griffith:—Yes, I used that term in the paper,—"White pelt weight," because I thought that would probably make it clear.

Mr. Vogel:—There is another interesting point in what Mr. Griffith just said, necessitating going a little further and getting an accurate white weight. After the hides are unhaired and they drain a little more, the loss of water would sometimes vary. Mr. Charles Parker, a brother of Dr. Parker, and a practical tanner, at one time spoke to me about a check weight. By this he meant he had a body of water in a wooden tank which had a constant weight of course, and which he would weigh, and in this he would put in ten butts and weigh them in the water, which would give him a constant weight. You see? The absorption of the water would be complete, and then there would be just hide substance, and these weights we would use in calculating. I thought it was very clever.

Mr. Hall:—I notice quite a number of men in the leather trade have noticed marks—so called rubs—the question has been in the trade papers several times and no response has been coming forth as to how they were caused, and it seemed to occur in the beam house somewhere between the soaks and previous to going into the pickle. This is not seen because of the white character of the skin, before going into any kind of color, and just as soon as they are in blacks or any other colors this is apparent. The The question is how and where they are produced?

PRESIDENT:—I think that Mr. Griffith has something to offer in explanation of that.

MR. GRIFFITH:—I tried to offer an explanation prior to the reading of the paper to the gentleman who put the question. Of course the question is of essential importance to the upper leather industry, and of course in order to arrive at the cause of any defect one must at least be given an opportunity of examining the defect. A description of a defect is not always very satisfactory, and I am not acquainted with the terms the questioner uses, although I am quite familiar with the somewhat—well I won't say vague, but it is not a conclusive description of the defect. One comes across it very frequently in the manufacture of calf upper leather. It is not exactly a removal of the grain because the grain is there intact; and it is not apparent when you glaze the leather, but it is apparent and quite visibly, and disintegrates the grain when that grain is colored into browns or blues, or even into blacks, if the black is finished into what is known as a mat. I followed that when I was in a tannery where I had been invited to solve the trouble, and I traced it to the lime yard. Now, of course, it must be understood in attempting to answer this question, that I am answering it within limits; that one cannot be expected to say that a thing is so. These things are largely a matter of opinion. The way that a chemist would get at any difficulty which arises in the tannery is by a successful process of elimination, and in order to be sure as to the cause one must go right through the whole process, and investigate each of those processes separately. Now I think, without knowing a thing about the methods employed in the tannery where this trouble arises—I don't know how long they soak or how long they lime—I think you can tell me how long they soak—three days— and how much lime they use I don't know, and just the condition of the lime I don't know. Now all those things have got to be taken into consideration; but I do know that by an observation of cleanly methods, not taking a chance with anything in the beamhouse, and being absolutely sure that your soaks are clean, that you have the right amount of lime and the right amount of sulphide or arsenic, which ever you are using in conjunction with the lime, and the washing of the lime out of the skin preparatory to bating,—all those things make for as near perfection as we can get in a very complex industry such as ours; and I can only advise you to look very carefully into the thing along those lines. I cannot offer you a definite solution of your trouble.

Mr. Hall:—I should say that the amount of lime and sulphide of sodium is practically the same the year round, and yet these rubs are not visible the year round, but from the time steam is introduced in the fall, say in the month of November, I have seen it follow for five months, and with the advent of warm weather and the discontinuation of steam, the lime and sulphide as a combination are not so accentuated, showing that of course the trouble is caused under water, and being in the beamhouse the white surface cannot be traced, but the trouble occupies a pretty large territory, especially in New England and along the coast here—in calf skin lines. It is a general complaint, though not made as public as one would think.

Mr. Griffith:—I would not like to assume responsibility for anybody, or for the stock in the lime where a steam pipe is introduced. You suggested yourself that the trouble is accentuated when your steam heat is introduced. There is the first point in your process of elimination. Eliminate your steam heat.

Mr. Hall:—Well, if the stock unhairs hard in winter would it be more practical to use more sulphide and less steam?

Mr. Griffith:—No; I think you would make a mistake in increasing anything in the quantity you employ. What you would have to do is to alter your methods. Instead of altering the time or altering the quantity of materials you employ, a slight change in your methods would be more practical. Give the skins the same time in liming; don't blow steam into the vat, but have a vat on one side containing water at a temperature of summer heat, and put your skins into that and unhair them out of that. That is where you want your heat, and you do not want to put a steam pipe into that even. You have got to arrange that by getting the temperature of your water before hand. You will probably raise it a little higher than summer heat, but arrange it so that when the skins are in you can approximate to summer heat. That would be a far more satisfactory way than blowing steam into a vat when the hides are in.

MR. VOGEL:—This is again very interesting to me because I have had experience along that line, and may I ask the gentleman what leather he was making?

MR. HALL:—Plain calf and glazed. I noticed in the glazed stock it does not make any difference but in the unglazed the trouble was very marked.

MR. GRIFFITH:—The fact that he said it occurred after he steamed his limes, or continued for a period of time when the weather was cold simply goes to prove just what I have found, and the steaming of the lime has nothing to do with it, or the heating or the treatment of the stock in the lime, but it is the washing in the wash drum in cold weather. Those are nothing but grain bruises. In the winter the pelt is hard and firm, and every time it strikes a pin that is a least bit rough it bruises the grain. That grain is then open and more receptive to any finish you wish to put on it, and it gives you these spots. If you glaze it that closes it down again, and the ultimate seasoning after graining would close up any bruises you have got.

MR. HALL:—I think the explanation Mr. Griffith gives is very good, but it is utterly impossible to say it occurs in the wash wheel because the skin is being worked—I always maintain that nothing can be seen of this action—the third, fourth, well, possibly the fourth or fifth day when the skin becomes sensitized and is in a large state nude when it reaches the sixth or seventh day, and when the man pushes down the spots and these spots rub against each other, why don't it occur then as well as in the wash wheel? You cannot tell it occurs in the wash wheel, because it is invisible. You and I might use the most powerful instrument and could not tell where it is done; but it is done in the beamhouse, but where and how? It is quite a problem.

MR. VOGEL:—I would suggest that the gentleman run his stock and unhair it and not wash it at all in the wash wheel, and follow it through the entire operation and see whether it has the spots or not.

MR. BLANK:—It is strange to say that skins known as double L, out of half a dozen skins not one of them showed these spots, but as the skins ran heavier the abrasion takes place; but with the thinner skins it does not.

LEATHER ANALYSIS.

By F. P. Veitch.

There is very little to be said on the question of leather analysis; that is, on this co-operative work that has been done. Unfortunately no members of the committee were able to do any work along this line, and the work which has been already printed in the November JOURNAL is entirely the work of our own laboratory. All those who cared to do so of course had an opportunity to read this, and it is unnecessary for me to read it here, or to do any more than to refresh your memories in regard to it. Certain changes were made in the instructions sent out this year. It has been pretty thoroughly determined that the use of basic lead acetate for the determination of sugar gives low results, and this having been proved it did not seem to me necessary to call for any co-operative work on that point. It simply made a change in the method; but in my own laboratory we found that there was quite a difference in whether normal lead acetate or basic lead acetate was used, and results were shown in my report where the difference was as great as two per cent. where the leather contained as high as thirteen per cent. of glucose. Now of the two samples sent out, one was unadulterated and the other was adulterated with four per cent.—samples of the same leather—adulterated with four per cent. of magnesium sulphate and with eight per cent. of glucose. The results of our own analyses gave us back practically these quantities; and you will remember that in last year's report the Referee was unable to get all the glucose back; there was quite a material falling off, and I think due to the use of basic lead acetate. Now with regard to the extraction, I have recommended that leather be extracted seven hours. I am entirely uncertain whether this is wrong or not. I recommended seven hours with the idea that the work could be finished in one day, but I seriously doubt whether this dissolves out all of the uncombined tannin. Longer extraction in our own practice is fourteen hours, and this gives us two or three per cent. more, and the two or three extra per cent. is practically all tannin, but I do not think that this can be said to be combined tannin, because on prolonged extraction we find we reach a point where the extract is practically constant,—where we are getting tannin at a pretty definite rate, and it is at that point, I think, where we can say that the leather itself is beginning to break up; and I do not think that in fourteen hours or some such period as that there is any material breaking up of the actual leather.

You will notice that the results show that there is less tannin extracted at 30 degrees than at 55 to 60 degrees, while the non-tannins are practically identical at both temperatures. This, I think, confirms the opinion in a general way, that the longer extraction has not broken up the leather but is simply removing the more difficultly soluble uncombined tannins. Glucose comes out at a lower temperature quite readily and we can readily secure all of that even at 30 degrees.

Now with reference to the question of other indicators, it seems to me that this is entirely a matter to be left largely with the individual analyst in the determination of nitrogen—in the titration of the excess of acid. Some chemists' vision is not sensitive to one indicator and more sensitive to another, and I think that cochineal or methyl orange, or anything that a man is used to using will give him satisfactory results, provided he uses the same indicator in his regular work that he used in making these solutions.

With regard to the other question which was referred to the committee, about the reporting of magnesium sulphate, whether with or without the water crystallization present, I am personally in favor of reporting with the water crystallization, as undoubtedly a material is in leather in this form and exists there when the leather is made or sold that way. I don't see why it should be cut down and given a lower quantity apparently than is actually present. I think that the work on the leather should be continued especially along the lines of improving the method of extraction. I think the sugar methods and the determination of ash and magnesia are fairly satisfactory, but that more work is necessary on determining the amount of uncombined matter, and also on fats where heavily greased leathers are used. It seems to me it would be well for the referee for next year to begin the use of greased leather. So far all the work has been done on practically rough leathers, and we have not been bothered with the complications that would be introduced with large quantities of grease.

DISCUSSION.

President Wilson:—You have heard Mr. Veitch's review, and I will call for a very prompt discussion now, as our time is getting rather limited and we wish to assemble at two o'clock promptly. Mr. Eachus, we would like to hear from you on this subject.

Mr. Eachus:—I haven't very much to say about it. I have analyzed a great many samples of leather, chiefly for adulteration, and used the official method as near as I could follow it. I report the Epsom salts as crystallized, because I believe it should be reported that way, as that is what the tanner adds. I extract with the Procter percolator for about one day with water at 50 degrees and analyze that solution for tannin and the grease is determined by extracting the air-dry-leather and evaporating down. Then I analyze the grease for the different ingredients in it—paraffine and things like that. I haven't anything further to say.

President Wilson:—Mr. Alsop, haven't you something to say in regard to the determination of sugar in leather?

Mr. Alsop:—No, I haven't anything to say. I precipitate with basic lead acetate, but to get the right results I think the method ought to be changed. I don't know personally; I have had no experience in testing that out. The matter of methods of extraction I think is something that should be standardized. I think it is more important than anything else that we should have a definite method that the different people could follow. I think it is pretty hard to get, it is so empirical. I think the method should be such that everybody does it the same way. I think the results agree very well. I think any reasonable extraction would extract all the sugar and salts.

President Wilson:—This matter of extraction of leather resolves itself down to exactly the same point as the extraction of barks and woods. We don't know where to stop; but just as Mr. Alsop says, there should be some definite time limit for everybody to use, because we do not know when we come to the point of breaking down the hide fibre any more than we know when we come to the point of breaking up the cellulose in our extraction of woods and barks. And there is another point in regard to the Epsom salts. In taking the moisture on leather you naturally get some of the moisture which is in the Epsom salts and is reported as the moisture in the leather. If any one else has any remarks on this subject now we would like to hear from them.

Mr. Reed:—Regarding the standardization of the methods, we voted upon the provisional method for leather analysis recently, and I might predict that that vote will be carried and we will have a standard provisional method for leather analysis such as is given here. And on the water soluble material it says, "Digest 30 grams of leather in a percolator over night, then extract with water at 50 degrees C. for three hours. The total volume of solution to be two liters." That will really be the standard in the absence of any official method for this association for the ensuing year at least.

Mr. Veitch:—That leaves in the present basic lead acetate?

Mr. Reed:—Yes.

Mr. Veitch:—Well, that has absolutely been proven to be wrong. Of course if the association wants to do it nobody can hinder them from doing it.

President Wilson:—Any further discussion?

Mr. Mardick:—I would like to ask if anybody here has found the relation between those different elements in the leather. The percentage of nitrogen for instance, is understood,—hide; supposed to be so much per cent. and the tannin so much per cent., and what has that relation to do with a given quality of leather? For instance, how much per cent. would a given quality of leather have of oil, how much tannin, how much hide matter? In order that the tanner might get some basis for comparison, you might take analyses a great many times and report to the tanner, "We find so much nitrogen and so much tan, and so much non-tan." That would not be any good unless we have some relation established between those different elements.

MR. WALLIN:—Doctor Wiley will establish that for us.

MR. MARDICK:—I think Dr. Wiley might do it later on, but there ought to be some understanding in the meantime. It is simply misapplied energy to make an analysis a thousand times and then throw it away in the waste basket without knowing why you do it and what relation it has. It seems to me a great deal of research has been wasted on the same basis. What the tanner wants to know is, whether a piece of leather that is tanned has certain relation to the hide matter or tannin; otherwise the leather analysis is simply a waste of time.

PRESIDENT WILSON:—Mr. Griffith, haven't you some observations to make on this line.

MR. GRIFFITH:—With regard to Mr. Mardick's question, I think the point with regard to the relation of tannin to hide fibre varies with the tanning material employed. I think if Mr. Mardick will look up some of the literature which has been published he will find some little information on it which might prove useful.

THE DEFINITION OF "TANNIN."[1]

MR. ALSOP:—In our official method for extract analysis we are required to take enough material to give a solution containing from .35 to .45 gram tannin to 100 cc. of solution. In making the non-tannin determinations we are told to use from 12 to 13 grams of dry hide, or that equivalent, and the non-tannin solution must not give a precipitate with a one per cent, gelatin, ten per cent. salt solution. Now, occasionally extracts or materials when shaken with 12 to 13 grams of dry hide will give a non-tannin solution that will give the precipitate with a gelatin salt solution. Now under this method what are we to do? Are we to increase the amount of hide or are we not to make the test?

PRESIDENT WILSON:—It looks as though we would have to

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[1] Discussion at Washington Convention.

have a sliding scale. Are there any opinions of any of the members on this matter? I would like to hear from them.

MR. REED:—I would say that the same point has been brought to the attention of the secretary by Mr. Nichols,—exactly the same points Mr. Alsop has raised, and he wished me in his behalf to bring it before the association for discussion.

PRESIDENT WILSON:—Well, we are ready for the discussion. Have you any suggestions, Mr. Alsop?

MR. ALSOP:—No; I want to hear some suggestions.

PRESIDENT WILSON:—You have introduced the subject; boost it along.

MR. ALSOP:—I introduced it, yes. I don't know what to do.

PRESIDENT WILSON:—It seems as though it is impossible almost to define any hard and fast rule in such a case as this.

MR. ALSOP:—I know of a case that came up of this kind. One chemist analyzed an extract and used that strength solution, and the amount of hide specified by the method and sent in his result, while another chemist analyzed it and found considerably more tannin; and one chemist took the stand that he did not have any right to add any more hide to the solution under the official method, and the other chemist took the stand he didn't have any right to report as a non-tannin a solution that had tannin in it, so he had to add more hide.

MR. WALLIN:—Where was the tanner?

MR. ALSOP:—The tanner, he didn't know what to do. Of course, that led to a scrap between the tanner and the extract man.

MR. HALEY:—What is the nature of this material that requires this extra attention and care? Is it an ordinary tanning extract?

PRESIDENT WILSON:—You will have to ask Mr. Alsop, Mr. Haley.

MR. HALEY:—What is it?

MR. ALSOP:—Extract!

MR. REED:—It seems to me, Mr. President, that this clause was drawn up to cover practically all what you might call *legitimate* tanning materials; and if we analyze a material that does not come up to the specifications of the clause following the official method for the amount of hide used, and if it did not detannize would report it according to that method and I would pay no attention practically to the gelatin salt test on it, because I would have some very grave doubts in my own mind whether the gelatin salt test in that case showed tannin or not.

Mr. Small:—The last remark of Mr. Reed's is one I would like to emphasize. I happened to run across two or three materials where it struck me that the gelatin salt test did show a very decided trace of undigested tannin, and it is an open question in my mind whether that test is applicable in all cases and whether it can be used to determine whether your non-tannin always is entirely free from tannin.

Mr. Eachus:—I have seen exactly this same thing happen in the case of mangrove bark which was brought in by New York importers and sold to the United States Leather Company, and you would have to use twice as much hide powder, or put acetic acid in it, or something like that, to get a non-tannin which would show up to the gelatin test.

President Wilson:—The question is, what that material is, whether it is tannin or coloring matter. If it were tannin it would appear that the amount of hide powder specified for detannizing all other tanning materials would be sufficient, and I quite agree with Mr. Reed that there is a possibility of that other material not being tannin at all. I have come across the same thing myself once or twice and it seemed to me that that was the way it then looked.

Mr. Alsop:—I had a mangrove bark not long ago which I extracted with the extractor, and the extracted solution was tested before shaking with the hide powder. It did not give any precipitate with the gelatin solution, yet it would give a big precipitate with the gelatin salt solution. And that bark was impossible to decolorize or detannize, or whatever you were supposed to do with it, with any amount of hide you could rise; but after shaking the solution up with hide powder you could get the precipitation. You couldn't get any with gelatin, but you could with gelatin-salt solution.

PRESIDENT WILSON:—I think this is an admirable subject for our research laboratory which we are going to have.

MR. WALLIN:—It seems to me that this question of rules is a matter that ought to be referred to some committee perhaps, and be settled. Now the tanner is immediately up against a selection when he buys this kind of tanning material; he will select some chemist who is running a laboratory for a Chestnut or Quebracho, or Oak extract manufacturer, and the man who is selling this kind of material, he will select some chemist who is looking after his interests; and the result is we have got two varying results, and that certainly ought not to exist. The association ought to get together on this matter. If I submit the matter to Mr. Reed as a tanner he will give me one result, and Mr. Saxe would submit it to some fellow who is not so much interested in quebracho extract as Mr. Reed is, and he will get some other results, and the Saxe and I have got to go out in the alley and fight it out, and that is hard on the tanner and extract manufacturer.

PRESIDENT WILSON:—I think Mr. Wallin's point is very well taken. This will be referred to the executive session before the close of the meeting.

MR. REED:—I think it has perhaps even a deeper significance than has been brought out so far in this argument. We all know that there are certain materials on the market purporting to be tanning materials that contain practically no tannin at all. I refer now to the waste products from the paper pulp mills. They are not legitimate tanning materials in the sense that we recognize legitimate tanning materials.

MR. WALLIN:—You mean by "We," quebracho manufacturers or chemists generally?

MR. REED:—I would rather not reply to that, Mr. Wallin.

MR. WALLIN:—That is a sincere question.

MR. REED:—I meant as a member of this association. And under the circumstances the same question was raised the year I represented the association at the Frankfort meeting, that the shake method, or at that time the filter tube method of the International Association returned as tannin matters that were not tannin at all in the sulphite cellulose products; and Professor

Procter has, I think, within the past year, called attention to the fact and recommended that the old Lowenthal method be used, which I believe on those extracts will represent possibly four per cent. of tannin in sulphite cellulose. I think, as I say, that the whole subject is of deeper significance than just the mere question of an analysis showing by the shake method some slight differences. I think it goes back further.

MR. SAXE:—Just a word. Possibly what Mr. Reed or the Association may not recognize to-day as tannin, possibly in ten years we may recognize as tannin.

PRESIDENT WILSON:—Physically but not chemically.

MR. SAXE:—Physically. Will any material that combines with hide powder and produces leather—can it be called tannin or not? I would like to ask Mr. Reed.

MR. REED:—No, I should say not; that does not necessarily follow.

MR. SAXE:—What is vegetable tanned leather? How is it produced? You cannot make it out of iron.

MR. REED:—Vegetable tannins usually contain what is known as tannin—tannic acid, which varies with the different compounds used—with the different materials—and tannic acid can be separated from the different vegetable materials.

MR. SAXE:—You speak of sulphite watse liquors as not being tannin. Do I understand you correctly?

MR. REED:—Yes.

MR. SAXE:—I can show you whole hides that have been tanned right through with it. It is not cloth, it is not broadcloth; it is not felt; it is leather. Now, are you going to classify that separately as something else and not leather? Yet there it is combined with the leather and producing leather. Shouldn't it be called leather?

MR. REED:—I should say not.

MR. SAXE:—What is chrome, then? Do you call hide tanned by the chrome process leather?

MR. REED:—Chrome leather, yes.

MR. SAXE:—What would you call hide tanned with sulphite waste liquors; would you call it leather?

MR. REED:—I would not call it leather.

MR. SAXE:—What is it then?

MR. REED:—I don't know yet, I would not call it leather.

MR. SAXE:—I would like to know what it is. I would like to show Mr. Reed some, and I would like to know what he would call it.

MR. REED:—I would call it waste sulphite tanned leather, perhaps.

MR. GRIFFITH:—Might it not be worth the whiile of the association to go on record for purposes of guiding litigation, to definitely state what in the opinion of this association, leather is? I had occasion recently to discuss that point with some attorneys and they turned up dictionaries, but in not one case was a true explanation, as I understand it, of leather given. If I may give my own ideas on the matter I would say that essentially leather is a preserved hide. It used to be the notion amongst the old time tanners that a tanner could not improve upon a hide, and that the nearer you kept your leather to the original hide construction—that is with regard to the fibre and so forth—the better your leather was, and the more foreign matter that you introduced in order to preserve your hide, the further you came away from what would be called good leather; while, of recent years, we have seen a variety of new tannages, the aldehyde tannage, the chrome tannage, and a number of vegetable tannages, and last but not least, the question of this recent new material tanned from an extract which is obtained from paper pulp. I think that there is a law in operation in our tanning which I have found to work fairly well. You take, say an alum tannage or an aldehyde tannage, the appearance of the hide does not undergo any change so far as the color goes. In bark or extract tannage we are guided very largely by the color of the tannin. And oftentimes the tanner can see that the leather is tanned when the penetration is completed. Of course tanners vary as to that. A good tanner is not satisficd with the tanning of his leather as soon as the hide is penetrated. But one of the great difficulties of the chrome tanners is that they are apt to conclude that the tanning is completed as soon as the color penetration of the chrome is completed, whereas that is not the case. Now with alum and aldehyde tannage you don't have that penetration, and the question becomes somewhat complicated. I have always laid it down as a law for my own guidance that a hide is tanned when it passes from the transparent to the opaque. Raw hide will always allow light to pass through it. Leather will not. As a fundamental principle I find that to hold good. Now I think it might be worth the while of this Association, seeing that we are responsible for a good deal that happens to leather in its preparation,—we ought to go on record with a definition of leather.

PRESIDENT WILSON:—I think that that matter requires considerable consideration before we take any action such as going on record to that degree. It is a matter which is not at all simple, and we certainly could not very well take any action on it at this assembly here without considerable forethought.

Are there any other remarks now with regard to the topic under consideration?

MR. MARDICK:—I think this method would be quite a clear if —there is a point of difference in buying the extracts. Some manufacturers sell their extracts by mixing with other lots; others do not. Now what we can do is one thing: Take the natural quebracho extract and analyze it; how much ash there is in it. Suppose one per cent. Take also the natural chestnut wood extract and analyze it. How much ash there is in it. Suppose we analyze a hundred different kinds, from 100 different carloads and find out an average which is very accurate. The ash is about so much in quebracho and so much in chestnut. They run very regularly if they are not adulterated. Then we have something to tell to the tanner, that natural quebracho extract has so much tannin and so much ash. Give him a standard for that extract. Same thing for the chestnut. If we go to other extracts when they are adulterated and find some insolubles about 212 degrees Fahrenheit, 118 to 212 degrees, non-tannin matters are held in solution by other salts and sold to the tanner, that ought to be, as Doctor Wiley says, on his brand. It is a mineral salt and non-tannin matters mixed together and should be sold as such and not sold as extract. Until you determine that question and establish a standard, you will never be able to be any good, or determine to the tanner what kind of extract he can buy or what it is. Then we have also the question of waste sulphite extracts or like extracts or treated extracts and so on. The question is whether the tanner is getting a natural extract or a treated extract. It ought to be branded. Then we know where we are.

PRESIDENT WILSON:—If there are no further remarks we will adjourn.

MR. HALEY:—I think this matter should be kept open during the absence of Mr. Saxe. I have been advised confidentially by Mr. Saxe that he would prefer waiting until his return. He has gone, I believe, to get some samples. Oh, here he is! Mr. Saxe, Mr. Wilson was going to close this discussion.

MR. SAXE:—I may be wrong in my premises, but I maintain that any vegetable matter that will combine with hide must possess tannin and produce leather. With Mr. Reed's permission I would like to ask him in all sincerity whether he calls this (handing Mr. Reed a sample) leather, or whether it is a piece of iron or a piece of broadcloth or a piece of felt.

MR. REED:—(Examining sample)—Well,—(interrupted).

MR. SAXE:—I am not asking about the quality of it now, because we all make poor and good leather, you know. That is tanned right through with waste sulphite extract. Don't let's talk about the quality; it is simply a question of whether it is combined with hide fibre and whether it is leather.

MR. REED:—I don't know whether it is combined or not until I analyze it.

MR. SAXE:—Would you accept that as leather or not?

MR. REED:—How could I until I analyzed it? I don't know the value of this material. I don't know its wearing qualities.

MR. SAXE:—That is not what I mean. Wouldn't that contain tannin to produce that result?

MR. REED:—Not necessarily, in my way of thinking.

MR. SAXE:—Would you mind asking any other gentleman here whether they would think it contains tannin?

MR. KERR:—Is that a piece of vegetable tanned leather or mineral tanned leather?

MR. SAXE:—Vegetable tanned leather.

MR. KERR:—It is? What tannage is it?

MR. SAXE:—Waste sulphite liquor tannage.

MR. KERR:—What is the composition of the tanning agent?

MR. SAXE:—The chemical composition? I can't give you that. If Mr. Kerr is getting at the chemistry of it it he has me beaten. If I was a chemist I would be an active member instead of an associate.

MR. KERR:—This particular extract made in the United States contains, I believe, about 4 to 6 per cent. of alum.

MR. HALEY:—Mustn't the extract manufacturer or the tanner expect that that is tannic acid from the report that the members of the American Leather Chemists' Association make upon samples of that extract submitted of their test? Isn't that the point at issue? What is the use of discussing whether or not this is tannic acid when the members of this Association stamp their reports that this material is tannin? Am I not right in that statement?

MR. REED:—Yes.

MR. HALEY:—I think this discussion is all out of order.

MR. REED:—I think Mr. Haley is right and that is why I said I think it has a deeper significance. Theoretically he is right.

MR. HALEY:—And practically too, because you stamp your report, "Analysis by the A. L. C. A. method 25 per cent. tannin." Why hasn't the tanner a right to conclude that your analysis is correct and that that is tannin? You take and analyze a sample of glucose, send it to your trades chemist, put it in your own laboratory and have your own chemist analyze it; call it glucose extract if you want to; and that chemist will report a certain percentage of tannic acid in pure unadulterated glucose, and he is obliged by the rules of this Association to report back to you that there is tannic acid in pure glucose. Take again our poor old resurrected friend palmetto, and you analyze palmetto extract for four hours with a certain amount of hide powder, and you increase the amount of hide powder and increase the time and your percentage of tannin according to your method will depend directly on the amount of hide powder used and the time consumed in contact. Now I don't mean to stand here and attack this method. It is not perfect and when conditions arise that call for change either in the method or in the method of reporting, it is up to this Association to embrace the opportunity, and it strikes me that that time has now arrived when some active measures must be taken to protect the integrity of the chemists' reports according to this Association's methods. Now we cannot stand here and say this is not tannin when you each and every one of you chemists report it as tannin. You are either prevaricating on your reports or else your method does not cover this special material and other kindred materials I could mention. In other words, if there goes into a laboratory an extract marked "X Extract," we will say; it is analyzed according to your official method. You send back to the source of the origin of that extract your analysis and you brand that analysis—that extract—as containing tannin, and you cannot come here and say that extract does not contain tannin. You are contradicting yourselves. I am not sponsor for waste liquor extracts, but I like to see justice done, and when this Association forces their members to report tannin in that extract you have got to stand back of it or change your method or change your method of reporting.

Mr. Reed:—That is what I said.

President Wilson:—I think that the whole matter hinges upon the matter of reporting rather than otherwise. When these methods were devised, as Mr. Reed remarked, they were not devised to cover all classes of materials which enter into the process of making the various kinds of leather which are on the market to-day. They were devised to cover those materials which at the time did contain real tannin chemically,—which were real tannins rather than supposed tannins. And in regard to these matters which were just mentioned, they are not true tannins but matters which combine with hide to make a so-called leather; and the whole fault lies in the method of reporting.

Mr. Haley:—You know that the foreign method—the I. A. L. T. C., do not report tannin. Their reports say, "Materials Absorbed by Hide." Now that may be tannin or it may be glucose. When the tanner drums glucose into his leather is that material absorbed by hide?

President Wilson:—Possibly some of it.

Mr. Haley:—Then according to our method of reporting it is tannin. This Association must keep ahead rather than trail in the rear, and when conditions like these arise this Association should devise ways and means of differentiating between true tannin and material that may or may not be used as a substitute for tannin. And I think that it is really a demand; it comes in the form of a demand upon this Association at the present time. It is perfectly ridiculous for a chemist to state that a material does not contain tannin when his own stamped and signed report gives it as tannin. Now we must change those things. It is not even a subject of argument. It is like giving testimony under oath and then coming off the stand and saying you don't believe what you have said. I do not think we ought to close this matter up with adjournment to-day noon, but rather keep it open. I understand that one of the speakers this afternoon is a gentleman directly interested in this material, and we would like to hear what he has to say on the subject.

ABSTRACTS.

The Measurement of Color in Fluids. A. T. HOUGH. *Collegium,* 1909, No. 388, pp. 417-22.—The author has sought, so far unsuccessfully for a practical substitute for the Lovibond tintometer in the measurement of colors of tannin solutions. A photographic method was tried, the principle being to measure the effect of the unabsorbed light after passing through the liquor, upon orthochromatized bromide paper. The element actually measured was the time required to produce an image on development. The results were "very erratic and out of all proportion."

As far as accuracy is concerned the Hüfner spectrometer has been found to give very precise results. A full description of a form of the instrument specially modified by Dr. Kenneth Mees, a photographic and color expert, is given, quoting his own paper as published (*Journ. Royal Photogr. Soc. of Gt. Britain,* July, 1904,) with illustrations. Any portion of the spectrum may be examined separately. The illuminated field of the spectroscopic slit is divided in halves, both coming from the same light source, one direct, the other after absorption in the colored liquid. A polarizing device is used to bring the two fields to equal intensity, effecting the measurement. The instrument is not likely to be adopted for technical analysis, being expensive (£55), and the numerical results would be difficult for the tanner to use practically. Also any given material according to the practical treatment would probably give as wide a range in the leather colors produced as the variation in solutions of different materials.

Irregularities in Tanning With Quebracho Extract. W. EITNER. *Gerber,* 1909, [35], No. 842, pp. 253-5.—In investigating the causes of some recent cases of incomplete tannage with quebracho, the author traced these to the use of Argentine solid extract for the entire process instead of for the after-tannage only where it is a cheap and efficient filling material. Formerly the solid extract could be used when the extract maker did not leach the wood to the utmost, as is now done. The extract of the present day contains 12% resins and 20% difficultly soluble tans; these last are precipitated on the hide and prevent penetration of the soluble tans. Another evil in some Argentine solid extract now sold is its adulteration with mangrove. This substance greatly assists in retaining the difficultly soluble quebracho tans in solution. The mixture does not, however, give good leather. Better results are obtained with the Argentine extract which has been mixed during manufacture with mangrove and myrabolams combined. This, however, is not claimed to be pure quebracho. but sold as blended extract. It is probable that the adulteration of the extract referred to is carried out in Argentine itself, for mangrove is plentiful in the coast regions and can be economically delivered at the factories.

Argentine Quebracho Extract. Forestal Land, Timber & Railway Co., Ltd., Buenos Ayres. *Gerber,* 1909, [35], No. 844, p. 288.—This communication is called forth by the strictures on Argentine extract in the preceding article. Absolute purity is guaranteed for the Argentine solid extract. Any adulteration with mangrove would be excluded on economical grounds alone. Mangrove is produced only on the distant seacoasts and freight costs thence, still more from Africa, would be prohibitive.

Cod Liver Oil. O. A. Jacobson. *Gerber,* 1909, [35], No. 847, pp. 329-30. —The writer, a Norwegian tanner, proposes that European tanners combine for producing this oil by more rational methods than at present in vogue, and provide themselves with an article of assured purity. Norway exports yearly some 25,000 hectoliters of brown cod liver oil, which is obtained from the residues remaining after expression of the medicinal oil. The quality of the brown oil which is used in leather dressing is not lowered by the increased production of medicinal oils, for it contains most of the "degrasgene," the chemically active ingredient in leather-making. Many producers of medicinal oil sell the residues to small concerns, which boil these for brown oil. The danger of fire is so great that the industry is carried out only in small isolated factories. To avoid this trouble, the oil is sometimes pressed direct from the residuum and presents a fine-appearing light brown product, which is, however, little suited for leather dressing, being liable to fermentation; it contains little degrasgene. The amount of degrasgene in residues appears to increase with storage. The writer thinks a combination of the pressing and boiling processes would be the ideal process. There is a large production in Norway of whale, bottle-nose, walrus and other marine oils, but blubber oil is not suited for leather, although most tanners cannot distinguish these oils. Blubber oil contains much mucous substance liable to later alteration. The oil is much improved by boiling, but is then, from the loss, dearer than brown cod liver oil.

School of the Tanner, (continued), **Control of Vat Liquors.** A. SCHMIDT. *LeCuir,* 1909, [2], Nos. 22, 24; pp. 510-512, 558-60.—In the ancient tanning processes irregularities in the liquors would on the whole adjust themselves, compensating for each other and at the close of the long tannage produce a good leather. In the rapid modern process this is not the case. If the old school tanner wishes to modify his system and shorten the tannage, he will have to be less lax in the adjustment of the liquors, for any irregularity will produce evil effects when he resorts to extracts. The old process itself, however, may often be shortened without recourse to extracts if the tanner knows his liquors. The following analysis was made of a series of vat liquors from a good tannery of the old school:

Vat No.	1	2	3	4	5	6	7	8	9	10	11
Tans	0.15	0.17	0.53	0.71	0.42	0.67	0.53	0.73	0.73	1.09	0.86
Non-Tans ..	1.07	1.58	1.73	1.80	2.01	1.84	1.69	1.86	1.78	2.00	2.21
Acid	0.05	0.19	0.68	0.90	0.90	0.92	0.79	0.79	0.79	0.66	0.62

These show great irregularity, especially apparent when plotted graphically. The vats 2, 5, 6, 7, 9 and 11 might as well be left out, and by leaving the hides a little longer in the others the whole process would still be much shortened.

Denatured Salt. W. EITNER. *Gerber,* 1909, [35], Nos. 844-5, pp. 283-4, 299-300.—In those states where a salt monopoly exists, the laws require that the cheap salt furnished for technical purposes be rendered unfit for use in food. The substances used in denaturing tannery salt are calcined soda, alum and petroleum. For the salt used in preserving hides, only soda should be chosen. Experience has shown that lumps of alum cause spots in the leather and even when the alum is evenly distributed, it produces a slight tannage of the flesh and interferes with the de-liming. The "blue oil" from petroleum residuum also causes irregularities. For the careful work of white leather manufacture, table salt is generally used. In pickling salt, alum is the best denaturing agent, as soda increases the consumption of acid.

Defects in Tanning; Stippled and Spotted Grain. B. KOHNSTEIN. *Gerber,* 1909, [35], No. 846, pp. 314-7.—Matt spots on the shell of circular form can originate from the crude hide being coated with dung. This should be quickly removed in the soaking. With long-haired calf-skins, such spots in the belly regions are also due to uncleanliness of the animal. Insufficient salting also occasions spots through decay. Also agents for denaturing the salt such as alum and soda will cause these defects. Carbolic acid, lysol or formaldehyde when used as preservatives should be applied very dilute, else matt or hard spots result. Sharply defined dark streaks on leather may often be traced to contact of the crude hide with iron, especially in the case of those animals having greasy pelts. There are so many opportunities for irregularities in dried hides, that for dyed leather, the tanner should choose fresh-salted stock, if possible. In the tanning operations themselves, the sources of defect accumulate.

In soaking, soft water from ponds or slow running brooks is liable to mitiate fermentation. Old limes strong in ammonia often give the grain a dull plush-like appearance. A neglect of frequent turning in the limes or long exposure to the air causes stippled grain. The dung bate is a prolific source of this mischief. Constant motion is the best preventive nor should the hides remain in the bate over night. For fine leather only bran bate is to be advised, or if dung is used, only fresh prepared strained solutions. In the tannage proper, lack of agitation and exposure to the air bring about the irregularities referred to. Also irregular liming shows up here. When dehairing has been effected by sweating or otherwise without lime, fatty spots in the hide may resist tannage. This may be remedied by treatment with borax. Finally these troubles may appear in dyeing, especially with vegetable dyes, boiled with alkali.

To Blacken Vegetable-Tanned Leather. *Ledertechn. Rundschau,* 1909, No. 48, pp. 379-80.—If the black refuses to adhere to the leather, it may be due to excess of grease in the currying. This is removed by saponification, using 20 to 30 grams of ammonia or soda to a liter of the log-wood liquor. The blackening is much promoted by heat, the liquor being at 50-55° C., and the leather being previously hung up in a warm room. Trouble in blackening may also be due to loss of tan in the leather through long storage. This is remedied by rubbing the leather with a strong decoction of tan-bark, or adding the same to the log-wood liquor itself; pure tannin is the most efficacious. Other hindrances to blackening are blooms on the leather from the dressing used. Glue, blood or gelatine glazes are best removed by luke warm water, casein and shellac dressings (made with water), by weak alkali, and waxes by ether, chloroform, carbon bisulphide, etc.

PATENTS.

Skiving Machine. U. S. Patent No. 944,103. W. A. PARMENTER AND A. B. ALDEN, Brockton, Mass.

Splitting Machine for Stripping off Flesh from Hides. U. S. Patent No. 944,488. A. H. KEHRHAHN, Frankfort, Germany.

Method of Removing Hair from Hides. U. S. Patent No. 945,221. L. CHEESEMAN, Scranton, Pa. The method of removing hair from hides consisting in treating the same with a composition of barium sulf-hydrate, barium hydrate, calcium oxide and water: the quantity of calcium hydroxide being sufficient only to convert substantially all the sulf-hydrate of barium into hydrated oxide of barium.

Apparatus for Evaporating Liquids. U. S. Patent No. 945,640. P. THELEN AND J. B. SPEED, San Francisco, Cal.

Tanning Machinery. U. S. Patent No. 945,878. G. C. VOGEL AND C. P. BOSSERT, Milwaukee, Wisconsin. A series of tanning vats, containing removable cages with curved bottoms which are used to contain the hides. A traveling crane transfers the cages from one vat to another, and a traveling paddle wheel serves to agitate the liquor in any desired vat.

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NOTICES.

The members of the Association are requested to communicate with the Secretary expressing their views for or against the reporting of analyses to the first place in the decimal. By analyses, is understood all official and provisional methods of the Association.

The Chairmen of the various Committees are earnestly requested to expedite the work as much as possible, as it is probable that the annual meeting will be held at an earlier date than usual.

The Secretary would urge that the reports be placed in his hands not later than September 1st, and as much earlier than this date as possible.

H. C. REED,
Secretary.

Stamford, Ct., Feb. 15, 1910.

THE DETERMINATION OF ACIDS IN TAN LIQUORS.[1]

MR. ALSOP:—I read the report of the committee this morning and the results the committee obtained, and the views of some of the members who collaborated, so I think it is up to the rest of them to make the discussion.

MR. REED:—Mr. Alsop, don't you think the question of the accuracy of the method is largely determined by the personal factor and experience? Isn't it true that of those collaborators many of them had no experience with the method before, and probably if now they would undertake it, with fuller experience, their figures would be more in accord?

MR. ALSOP:—I think that experience is seventy-five per cent. of the whole thing. A person with experience in this method in 90 per cent. of all the cases would get useful and concordant results. In fact, I know that concordant results can be gotten, because I have tested a good many thousands of liquors by it. There might be a few cases where it would not work well, but I think the same can be said of any method that can be devised, so far as that goes.

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[1] Discussion at the Washington Convention.

Mr. Oberfell:—I have used the gelatin-hematin method on perhaps 150 liquors in the last year, and find I can get concordant results a whole lot better than by the official method, and on the quebracho I believe my results ran fairly close to Mr. Alsop's, which would go to show that the experience would give concordant results; but I noticed in Mr. Alsop's report that he thinks the basis of the trouble on the method is the indicator, and while what I have to say may be wrong, for some reason which I have not been able to see, still I have been able to find that the hematin can be made very sensitive by using it in a very dilute solution; that is, the solution containing the acid from the liquor to be dilute. I took five cc. of liquor—tan liquor, added 15 cc. of gelatin solution, and diluted to 250 cc. and added the regular amount of kaolin and filtered it, and then I took 30 cc. of the filtrate and titrated it, and by using just one or two drops of the hematin indicator I found that the color changed just as accurate as by using cochineal or methyl orange or any volumetric indicator. The change is correct, and it is permanent. Now whether there is anything wrong with that idea of using a dilute solution, I cannot say. The one trouble would be that just the proportions I gave gives the percentage of acid as acetic direct from your burette reading, and in liquors where the acidity runs down to say two or three-tenths per cent. you would only use two or three-tenths per cent. of N/10 sodium hydroxide solution; but I made up a twentieth normal solution, and even twenty-fifth normal, and tried out that acidity. I used a greater volume of filtrate solution, and I think that improved the accuracy of it. I tell you what it does, it gives less acidity, but that would be more than likely what we would expect from the fact that when you start to get your color change on the regular method it runs from a very faint color to a distinct color when you stop your titration, and that can be traced to the fact that it is consuming more alkali than there is acid in the liquor to be titrated.

Mr. Alsop:—My objection to the indicator isn't so much in one given case, but there are different materials and different liquors; it has different color changes.

Mr. Oberfell:—Of course, I can only speak from just a limited class of liquors; I haven't a very wide class to work on.

MR. ALSOP:—That is one reason why the results vary so much. You have to get used to the color changes that occur in different kinds of liquors. That is the principal trouble with it. The gelatin precipitation method I think is accurate enough. I do not think there is enough acid lost by that method either with the alcohol or water solution to make any serious difference.

MR. SMALL:—I was one of those that had a good bit of difficulty with the method, and perhaps my point of view might lead to a little more active discussion in the matter. I did the work Mr. Alsop sent out in the first place and sent him in a series of liquors and he sent me back word he thought he would better not publish them and it would be a good scheme if I tried the thing over again, so I proceeded to try the thing over again, and I see I am still not very well in line compared with the general average. Now, I made those titrations and got a perfectly definite color change. I had absolutely no trouble whatever in making duplicate determinations—getting the duplicate determinations to agree perfectly well, and so far as I was able to make out, the trouble was that I did not titrate to the particular color that the rest of the men did. I titrated to a color change, and the color change was perfectly defined and I got a perfectly definite color and I could duplicate it time after time. The next thing I did when I found that my results were not being particularly in line, was to go ahead and take a known amount of acid and make a blank experiment by putting in the hematin and adding the amount of alkali that I knew would absolutely neutralize the amount of acid I started out with, and that gives you a certain color change for your hematin, but you go to titrate the tannin solution to the color you get that way, and you don't get that color at all. Now, granted that you are titrating, using hematin for an indicator, you are titrating to some end point, but what authority have you for saying that the particular color you are titrating to corresponds to an end point which agrees with the neutralization of the acid that you have in your solution? Admitted that you titrate to some color and that you duplicate that right along, how do you know that that color that you titrate to is the color that corresponds to the end point of your reaction? You fellows are getting results in agreement and apparently you are titrating to something like a similar end point, but how do you know that that end point is the end point corresponding to the neutralization of your acid? Another thing: Mr. Oberfell speaks of working in very dilute solution. That is all right; you increase the sensitiveness of your end point but do you increase it in anything like a degree corresponding to the dilution of your liquor? When you dilute your liquor down to one tenth its original strength, is your end point ten times as exact—ten times as delicate? If not, you have not gained anything at all by the dilution of your liquor.

Mr. Reed:—I would like to ask Mr. Small when he titrates and calculates it as acetic, how he knows that that calculation determines the acid that is in there. Suppose it is lactic?

Mr. Small:—That is quite true; I am not trying to say that the method hasn't any use. Personally I would say it is very decidedly useful. The fact that Mr. Alsop and Mr. Oberfell, who are handling quantities of acid determinations right along week after week and are able to keep the yards in line by the results that they get,—seems to me to indicate that the method certainly is useful and that it has a place. It certainly is way ahead of the old charcoal method. The point I am making is that the method seems to me still far from ideal, and that the conclusion of Mr. Alsop's paper that we should not abandon our search for an indicator, is the only proper conclusion to draw; and I do think it is wise to call attention to what seems to me a decided defect in the method that exists at the present time, namely, that while you do titrate to a certain color change and get a certain acidity, you do not know that that acidity is the actual amount of acid, or anything of the sort, that there is in the liquor.

Mr. Reed:—I don't know whether Mr. Small recalls that when the method was first proposed I did a lot of work on known acids and mixtures of known acids, of lactic and acetic, which proved that they did titrate to the correct end point of those mixtures.

Mr. Small:—Well, as I stated, it is quite possible to make up a solution of any acid and find the end point that corresponds and then titrate other solutions of that acid to that same end point, but the trouble is that when you get your tan liquors the end point is not the same.

Mr. Reed:—These were also tried by mixing the known acids with fresh tans and with tan liquors.

Mr. Small:—That again does not seem to me at all conclusive even, because in those cases you are working to a same end point all the time, and the adulterants that you put in, the things you put in to mix with it, do not necessarily change the color of your end point.

Then there was one other thing that I would like to mention which struck me as being rather interesting, although how much value it may have I do not know. In my own experience I found a certain class of liquors which gave me very decidedly different results, using the water gelatin and the alcoholic gelatin. The results were not in agreement at all and I sent Alsop some of the samples of liquor for him to test out, and he did not agree with the results which I found in the least. He was able to make those same liquors check up very fairly well with both the alcoholic gelatin and the water gelatin, but I could not—running to what I regarded as an over end point in every case,—one where it seemed as though I had gone way beyond a legitimate end point—I was still unable to get results by the two methods which would correspond, and I still was unable to get results which would come up to the figure that Alsop found on those same liquors.

Mr. Reed:—I should presume that to arrive at the point that Mr. Small considers desirable we would have to go to work and determine just what the nature of the acids in tan liquors are first. Isn't that true, Mr. Small?

Mr. Small:—Well, there is no use attempting the impossible. You have to go slowly. I should consider that eminently desirable, certainly.

Mr. Reed:—*Necessary*, to arrive at your conclusion.

Mr. Small:—Necessary to arrive at an absolute truth of your tannin in your plumping process, yes.

Mr. Alsop:—I have tested this method in a great many ways. I have tested it by comparing it with the best methods for determining acidity in liquors,—if there are any. Some liquors you can titrate fairly well with phenolphthalein; others you cannot. Those you can titrate with phenolphthalein give practically the same results. I have tried it by determining the total acid in the liquors and distilling off the volatile acid and titrating the residue and the two titrations agreed very well. I also titrated the distillate with phenolphthalein and those results agreed with the other. In some cases I could titrate the residue with phenolphthalein. In fact I tested it in most any way I could think of. I tested it for months and months before I started to use it as a regular method. I suppose I have tested twenty or thirty thousand samples since with it and I find it by far the most satisfactory method, and while it may not give the exact acidity, and I do not pretend to say it does, it gives results that are comparative, and will show low acid and high acid, and you can compare the acid from time to time from the same yard, which seems to me is the thing that we want practically, anyhow, as long as we haven't got any exact method, and I don't think we ever will get one that will apply to all classes of liquor.

Mr. Oberfell:—I would say that I used a solution just about one-tenth regular strength and the sensitiveness of the indicator was increased that much at least—just as sensitive as I said as most any indicator; just as sensitive as if you took a water solution, diluted an acid with water and put the liquor in and titrated with a clear solution. The indicator was just as sensitive as that.

Mr. Reed:—It seems to me that we are rather in an unfortunate position in having an official method which every member of this association recognizes,—I mean the charcoal method—an official method which is not any good at all. I do believe we should make this method a provisional method, and if I am in order, Mr. President, I would move you that the gelatin-hematin method be made a provisional method.

President Wilson:—I think that Mr. Reed is decidedly right in making this motion. It had been my intention to put this motion before the house before the meeting adjourned. However, the method that is incorporated in our little book is altogether out of place, as we all realize that it is almost worthless, and I would call for a second to Mr. Reed's motion that this method become a provisional method.

MR. OBERFELL:—I second it.

PRESIDENT WILSON:—Any discussion on this motion now? (after a pause) If not, I will put the question. All those in favor of adopting the gelatin-hematin method as a provisional method signify by saying aye. Contrary? The motion is carried.

MR. NORRIS:—Which gelatin solution do you suggest using,—the alcoholic or the water solution?

PRESIDENT WILSON:—So far as I personally am concerned it does not make much difference. I never could substantiate Mr. Small's objection to the water gelatin solution; I could not find the differences that he records. Now, I do not know why that is, and I presume we will have to decide that matter by a little discussion before making any final decision with regard to it. What would be your idea, Mr. Reed?

MR. REED:—I did not hear the question.

PRESIDENT WILSON:—Mr. Norris brought up the question whether or not that would be alcoholic or water gelatin.

MR. REED:—Mr. Small is the only gentleman present who has raised any question as to giving consistent results. I have never found any difference between the alcoholic and water solution. My practice is now to use practically all water solution. I do use a little alcohol with it to knock the foam off so that you can pipette the supernatant solution more readily. I think the water solution is just exactly as good as the alcoholic and certainly is very much cheaper.

MR. SMALL:—I should mention in that connection that I should think the use of a small amount of alcohol might overcome the discrepancy to which I referred, for the fact that Alsop could not corroborate the results that I got I ascribe in the first place to the fact that the solution I sent him had been treated with chloroform in order to preserve it, and I found the addition of a small amount of chloroform, strange as it may seem—the addition of a small amount of chloroform to the solution where I used the water gelatin solution for precipitating, made the end point correspond precisely with the alcohol; but without the addition of this chloroform the end point was widely different; and I had the idea that the addition of a small amount of alcohol would bring about the same result.

PRESIDENT WILSON:—I should think it would be quite necessary, of course, to use some sort of a preservative either alcohol or chloroform or something of that kind, as the gelatin is not at all stable and spoils very readily.

MR. REED:—I should think it might be in order, Mr. President, to move that the committee on determination of the acidity of tan liquors be continued and instructed to draw up a method in proper form.

MR. EACHUS:—I want to know if there is any objection to using denatured alcohol? We use the gelatin-hematin method as originally published, but we use denatured alcohol and find it does not give any different results from the others. While investigating the subject we might as well investigate that.

MR. REED:—I had some rather bitter experience with denatured alcohol and then I quit; but I suppose it depends largely upon the method used for making the denatured alcohol?

MR. EACHUS:—Of course you can make different kinds of denatured alcohol. We prepared it with the pure 95 per cent. alcohol.

MR. REED:—But if you use a water gelatin solution, say—I use about 50 cc. of 95 per cent. alcohol to the liter; and there the item of cost would not amount to much.

PRESIDENT WILSON:—Mr. Reed has a motion before the house that this committee on acidity be continued with the object that they shall draw up a proper method of procedure; and I would include in that motion that they might try the denatured alcohol in connection with that.

MR. SMALL:—Won't that throw this thing over for still another year? Can't we leave it so that that committee will present something before the close of our gathering here so that this can be acted upon without quite so much delay.

ON THE QUESTION OF THE VARYING EFFECTS OF TAN LIQUOR ACIDITY.[1]

MR. HALEY:—If the scientific part of the acid determination is in such condition that it has been referred to a committee,

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[1] Discussion at the Washington Convention.

it strikes me since we have here a representation of the tanners and a full representation of chemists, part of whose work is to report to the tanner the percentage of acid that is in his liquor, that it would be well for us to look upon the practical side of the acid determination and its interpretation. We have both factors here now, the scientists and the practical men, and I think some method should be devised to lead the tanner to a more thorough appreciation of the chemist's reports and the chemist also to learn something of why his reports are not borne out in the tannery in practice. Now, as I understand the tanning process, be it a dyeing process or a chemical process, there are two general constituents of the liquor that go to make leather,—that is profitable leather. The tanning agent in the liquor is an astringent; the acid factor in the liquor is of exactly the opposite of fact from the tanning agent. It is the property of the acid to distend the fiber of the hide and contemporaneous action of the tannin is to tan and preserve that distended hide, and the better preservation and the more distension results in the end in profitable leather,—that is plump leather is profitable leather. I am speaking now of the heavy leather. Now I would like to know from some of these chemists who have had experience how they can explain that. John Jones or John Doe, as Jerome uses it,—John Doe operating two tanneries will get the plumper leather from the tannery which has the lesser amount of acid, and vice versa. Now I have listened to this discussion of the determination of acid with a great deal of interest, because, while it has been several years since I had any practical dealings with the scientific side, yet I find that it is not any further forward to-day than it was ten or twelve years ago; that it is still hazy in the chemist's mind when he reports to the tanner the percentage of acidity present in the liquor that has been tested, what that acidity means. As I understand the reports to-day, the chemist says 0.5 per cent. acidity. Now, shouldn't you go a step further and if you have in a liquor these two what you might call antagonizing forces, present to the tanner some definite data as to the relative percentage, the relative amounts of each of those two materials present in the liquor that will go to make the most profitable leather, and I do not think there is any better time for discussion of this point than the present, for the reason that you have science and practice here in one room under one roof; and let's get at the bottom of this thing. Now, if no material development has taken place in the determination of acid in the last ten years it is full time that the scientific man was meeting the practical man on a common footing to fight this matter out, and such an opportunity is offered now. I don't think there is anything more important to the tanner than the question of acidity in his liquor and the effect of that acidity upon the manufacture of profitable leather.

MR. REED:—I don't know, Mr. President, whether I am capable of going on with this discussion along the lines that Mr. Haley has brought up, but it looks to me something this way; I think every tannery is a law unto itself; that the question of the right amount of acidity in any given tannery will not hold necessarily for any other tannery, but for that one single tannery there is a certain range of acidity that is possible for that tannery. Once having gotten that, then the value of the acidity test comes in to keep your range of acidity as nearly constant for that tannery as you can. As a man who has no connection with a tannery, that appears to me to be the determining factor.

MR. WALLIN:—That is by a cut and dried method that the tanner has had to upset during the last fifty or one hundred years. It is like the rule of the nurse who did not have to use the thermometer in the baby's bath, because if she brought the baby out and it was all blue she knew it was too cold; if she brought the baby out and it was all red she knew it was too hot. But it seems to me the chemist ought to get at that acidity factor and not say "Well, one tannery wants this and another tannery wants that, and we don't know what any one tannery wants by any experience in another tannery." It seems to me that Mr. Haley has struck a very important note when he suggests that the chemists ought to, after a while, give us some facts about acidity in tan liquors and some facts that we can be guided by. I know, and every tanner knows, that one man says "I want this high acid," and another man wants low acid, and we cannot govern another tannery at all by the experience in a different tannery. Now, there must be some things in those liquors which the chemists ought to fish out, that is modifying the effect of that acid in one tannery as against another tannery, and I think some research along that line should be undertaken. There are men here selling acids that are making a study of acids, and an honest and sincere study of them, and it seems to me if the chemists could devote some time in the future towards co-operation along the line of the study of acids and what kind of acids will do what kind of work—and perhaps there are some other agents in there other than tannin that are neutralizing the acids—it would be a very great help to the tanners.

MR. SMALL:—This very same matter was brought up at the meeting in Boston last year and so far as I know there has been practically no work done along the line, although I suggested it to Mr. Alsop as being along the line of work as being eminently interesting for his committee to take up this year. The gem of the solution of the problem lies in a suggestion that Claflin and Griffith made in an article in the JOURNAL something over a year ago, of combining with your acid determination a determination of the "plump." That is, simply taking a piece of hide and putting it into your solution, and getting at the plumping effect of the hide at the same time that you make your acid determination.

No chemist will ever be able to tell a tanner by a simple determination of the acidity of his tan liquor how plump leather he is going to get from it, nor will he be able to do that if he determines the acidity and then determines the percentage of tannin in there; nor can he get any ratio out of the two that will tell him how much his liquor is going to plump his hide. No more will the chemist ever be able to tell the tanner how much "plump" he is going to get into his hide if the tanner goes ahead and changes his water or changes his tanning materials or changes any one of a dozen other things.

If he starts in using a quantity of mangrove in his yard he is going to affect his "plump;" if he starts in using a quantity of palmetto in his yard he is going to affect his "plump" very decidedly. If he starts in using a hard water where he has been using a soft water he is going to affect his plump. The answer to Mr. Haley's question as to whether one man with a high acidity gets a low "plump" and another man with a low acidity gets a high "plump," is very simple. It is simply due to the fact that the plumping effect depends on ionization of your acids; that in the presence of certain salts and other materials, the quantity of acid being the same, the ionization is very much diminished. The chemist can do it for you all right but you have got to recognize the fact that it is not a simple process for him, that it is going to mean a lot of work for him and that he cannot make an examination of that sort three or four hours a day for you.

MR. WALLIN:—Has there been any effort made to examine these other materials which you have described as having some kind of an effect on acid,—any attempt to determine what that is and how much there is?

MR. SMALL:—Well, the principle on which it is based is an old principle and perfectly well known. You probably are familiar with the pickling process whereby skins are put into a mixture of sulphuric acid and salt: now if that salt were not there, if the skin were put in the sulphuric acid alone, the skin would plump so that it would burst, but the presence of the salt in there—I cannot very well put this into very plain language, but the acid does not exist in the solution probably as acid but it is split up into two parts,—a hydrogen part and another part, the hydrogen part being the effective part. Now, in the mixture of sulphuric acid and salt the sulphuric acid is not split up into hydrogen and another part in the same way that it is when the salt is not there. Now in the one case you have got your sulphuric acid split up into hydrogen and another part, and in that condition the acid is very effective and it plumps your skin or your stock or whatever it may be very decidedly. In the other case, the salt being present there prevents this splitting up of the acid and there isn't anything like this same chemical action in there, and therefore the acid does not act on the skin as acid ordinarily does, and consequently the skin is not swollen.

MR. WALLIN:—That leads right back to the suggestion that has already been made. When you give us the percentage of acid you ought also to give us the percentage of some of those modifying salts if they are easy to find.

Mr. Small:—It is not an easy determination.

Mr. Wallin:—Or if they can be found.

Mr. Small:—But it is not a simple matter by any manner of means to find out how many and what things are in there that retard or diminish this ionization process of your acid. For instance, if you run lime into your yard in your soak, the lime will combine with your acid in there, and form with the salts or with the acid supposing it is acetic acid it will form a certain amount of calcium acetate and your calcium acetate will act exactly the same as your common salt will in your pickling process. Now a chemist can go ahead and determine how much of these salts is present there, but then there is still something else that comes in there that is likely to complicate that, and that is the question of the effect of a large amount of non-active vegetable materials that are in there. For instance, one man tanning with oak bark will accumulate a tremendous amount of non-tannin in his yard. A man tanning with chestnut wood may not accumulate anything like as high a percentage of non-tannin. Now it is a question whether in those two yards the same percentage of acid will give you anything like the same "plump" on account of the decided difference in the amount of these non-tannins that are present there.

Mr. Mardick:—The most important point that we forget in connection with acid liquors is the purity and foulness of the yard. Several years ago when I took control of tanneries I observed that there was a marked difference between the two yards that Mr. Haley spoke about; for instance, one of our tanners wouldn't throw away the liquors but would pump over the leaches. He very naturally has about one per cent. acid, yet he would not get as much "plump" as the other one who has a smaller percentage of acid yet who has an outlet for his tannery. Now this is the most important point that we have to consider in connection with leather; whether we keep our yard clean and pure and have an outlet for the liquors, or whether we have not. Now, most of the sole leather tanners do not de-lime but lay the lime right down in the liquors or in their rockers. Just imagine one side weighing about forty pounds, say, contains about two ounces of lime on an average, I suppose. You imagine five hundred sides a day going into a tannery, having about one thousand ounces of lime in your liquors! They are flooding your yard with lime which is killing your tannin, fouling your yard and depleting your hides and eating your acid, and this process is going on all the year round because there is no outlet. What kind of plumpness and what kind of leather do you expect in that yard? Therefore I say, the question is a matter of cleanness of the yard, foulness of the yard, and how much lime you carry in your liquor. If the chemist can determine how much lime there is in his liquors,—calcium tannate,—gallic acid—those are the most important fouling matters in the yard, and the others—he can tell very well whether the acid he has, the genuine acid, would plump or not. If you have one-half per cent. of acetic acid and you add one per cent. gallic acid and some other quantity of lime and mix it altogether and throw the mass in it you would not get any plumpness; but if you take pure, clean, acid, also tannic acid, and put your hides in, you will find that your hides will plump immediately. The only thing we can suggest which would be practical without giving any undue trouble to the chemist would be to keep your yard clean by having an outlet. We must get rid of this idea that we can tan or make leather by foul matter. So long as the tanners cling to that idea we will have trouble always.

MR. OBERFELL:—Given that the chemist can determine all these different materials in there, what is the tanner going to do when he changes the sorts of his hides? Because I know that hides cured in different ways going into the same liquor with the same acidity will plump differently.

MR. GRIFFITH:—I think Mr. Haley has raised a very practical question, and in answer more particularly to Mr. Wallin's request for an interpretation of the chemist's results, as Mr. Small has been good enough to say, the question is susceptible of being handled by the chemist, I think. And with regard to what Mr. Reed said, I think that I must differ with him so far as the question of each tannery being a separate unit. I don't think so. I think what we have to do, as chemists, is to establish principles, get these principles and then we will find that the principle will hold good under every condition.

Now with regard to the salts which Mr. Small referred to in connection with the work I did with Mr. Claflin some months ago, I think it is very immaterial what those salts are, because all salts act towards acid very much the same, only in various degrees, but the principle of the relation between acid and salt is a simple one. Now when the tanner wants to know what the salt is, it is really immaterial that he should know, and if he understood that if he were to ask the chemist for the ash determination of his liquors, that ash could be interpreted into its equivalent of salt, and that ash would always be more or less uniform according to the amount of salt that was there; the ash would always vary with the amount of salt: a greater amount of salt, a greater amount of ash, and so on. But the question is even a greater one than that. That is, of course, a very important point with regard to the actual practical condition that can be observed by the practical man irrespective of what results could be given on paper. The other question is the nature of the acid which does the plumping. Of course, we have in a natural fermented bark liquor all organic acids, the volatile and non-volatile. Now I have permission to refer to some very excellent work which has been done by Mr. Alsop on this question, and Mr. Alsop found that there is quite an appreciable difference in the effect of a volatile acid and a non-volatile acid. That is the effect on the hide. I will not go too deeply into this, because you know I am interested in the acid question. I have studied it very carefully with all the practical data I have been able to summon, and that is a point which is worth considering,—the value of volatile and non-volatile—you know what I mean by those two—the value of the relations in the acids of volatile and non-volatile acids, and also their relations to the practical part of it.

MR. WALLIN:—Do you regard this ash determination as being of importance bearing upon the plumpness which your acid will give you?

MR. GRIFFITH:—Yes, because the ash always indicates the presence of salt. The greater the ash the greater the presence of salt.

Mr. Wallin:—Then, other things being equal, the greater the ash the less plumpness?

Mr. Griffith:—Exactly; and irrespective of the amount of ash there, there is an equilibrium set up between the salt and acid which nullifies any tendency toward plumping, so in a yard where you have a very high percentage, even as much as one per cent., if you have quite an appreciable quantity of salt, which would be indicated by the amount of ash, you would not get any plumping. We all know that one per cent. of acid in liquor is an outrageous amount to have, and we know of instances where that amount has been present. Now there must be a cause for that, and in every case which has come to my notice we have traced the cause to the presence of salts which produce an equilibrium in the liquor and nullify the influence of the acid in its effect on the hide. Now we are working on hides and as chemists we always ought to recognize that is our goal. It is not the influence of one thing on another, but the ultimate influence of that liquor on the hide, because that is what the tanner buys and what he ultimately sells. Now a hide that is not plump or is not worked through the earlier liquors will not—I refer now to what Mr. Vogel referred to in his paper on the amount of extract that the hide will hold. Now there is a limit to what you can fill a hide with, because you can go up to a certain weight of leather and of course you can increase that weight but you make it unsaleable because there is a relation between the weight of the hide and the iron or substance of the leather. Now the problem is to give a light weight hide, weight in proportion to that substance. If a hide would come out of the rockers or handlers in a good condition it will hold considerably more weight when it comes to the extract, which is the final operation; much more than the hide would if it had been allowed to pass through the handlers without being observed and checked up at that stage, because it is my experience that if they are corrected at the time they come out of the handlers it is better than to have them corrected afterwards.

President Wilson:—I think Mr. Griffith is quite right in regard to the kind of acid, whether it is volatile or non-volatile, and also in regard to the salts in the liquors; but I agree with Mr. Reed nevertheless that every tannery is peculiar to itself. You take one tannery which has an acidity in the liquors of say 0.3, and that leather may be as hard as bone,—brittle. You take another tannery running on the same class of goods, which may have an acidity of three times that, and the leather will be mild and soft, and in each case the tail liquors are being run away. How is a man going to stop the peculiar fermentation in one yard and make them all harmonious without impregnating the whole yard, and making a certain ferment.

MR. GRIFFITH:—I think the thing goes further than that. It is not altogether a question of the water or a question of the acid in the tail liquors, unless you have recognition of the presence of the salts. Now, the salts get in to the tan liquors not only by way of the lime yard; they also come through the yard from the other end in the form of the salts which are present to more or less extent in the handlers. Now, that opens up a very big question, but nevertheless I still hold that the principle is sound irrespective of the salts being separate units. Of course, we know the water is a very important factor, but then water varies,—the salt contents of the water varies.

PRESIDENT WILSON:—If the water varies and the salts in the tanning materials vary, how are you going to get all your tanneries on the same basis in the governing of the acid?

MR. GRIFFITH:—Well, that is a question of adjustment; that is purely a question of adjustment.

PRESIDENT WILSON:—You cannot adjust them all in the same basis; you have got to have a certain acidity for one tannery and a certain acidity for another one.

MR. GRIFFITH:—Are you assuming that the conditions are identical in every other respect?

PRESIDENT WILSON:—Yes.

MR. GRIFFITH:—That they are using the same materials?

PRESIDENT WILSON:—Just as I spoke to you last evening, and Mr. Reed. You take one yard and leave the cover off the vat and it will smell like a winery.

MR. GRIFFITH:—That is the point I have referred to in connection with the acid.

PRESIDENT WILSON:—How are you going to make those conditions equivalent in the two yards. How are you going to change the ferment in one to correspond to the ferment in the other?

MR. GRIFFITH:—That is the point I raised. You will have to consider the nature of your acid, as to whether it is volatile or non-volatile.

PRESIDENT WILSON:—That is perfectly evident.

MR. GRIFFITH:—I put that in as a factor to be considered. Now, if you raise the question of ferments, that rests largely upon a question of cleanliness, because the cleaner the yard the less tendency there is to fermentation; that is an acidous fermentation.

MR. WALLIN:—There have been three elements spoken of here by the chemists as being determining; one, the total amount of acid; another is whether volatile or non-volatile, and the other is the total amount of these salts. Now, as I understand it, chemists heretofore have furnished us only one of these elements, have given us the total amount of acid, and when the tanner could not understand why he did not get certain results with that total amount of acid, he got nothing more. Now, if those three elements do determine, as has been nicely explained by Mr. Small in his pickling process, it seems to me the chemist might give us perhaps the volatile and non-volatile acids, if they do determine, and the salts if they do determine. Instead of giving us one element give us the three, and later on you may have to make it a dozen.

MR. MARDICK:—Wouldn't it be a more common-sense idea to strike the question at the bottom by not allowing any kind of salt in the yard where you cannot plump leather? That is, try to eliminate in any way possible the contamination of any kind of salt in the yard. Wouldn't it be the most feasible thing, than afterwards to trouble yourselves for months and years in trying to find out what you are going to do? Wouldn't it be a better idea first to remove, as much as you can, all those compounds in the hide or with tanning material that produced so-called salts which will interfere later on in plumping? That is the way I would look at the matter, and a very natural thing is therefore get rid of just as much of it as you can before you hang your hides in your rockers, and also to see that the tanning materials used are free from salts; and then you are certain this is the cleanest and neatest way of tackling that problem I know of.

MR. SAXE:—Isn't there a very interesting point there regarding the bacteriology in the tan yard? How much work has this association done in that connection?

PRESIDENT WILSON:—I am sorry to say that the association has done very little as an association. About the only member who has done anything along that line has been Mr. Alsop, but I think he has no report to submit yet. He has been investigating that subject for some time but without any definite conclusion.

MR. ALSOP:—I think it would be a very nice thing to have a committee on that subject, if the tanners didn't growl if they worked on that and nothing else; but it would be folly to have any work done along that line unless a person's whole time could be devoted to it.

MR. SAXE:—Isn't it a very important factor if you come right down to it?

MR. ALSOP:—I think it is. I think the whole subject we have been talking about is a very complicated one. I do not think it depends on the acids or salts or any one thing; it depends on a whole lot of things; and I think that perhaps both Mr. Griffith and Mr. Reed and also Mr. Small are right. (Laughter.) Not altogether right, but partially right. I do not think each tannery is a law unto itself, but it is to a certain extent. naturally acid plays an important part in the plumpness; also the bacteria in the liquor, and a good many things; and for any tanner to expect to get all that information for fifty cents—(Laughter).

PRESIDENT WILSON:—Is there any other discussion?

MR. SAXE:—I would like to ask Mr. Alsop if he thinks the day is coming when we are going to inoculate the yards with the various species.

MR. ALSOP:—I have heard a good many prophesies here today; I don't think I will prophesy. I am going to do some work on it, but I think it is very hard to tell. I think maybe I can tell you better a year or so later.

MR. SAXE:—Beardmore here, has been in England, and he tells me they have tried that method in England, and are working at it now, inoculating yards with various species of bacteria.

PRESIDENT WILSON:—Perhaps Mr. Beardmore could give us some information along that line.

MR. BEARDMORE:—I just want to say that I do not know how the work is going on, but I heard they had been trying to inoculate one yard from another; but I do not know how it is being worked or anything about it. However, I heard they had tried it over there. So, I cannot tell you whether it has been successful or not.

MR. ALSOP:—The work of bacteria in liquors is very interesting. There are quite a number of them in the liquors, for the one thing, of different kinds, and it is difficult to get them separated and pure cultures made of them, and it is rather difficult to get the proper mediums for them to grow on, so we can get them separated. You haven't very much to go by and the ordinary mediums used do not seem to work very well, about all I have succeeded in getting done is to find something that a good many of them will go on and get them separated out, without having been able to try what I could do with the individual bacteria themselves. I have separated a number of yeasts out of the different liquors which gave rather curious results. I took ten different yeasts and sterilized a liquor which contained 0.8 acid, sterilized it in bottles and inoculated ten of those bottles with yeast and also ran one blank at the same time. I let those stand for two weeks and then tested them for acidity. Five of those yeasts were surface yeasts, running on top of the liquors, forming a film on top of the liquors; the other five were yeasts that grow under the liquors and do not form any film. The ones that grow under the liquors form carbonic acid and alcohol. When I tested those liquors I found that the five yeasts growing on the surface had used up two-thirds of the acidity of the liquors during that time, and that the five yeasts that grew under the surface had not changed the acidity at all. That is rather interesting as showing what those surface yeasts tend to do.

MR. SAXE:—Did you learn what species they were?

MR. ALSOP:—I have them by numbers, so far.

PRESIDENT WILSON:—I think that point Mr. Alsop just brought up has a direct bearing on this acidity question in the yard liquors.

MR. ALSOP:—There is no question about it.

PRESIDENT WILSON:—Take those yeasts which grew from the bottom of the vat: you go in some yards and see what they call mother; the liquors will be perfectly clean on top and the leather from those liquors is entirely different from leather where the mother is on top of the liquor instead of on the bottom, with the same percentage of acidity in both. So it looks to me as if it were a question of ferments rather than the amount of acid.

MR. ALSOP:—I think ferments have a whole lot to do with it. Another time— I had heard that in order to promote the growth of acid they had taken the mother off the top of the liquor in some vats and put it into others to make the acidity more. Well I got some of this mother off the top of the liquor and examined it and I could not find a single acid-producing bacteria in it; nothing in fact but yeast; but when I went down under the liquor and got some mother, as I suppose you might call it, off of the leather itself, I examined that and found there was practically no yeasts in it at all, and it was practically all bacteria,—presumably acid-producing bacteria. But these bacteria out of liquors are very particular how they grow, and it is pretty hard work to make them do just what you want. It is rather discouraging work too. You work a good while and get a hold of something and then it don't seem to amount to anything afterwards.

Speaking of the percentage of volatile and non-volatile acids in liquors, I find that to vary a great deal. In fact I find it to vary as high as from 90 per cent. volatile acid, down to 25 per cent. volatile. It seems to me that must have some influence upon the tanning process. I also found that the acids in liquors vary somewhat; well, I don't know as I have gone far enough to say they vary somewhat in the way they act, but I do know this: if you take a liquor that has volatile and non-volatile acid in it and neutralize that acid, that the amount of non-volatile acid is all neutralized before the volatile acid is touched at all. You start with a rocker liquor say with 40 per cent. volatile and 60 per cent. non-volatile acid, and as that goes through the acid is used up until there is only 40 per cent. of acid there, and that 40 per cent. will be volatile acid.

THE BLEACHING OF LEATHER.

By C. M. Procter.

When you asked me to make a few remarks and chose a subject for me, it is quite a coincidence that in some of my visits around the different sole leather plants, that almost always the conversation gets around to the bleaching of sole leather, and its remedies. I don't want to make any set address; I would rather just make a few remarks and then if there are any questions you will have it back and forth.

In the bleaching of sole leather—of course it is a subject that interests simply one class of tanners, and as I presume there are other tanners here, we will of course try to make it as interesting as we can for all,—the tanner and the leather manufacturer, or the leather dealer and the shoe manufacturer, have found that in addition to good leather, color seems to play about as important a part. You take a leather buyer in a large shoe manufacturing concern, and he will on one of his purchasing trips go into the sole leather store and ask to be shown different samples, and almost invariably he will pick out what is pleasing—what is *then* pleasing—to the eye. Of course a tannage that is pleasing to the eye gets first call. Of course in shoe manufacturing concerns nearly all purchases of leather are made under what is called the sampling process, that is ten, fifteen, twenty-five or fifty rolls are taken and cut across, but still if a concern is handling four or five tannages and a buyer goes into that store he almost always picks, as I say, that which is most pleasing to the eye. Well, it is of course for the tanner to make his stock not only of good fiber, but pleasing to the eye, and during the last ten or fifteen years with all the changes that are going on in sole leather manufacturing and where the tanner wishes to keep a distinctive color of the leather that he has sold for a number of years, of course he takes the bleaching process as the final mill to rectify all shortages or mistakes or changes in his tannage. The leaching has changed a good deal the last few years. Most of the sole leather tanners are leaching better. Some are over-leaching. Of course in that case they have a large amount of insolubles and red matter, and non-tannins to take care of. That will change their color, and of course the introduction of extracts has changed the distinctiveness of a good many tannages. In that way a tanner will try to color his old original tanning material; supposing it is hemlock bark or oak bark, he will commence his process by coloring his leather, and then using his different tanning materials and extracts during the intermittent process, and possibly finishing his tanning process by going back to the original tanning material that he has tanned with so many years, and then by bleaching he hopes to bring back that original color that he has sold under so long.

Of course you cannot lay down in the bleaching room any set of rules for tanners, because every plant has certain local conditions. We know that principally the ingredients used are your alkalies—sal-soda, or concentrated alkali—and the sulphuric acid. That is the most common method; but we have all found out that no matter how lightly we may bleach we are bound to lose some of that work which we have previously put in. Of course up to within a few months that weight has all been put back by adulterants, but I think that is not practiced as much to-day as a few years ago. There is a feeling in the trade against it. A little amount of adulterant will do the leather no harm, but 10, 15 or 20 per cent. put back into the leather, or put into the leather in addition to the loss in weight, caused by bleaching —I think the day for that is pretty much gone by. Of course the method of bleaching is after the stock comes from the yard, it is washed and taken to the bleaching tubs and the arrangement of those in most sole leather plants is this: They are built in a set of four tanks—I think four is preferable. You first have your soda tank and then a tank for warm water, and then a tank for your sulphuric acid and a tank for cold water.

As a rule the amount of soda or the amount of sulphuric acid depends on how your stock is coming through the tannery. Of course there are seasons of the year when it may be off color, and the bleaching ingredients are increased, and other times when they are brought down to normal. I think that it is a good plan to always wash the leather between the soda bath and the sulphuric acid bath and also thoroughly wash it in cold water before it is taken to the wringer. Over-bleaching will a number of times bring out the reds from various tanning materials, especially quebracho, but most tanners do not—my observation is, they do not over-bleach. It is always on the other side. In fact you talk with the owner of the plant and his question is, "how can we do away with bleaching? Can't you suggest some way to rid us of this curse?" The tanner, of course, does not always see it in that light, because he wants to get his color where the shoe manufacturer desires it, and he has his reputation at stake.

The question has come up a number of times whether the sulphuric acid in leather causes it to deteriorate. I think not. I think leather will stand quite a percentage, and although it may be packed or piled in the warehouse a number of months or even a number of years, it will show outside possibly a change in color if it is exposed to light. I think the sulphuric acid does not hurt the fiber.

I think that the time may come when bleaching will be done away with. We cannot see that time now in a good many tanneries because they use a number of the cheaper tanning materials and try to get a good color with them. If the shoe manufacturer was not so particular about his color and was only after a good, strong fibered stock, why the bleaching question would solve itself. As I say, there are no particular rules to lay down. You can do it only in a general way. I think though that the soda and sulphuric acid plan is that practiced by most of the large tanners to-day. Of course you can use oxalic acid, and although you may get along with possibly a third to a half as much, I do not recommend it in the average sole leather plant. You can use a tanner's alkali that is prepared to-day. Although that costs more than the ordinary sal-soda, it contains twice as much strength; and it is six of one and half a dozen of the other there. In reference to the use of extracts in the yard and trying to rectify the color of the same in bleaching—of course extract tannage has come to stay in this country, and come with a vengeance. Of course the color of English leather is the standard the world over to-day, and we are trying to bring the color in all the standard tannages here to that. Of course they get it by using a number of the tanning materials, extracts and so forth, that give light color. That will help out a good deal on your bleaching end. You will not have to bleach as strongly or as hard. In buying tanning materials therefore, I presume the tanner should look pretty well to getting as many light materials, that is light color-giving materials, as he can consistent with the cost of tannin.

DISCUSSION.

MR. KERR:—I would like to ask Mr. Procter if he has any data as to the loss of weights in bleaching sole leather?

MR. PROCTER:—Yes sir; the losses in weight run, my experience has been, from three to eight per cent.; generally five per cent. on a year's run with ordinary bleaching.

MR. KERR:—What would you figure that costs the tanner in addition to the cost to which he is put; that is in weight?

MR. PROCTER:—Well, that is almost too stupendous to figure. You take a large sole leather plant and figure the actual amount of money he gets for his finished leather and deduct five per cent.—of course you understand it has been the habit in all the large plants, in fact in most all the tanneries in this country, to put that weight back at a small cost.

MR. KERR:—Yes, but I understand the tendency now is not to put it back.

MR. VOGEL:—I would like to ask Mr. Procter how he arrived at his figures of percentage of loss due to bleaching.

MR. PROCTER:—Only on tests of one hundred sides or fifty sides at a time. Of course that would not be an exact condition, but it is as near as you can get at it though.

MR. HEALEY:—I would like to state this may be gotten at another way, I believe. Not I personally, but other members of our company have arrived at it in a little different way by estimating the total solids in the liquors after bleaching, or during bleaching. We know exactly how much acid, how much pure water and how many hides go through, and by an analysis of the same liquors afterwards and the calculation on total solids we can arrive at pretty nearly the same conclusion. I think it is about the per cent. mentioned by Mr. Procter.

MR. VOGEL:—What per cent., Mr. Healey?

MR. HEALEY:—Three and a half to four per cent.

MR. VEITCH:—If a tanner was aiming to put back just what he washed out with the bleaching process, would it cost him as much to put that back—or rather, does the bleaching cost him less than it would cost him to not bleach at all,—that is putting it back?

MR. PROCTER:—No; supposing for example you take a twenty pound side of leather and take out five per cent.; that is a net loss of one pound. Now, in the average side of leather to-day that is worth twenty-five cents, and the cost of bleaching, the labor and ingredients, and figuring the building it is done in and the insurance and everything you can figure in, and also the cost of the weight added—that is the adulterant afterwards—I think that it would not figure up much over five or six cents to put that back.

MR. SMALL:—There is one phase of the question which Mr. Procter mentioned in passing which I think I shall have to take exception to his point of view, and that is with regard to the effect of the acid that is used in the bleaching process and the amount of it that remains behind in the leather. I had occasion to analyze, not so very long ago, a sample from a carload of bellies which showed only a little short of one per cent. of free sulphuric acid left in the belly. Now those bellies don't have to stand around such a tremendous length of time before they show a very decided effect from the acid that is left in them. That was one of our standard tannages in this country too; and you can readily see that if a shoe man is buying any soles made out of bellies that contain any such percentage of free sulphuric acid as that, and the bellies lay around, or the inner soles lay around very long, before he goes to use them, he is likely to have some remarks to make when he goes to channel them. Moreover, sole leather with any percentage of acid like that in it is not going to be particularly attractive in wearing qualities when it is used by the consumer. I doubt if a great many of the people who are bleaching leather realize anything like the amount of acid which is left in there, nor how great the deterioration is to the leather due to the amount of sulphuric acid that is left in the leather. And the shoe man when he insists on his color, if that color is obtained by a bleaching process, has no suspicion of the damage that he is doing to his business; unless of course he is looking after turning out a shoe that will wear out quickly so that he can sell another one.

MR. PROCTER:—I agree with you to a certain extent, but I think you will find in most of the tanneries they are very careful about the bleaching and that by an after-bleaching they get out most of the sulphuric, on the surface anyway.

MR. SMALL:—That is where I have got to disagree with you. I do not think the amount taken out by that washing is anything like the amount that goes in.

MR. KERR:—I think on exact analysis—I have seen some comparative tests, I think on a dozen tannages, about 0.4 of one per cent. The difficulty is we haven't a method by which we can readily determine the free acid. There is where we are handicapped. We can't learn. If we had a good method we would be able to; but there is no doubt about it, the leather will certainly take acid readily, and I do not believe, as Mr. Small says, that just one rinsing in the water will take out anything like the amount of acid that goes in.

MR. PROCTER:—I don't think so myself; but if it is done slowly or done hastily, of course there is a difference. If a man is careful he is bound to have his stock in a better condition than if he rushes it.

MR. VEITCH:—It seems to me that this is really a more important matter to the consumer—most of us are consumers—than it is to the tanner or to the tannery chemist; and personally I would like to see more interest taken in the matter of doing away with these harmful processes of manufacturing leather. If we could leave out the bleaching entirely, if we could educate the shoemaker to the point where he would not demand only color but would demand quality, I think it would be a very desirable thing, not only from the point of view of the consumer, but I really think it would be beneficial to the tanner and the shoemaker as well. Let us have as good material as we can possibly get hold of. We are coming to it ultimately.

Mr. Saxe:—I would like to ask Mr. Procter whether you can get as much "dope," as they call it, into sole leather that has not been bleached as that that has been bleached?

Mr. Procter:—You can get more in after it has been bleached You are pinning me right down, aren't you? But I have that question put to me only about once a week, so that it is all right.

Mr. Saxe:—I don't understand, as long as the color of the sole is black, what difference it makes.

Mr. Procter:—In talking to a shoe manufacturer only ten days ago, he admitted it all but he said, "Gracious, my buyer gets into those stores in New York and Boston and I know just how it is. That pile looks pretty there and this pile over here has a dark cast, and naturally he gravitates to the nice looking leather.

Mr. Procter:—That was my argument in starting off, that not only the quality of the leather but the color enters into it a good deal. They will sacrifice part of that quality in order to get the color. Some of the poorest looking leather you have ever seen will be the best tannage.

Mr. Kerr:—I would like to ask Mr. Procter how the color of English sole leather bends compares with American? I have seen considerable English sole leather, and some American, which did not seem to be colored at all. The English leather is the standard of the world. I never saw an English sole leather which would be passable in this country, from a color standpoint. There may be plenty of it but I have not seen it, that's all.

Mr. Procter:—I used that argument, that English leather was the standard. I think it is the standard across the water. Of course we are all the time improving in this country, and I think we won't find it a very hard task to beat out our brethren on the other side of the water.

Mr. Haley:—As a matter of fact, drawing your conclusions from analogous industries isn't the leather in the ideal condition to be bleached and get what color you want on it after the so-called bleaching process in the tannery is concluded? For instance, you bleach hemlock leather—that is, I have always been under the impression that the term "Bleaching" is wrongly applied in the usage of alkali and acid to effect an end. As I understand the so-called bleaching process it simply consists in dissolving out of the grain by means of an alkali the excess of coloring matter that is present there, and also darkening by the action of alkali the tannin that is combined possibly with hide in the grain. The subsequent treatment by sulphuric acid neutralizes the alkalinity of the grain somewhat, with the resulting effect of a so-called bleach. Now your leather when it is in that condition is in the ideal condition to put upon that grain whatever color you want. If you want to give it a Mimosa color, or whatever color you want, put it over into that liquor when the grain is free and clear from all foreign coloring matter and thereby get back into your leather the weight you have lost in the alkali and soak process. Now, if you take your leather out of your sulphuric acid there and run it through your wringer to remove the excess of moisture and then put it into a sixty or eighty or one hundred degree liquor, of whatever color you wish to produce your finished leather, that, according to my mind, is strictly bleaching that leather; it is changing the nature of the tanning material in the grain, and each individual tanning material has its individual color. Now, as I understand the English tannage, they do not bleach. A year or so ago the tanning trade of this country was favored with the visit of an eminent English chemist, and the first tannery that he went into he saw sulphuric acid and sal-soda and he saw the leather progressing in the profitless business of bleaching through those various stages, and he wanted to know what that was. The tanner told him he was bleaching his leather. "Well," he says, "I have been in the leather business all my life and I have been in almost every tannery of any importance in England and Continental Europe, and I never before saw the use of sulphuric acid and sal-soda for bleaching leather." Now, if they can do it in Europe we can do it here, and if I understand the reason why they do it in Europe and not here by the same processes followed in Europe, it is largely due to the labor expense. The tannery laborer in Europe gets probably in a week what our average tannery laborer secures here in a day or two days, and he is able to put more labor toward the ultimate object of securing a satisfactory color, and he does get that color without detriment to the natural property of the leather itself; and that is where it affects the consumer, as Mr. Veitch says. We have to put it through that process in order to get the desired color.

Now I do not know whether any tanners here have tried the bleaching of leather after the grain has been cleared by the action of sal-soda and sulphuric acid. If they have I should like very much to hear their experience in it. I should also like to hear from the chemists and tanners what objections they can offer to such a process.

MR. MORRISON:—I wish to say to Mr. Haley: He asked if any tanners had tried this bleaching process after going through the soda and the sulphuric acid; I have tried it repeatedly but I have not been able to get a satisfactory color afterwards for the simple fact that the tannin oxidized on the grain in drying—dried black on the edges—dried out spotty, and when you put it in the market you cannot sell it.

MR. WALLIN:—Did you wash it after you took it out of the extract vat?

MR. MORRISON:—Yes, and still it spotted.

MR. PROCTER:—On thoroughly tanned leather you can do what you say it will do; just as you say, it will spew out because there is no space for the tannin to go in. There is a small space made by the bleaching, but you try to put back so much in the coloring. My experience has been such as yours. I got blackened edges, and I think it is due to the fact that the stock is thoroughly tanned and won't take any more tanning material, but it would take some, say, glucose or sugar on the surface.

MR. WALLIN:—I have had a lot of experience but it has not done me any good. I was hoping Mr. Procter would come here and show us some way to relieve us of this curse he has spoken of. So far nearly all American tanners have found that the standard color which is required necessitates the bleach. I suppose in England shoe manufacturers haven't got educated to this higher color, and doubtless use tanning agents which give a better color than we get naturally.

MR. GREENE:—From what little I know of tanning on the Continent, I understand the tanning cost is higher than in this country, and I have wondered if this increased cost has not come from the labor and a good many other factors on which we are much too saving; and maybe this increased cost has come largely from the expensive tanning materials and extracts possibly which they have found necessary to use in order to make a nice appearing piece of leather. I would like to ask Mr. Griffith or Mr. Vogel what they have to say about the English practice.

MR. VOGEL:—Mr. Chairman, the reason that the English sole leather tanner does not have to bleach his sole leather lies in the fact of his high cost of tanning material. The tanning materials that are used—chiefly I mean extracts now—are very expensive because of their clarification with blood albumen. They have no adulterants, no bi-sulphites, and the blood albumen clarification takes out considerable tan but leaves a very clear extract. On top of this the material that they use in their leaches is only used after it has been in the yard in the form of dusters. It has been dusted first into the butts and thoroughly absorbed and all the blooms and reds and insolubles have been washed away, so to say, by the liquor, or deposited mostly in the grain. They then go to the leach house and are leached and the resulting liquor is then clear and has no resinous matter. What bloom or insolubles is deposited in the grain through the dusters gets to be a sort of a pasty mass which I described to you yesterday, which is easily handled and scrubbed by means of the scouring machine which they have developed. They therefore can remove this very easily and by means of these clear extracts in the later layers they penetrate the grain and butt with a clear tan which leaves no deposits. On the other hand what do we use? Hemlock bark—resinous! Quebrachò extract—resinous! We use mangrove bark, which has large deposits—resinous! And what is the result? When the stuff comes out of our vats it is full of dirt and filth, and how are we going to get rid of it? We must bleach it, unless we go to the expense of using highly clarified extracts, and if you want to do that you will have to increase your tannery costs to a great extent with the result that the cost of leather will be higher than it is to-day.

MR. WALLIN:—Suppose you use bi-sulphite extract? Don't they do that in England?

MR. VOGEL:—They use bi-sulphite extract at the last.

MR. VEITCH:—This high color of which you speak is no detriment to the leather. There is no real necessity for removing it, is there?

MR. VOGEL:—No, excepting the shoemaker demands it.

MR. WALLIN:—It seems to me that is not quite true that if you leave that coloring matter in the grain out of a strong hemlock liquor, for instance, your grain is very much more apt to be tender than if it is thoroughly bleached out.

MR. VOGEL:—Even if it was thoroughly washed out?

MR. WALLIN:—Well, I suppose you might wash to the same extent—get the solubles out of the grain to the same extent as you would with bleaching; but wash it clean and you will not have as strong a grain, as good a grain, I think, as if you bleach; in hemlock leather I am speaking of.

THE ASBESTOS-KAOLIN FILTRATION METHOD.[1]

By F. H. Small.

The Council at its meeting on December 30th, 1908, expressed its desire that some definite conclusion regarding the usability of the asbestos-kaolin method of filtration should be reached during the current year. To this end it requested the author of this report to make a careful and thorough investigation of the method and granted him authority to call upon the full membership of the Association for assistance. This method was originally proposed by Reed in a paper presented at the meeting of the A. L. C. A. in 1907, and published in the JOURNAL of the Association for November, 1907, pps. 420-426. It was investigated by a Committee of the Association during the following year and the report of this Com-

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[1] Report of the 1909 Committee.

mittee was published in the JOURNAL for August, 1908, pps. 214-227. The general conclusions reached by this committee were that the method requires a somewhat bulky and cumbrous apparatus and calls for some dexterity of manipulation; that conversely it saves time, is conducive to more brilliantly clear filtrates and to greater accuracy; that therefore it should be given a more thorough try-out to the end that it may be adopted as at least an alternative method of soluble solids filtration.

In pursuance of the instructions of the Council a letter was sent to the active members of the Association, giving them the above information, requesting them to familiarize themselves with the method by practical trial and to forward criticisms of the method or suggestions for improvement. On the chance that some one interested might have been overlooked, a notice emphasizing the points made in the letter, was published in the April issue of the JOURNAL. The net result of these appeals was a grist of letters explaining inability to participate in the work and some half dozen suggestions or reports. These will be referred to again later on. As this line of attack did not seem fruitful of results, it was decided to prepare samples and send them out with instructions for the work desired. Samples were therefore prepared and sent to some thirty of the members, the list including all those who seemed to the author at all likely to do the work. Much to his regret he was able after vigorous prodding to obtain reports on less than a third of the samples sent out. Moreover as several of the reports are of work done either confessedly or obviously not according to the instructions sent out, and the deviations involve matters essential to successful use of the method, the author has to confess at the outset that he feels he has failed in his appointed task and that what conclusions he draws are based on so few reports as to be no more conclusive than were those of last year's Committee.

In response to his first letter Alsop submitted two designs of apparatus which might be used for the method and in conversation with the author explained that he thought much of the trouble experienced in the use of the method was due to the use of filter plates with too large and too few holes. The designs are reproduced here. Wilson using an apparatus modeled after Fig. 1, obtained the set of results shown in the following table and drew the conclusions following:—

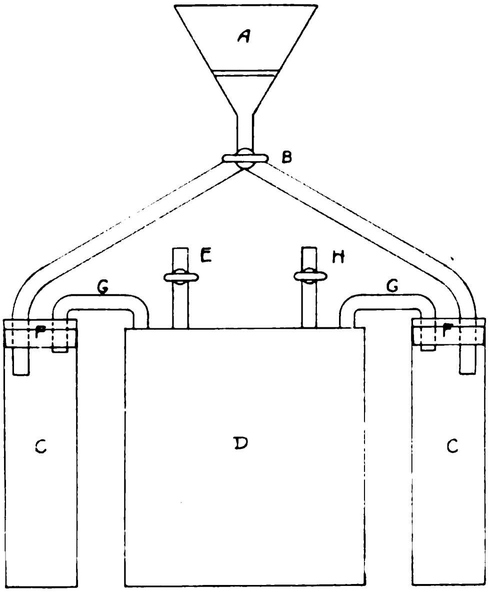

Fig. 1.

A, filter and reservoir to hold sufficient liquor for determination. B, two-way stop cock. C, receiving bottles. D, tank for vacuum. E, valve to break vacuum. F, rubber stoppers. G, could be made of copper or brass; also D. H, to pipe line connected to pump.

Personally I have some objections to the method in spite of its rapidity.

1. The asbestos fiber is not so easy to prepare as might be imagined.

2. Especial care must be taken in placing the asbestos on the funnel to secure a perfect mat.

3. The installation of special apparatus which many will object to and not do.

4. Probable cumbersomeness of apparatus.

It was found more expedient on all filtrations to use 3 grams asbestos and 2 grams kaolin. This may have been due to the slightly larger diameter of the filtering disc.

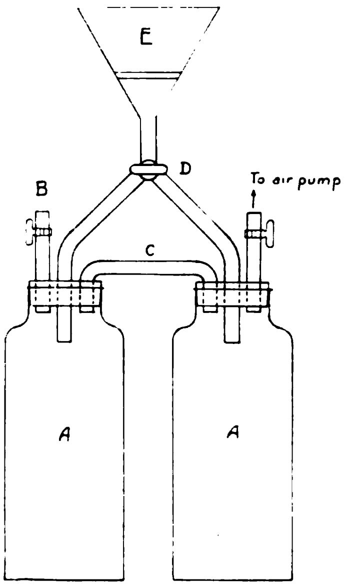

Fig. 2.

A, bottles 500-600 cc., or larger if necessary, or one large and one small, *i. e.*, 500 cc. and 200 cc. B, to break vacuum if set up in series to one pump. C, to connect bottles. D, this can be a two-way stop cock or a Y with two cocks. E, filter and reservoir to hold sufficient liquor for determination.

SOLUBLE SOLIDS.

	Total solids		Official		Asb.-kaolin			
Material	Wt.	%	Wt.	%	Wt.	%	Official	Asb.-kaol.
Ord. Queb.	.4991	82.87	.4470	74.22	.4497	74.67	75	40
			.4456	73.99	.4510	74.88	90	60
Clar. Queb. ...	.4517	44.07	.4471	43.62	.4470	43.61	50	25
			.4469	43.60	.4479	43.69	50	30
Chest. Ext. ...	.6108	53.62	.6028	52.92	.6074	53.31	50	5
			.6044	53.01	.6081	53.37	50	6
Handler Liquor	.6921	2.28	.6616	2.18	.6651	2.19	45	8
			.6641	2.19	.6648	2.19	45	11
Handler Liquor	.7848	3.22	.7574	3.11	.7584	3.11	38	6
			.7594	3.12	.7590	3.12	38	12
Sapped Liquor.	.7262	2.76	.7218	2.74	.7242	2.75	38	8
			.7214	2.74	.7222	2.74	38	12
Sapped Liquor.	.7246	4.73	.7010	4.58	.7018	4.58	38	10
			.7048	4.60	.7022	4.58	38	15
Sapped Liquor.	.7370	7.15	.7268	7.05	.7252	7.03	45	14
			.7230	7.02	.7240	7.02	45	18

Notes.

1. The time required for the suction filtrations was much less than that for the filter paper.
2. Vacuum on extract filtrations was 14″.
3. Time required to clear solution by suction was about equal to the time of the first 100 cc. portion.

Nichols made some tests and reported as follows:—

SOLUBLE SOLIDS.

Official	Asbestos-kaolin	
.683	.670	Liq. Quebracho.
.646	.639	Oak
.879	.867	Special
.561	.544	"
.555	.530	"
.576	.570	"

Kerr sent the following letter:—

"We have not found it necessary to carry as much as 16″ vacuum; in fact, we found by covering the perforated bottom of the porcelain funnel with a piece of brass wire cloth, and thereby improving the drainage, that the necessary quantity of liquor could be obtained with a 4″ vacuum, using a vacuum flask of 1,000 cc. capacity.

A much better mat can be thrown on the gauze than on the porcelain funnel bottom, and all danger of stopping the perforations is avoided. A much more uniform mat can be obtained when the asbestos is thoroughly pulped in 100 cc. of liquor than in 50 cc.

The funnel should be made to contain the full quantity of liquor necessary for the filtration. When it is so small that it is necessary to add liquor from time to time, there is considerable danger of disturbing the mat. As the porcelain funnel we used held only about 100 cc. we guarded against this by laying a small piece of gauze, with the corners turned up, on the mat, thereby preventing the stream of liquor from washing a hole in it, or disturbing the coat of kaolin.

After working on the method to the above point, the writer decided that if the filtration could be made without employing reduced pressure, it would be much simplified, and as the improved drainage obtained by using the wire cloth enabled us to reduce the vacuum employed, he decided to experiment in this direction, with the result of finding that in the case, at least, of any ordinary extracts or liquor, a vacuum is unnecessary to obtain rapid filtration and clear filtration.

I attach a sketch of the apparatus that we are now testing, and will say, so far, it has not failed to duplicate the results obtained in the vacuum apparatus.

The whole question is one of drainage, and you will note I have doubled the area of the funnel bottom, and instead of an occasional perforation have increased the number until at least 50 per cent. of the whole bottom is open. With the wire cloth screen on top of this, I find the drainage to be rapid enough to do away with all other apparatus than the filter tube. At this time we have made a considerable number of filtrations, ranging from common solid quebracho liquors to chestnut, and so far have not encountered any mechanical difficulties. Should our work be confirmed in this respect and the asbestos-kaolin mat be determined superior to filter paper, it would seem practically all serious objections to its adoption would be removed."

The author spent some considerable time trying to make the method work along the lines suggested by Kerr, *i. e.*, using no vacuum, but he was forced to confess absolute failure. When a mat was secured which yielded a clear filtrate, filtration proceeded at a prohibitively slow rate; when a mat was secured which allowed filtration to proceed at a reasonable rate, the filtrate was far from clear. As other members reported similar experiences, the author concluded it unnecessary to carry this line of investigation further.

The apparatus suggested for the collaborative work was patterned after one used successfully in the author's laboratory. It does not pretend to be the best possible, but it will do the work comfortably and satisfactorily. The directions given did not pretend to describe the only possible procedure for successful operation of the method, but did describe a procedure used with success and satisfaction. The samples sent out were of ordinary quebracho, of clarified quebracho and of chestnut wood, together with a sample of asbestos. The directions accompanying were as follows:—

"Do all work in duplicate.

Use the following amounts of extract in making up your solutions for analysis:—

6 gms. of Ordinary Quebracho, to	1000 c.c.
6 gms. of Clarified Quebracho, to	1000 c.c.
14 gms. of Chestnut Wood, to	1000 c.c.

1. Determine total solids by the official method.
2. A. Determine soluble solids by the official method.
   B. Determine soluble solids as follows:—

Digest 1½ grams of asbestos with 50 cc. of analysis solution in a small beaker.

Digest 1½ grams of kaolin free from soluble impurities with 50 cc. of analysis solution in a small beaker.

(These amounts of asbestos and kaolin are right for a filter plate 2¼" in diameter. For larger or smaller plates, correspondingly larger or smaller amounts of asbestos and kaolin must be used.)

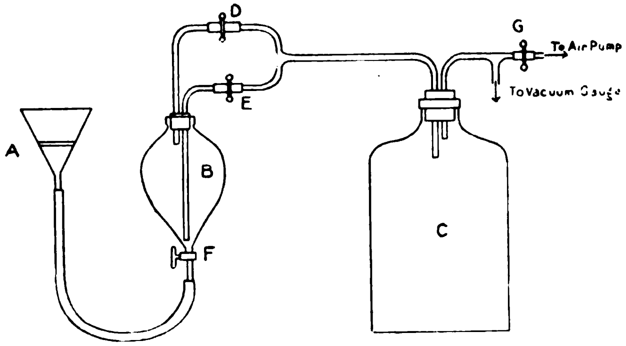

Fig. 3.

Using the apparatus shown in Fig. 3, start the suction pump going and throw the solution containing the asbestos on the filter plate A, cocks E, F and G being open and D closed. Pull the asbestos down to a firm mat by suction. (A little care and practice are necessary to insure a good mat covering the plate uniformly, but such a mat is essential if the filtration is to proceed properly.) Next throw on the solution containing kaolin and allow the vacuum to run up to 16" hg. Close cock G. Allow most of the solution to be drawn through the filter, then add approximately 100 cc. of fresh solution and keep approximately this volume of liquor in the funnel throughout the filtration by adding fresh solution as needed. Once the solution containing kaolin has been thrown on the filter it is imperative that the mat be kept covered with solution. At least 150 cc. of solution, including that used for digesting the asbestos and kaolin, should be allowed to pass through the filter before beginning to collect for analysis, and more if the filtrate shows any indication of not being brilliantly clear. Then cock D is to be opened and E closed and the 100 cc. to be measured out is to be collected in B.

In the apparatus shown (Fig. 3), A is an ordinary glass funnel in which has been placed a porcelain filter plate 2¼" in diameter. The funnel is connected to the heavy walled 150 cc. separatory funnel by heavy walled rubber tubing. C is a common heavy-glass bottle of about 4 liters' capacity. This is connected to the separatory funnel by the glass and rubber tubing shown, the latter having pinch cocks at D and E. C is also connected to an ordinary mercury vacuum gauge and to an air pump. It is not necessary that you prepare an apparatus exactly as described here. Any apparatus which will accomplish the same end is permissible. Of course, the air pump must not be allowed to act on the collecting liquid during the actual filtration. The apparatus must be arranged so as to permit a change of collecting flask without altering the pressure on the asbestos mat. A vital point in the proper working of the method is that the porcelain plate must have as many and as fine holes as possible. In much of the preliminary work of the Committee, failure resulted from the use of a plate having too large holes. In several cases this was remedied by covering the plate with 100 mesh brass wire gauze.

The asbestos sent you is the mixed long and short fiber acid-washed asbestos prepared by E & A for Gooch crucible work. It has been further digested with HCl in the Chairman's laboratory and washed free from chlorides.

You are requested to use also an asbestos obtained from some other source. This asbestos should be digested with fairly strong

HCl washed free of chlorides and dried. An asbestos of mixed fiber such as is in use for Gooch crucible work is desirable.

Report results on the accompanying sheet showing the duplicate values obtained."

A summary of the reports received is as follows:—

ORDINARY QUEBRACHO.

	Total	Official		Asb.-kaoln.		Time	
	sols.	Sol. sols.	Insol.	Sol. sols.	Insol.	Off.	A.-k.
Faust, Yocum-Eachus Lab..	85.58	77.43	8.15	78.33	7.25	150	40
				76.30[1]	9.28		40
Fox, U. S. Lea. Lab.	84.00	73.08	10.92	72.00	12.00	300	170
Hilbert, G. & K. Lab., A ...	84.59	76.65	7.89	75.50	9.04	313	98
B	85.12	77.08	8.04	76.11	9.01	340	113
C	85.91	78.16	7.75	77.02	8.98	305	56
Hutchins, Sheff. Sci. Sch....	85.79	77.56	8.22	76.24	9.55	540	180
Maxwell, Kistler-Lesh Lab...	84.74	77.20	7.54	77.03	7.70	204	107
Paessler, Freiberg, Ger.	87.3	76.8[2]	10.5	77.5	9.8	90	128
Parker, London, Eng., A ...	90.1	82.4	7.6	80.15	9.95	155	50
B ..				79.70	10.50		60
Pichette, Pfister-Vogel Lab.	88.43	77.62	10.81	85.63[3]	2.80	180	20
Worthen, G. & K. Lab.	85.08	78.62	6.46	77.04	8.04	285	80

[1] 2 grms. each kaolin and asbestos used.

[2] Berkefeld candle-filter method used.

[3] No kaolin used.

CLARIFIED QUEBRACHO.

	Total	Official		Asb.-kaoln.		Time	
	sols.	Sol. sols.	Insol.	Sol. sols.	Insol.	Off.	A.-k.
Faust, Yocum-Eachus Lab..	87.95	87.58	.37	87.45	.50	85	12
Fox, U. S. Lea. Lab., A	88.33	88.21	.12	88.33	.00	110	10
B				88.33	.00		10
Hilbert, G. & K. Lab., A ...	87.16	87.10	.07	86.96	.20	135	11
B ...	86.89	86.81	.05	86.84	.05	120	5
C ...	87.48	87.41	.07	87.42	.06	104	9
Hutchins, Sheff. Sci. Sch....	88.08	87.62	.46	87.29	.79	150	15
Maxwell, Kistler-Lesh Lab...	86.90	86.77	.13	87.01	...	118	9
Paessler, Freiberg, Ger.	91.3	88.8[1]	2.5	92.0	...	20	50
Parker, London, Eng., A ...	89.4	89.3	.1	88.74	.66	75	40
B ...				88.83	.57		45
Pichette, Pfister-Vogel Lab..	90.16	89.80	.36	88.65[2]	1.51	120	15
Worthen, G. & K. Lab.	86.89	86.96	....	86.89	.00	98	10

[1] Berkefeld candle-filter method used

[2] No kaolin used.

Chestnut Wood.

	Total	Official		Asb.-kaoln.		Time	
	sols.	Sol. sols.	Insol.	Sol. sols.	Insol.	Off.	A.-k.
Faust, Yocum-Eachus Lab., A	41.49	41.21	.28	41.34	.15	85	11
B	41.70	41.32	.38	41.44[1]	.26	85	12
Fox, U. S. Lea. Lab.	41.59	40.81	.78	40.58	.74	120	25
Hilbert, G. & K. Lab., A ...	41.36	40.87	.49	40.87	.49	142	15
B ...	41.35	40.87	.48	40.84	.51	125	10
C ...	41.46	40.82	.64	40.77	.69	120	9
Hutchins, Sheff. Sci. Sch....	41.30	41.07	.23	40.80	.50	240	30
Maxwell, Kistler-Lesh Lab., A	41.57	41.10	.47	40.97	.60	125	10
B				41.04	.53		
Paessler, Freiberg, Ger.	42.0	41.1[2]	.9	41.7	.3	25	45
Parker, London, Eng., A ...	42.3	42.1	.2	41.9	.4	70	30
B ...				41.8	.5		35
Pichette, Pfister-Vogel Lab..	42.4	42.03	.36	41.60	.80	120	15
Worthen, G. & K. Lab.	41.53	41.00	.53	40.89	.64	110	10

[1] 2 grms. each kaolin and asbestos used.

[2] Berkefeld candle-filter method used.

[3] No kaolin used.

The comments of the collaborators were as follows:—

Mr. Alsop:—No report. I filtered a few extracts and obtained very good results with chestnut and clarified quebracho and was not so successful with hemlock and ordinary quebracho. I am not especially impressed by this method but would be willing to have it added to the method, but would not consider voting to have it supersede the present method.

Mr. Faust:—I had difficulty in getting clear filtrates with the prescribed amounts of asbestos-kaolin, consequently raised the prescribed amounts of asbestos to 2 grams, the kaolin to 4 grams which improved the filtrates greatly. I find no difference between results obtained by using the prescribed asbestos and by using some which we had on hand. My results are all quite similar to those given by the official method with the exception of ordinary quebracho when a brilliant filtrate was obtained, lowering the soluble solids over 1 per cent. I made a number of filtrates with ordinary quebracho and while I had trouble getting concordant results, believe that could be overcome with practice. For materials other than ordinary quebracho I think the official method gives better results with easier manipulation.

USING 2 GRMS. ASBESTOS AND 4 GRMS. KAOLIN.

		Soluble solids		Time	
	Total sol.	Official	Asb.-kao.	Official	Asb.-kao.
Ordinary quebracho[1]	83.70	78.52	79.03	2.30	.40
	79.57	74.20	73.26	2.20	.35
	79.26	75.90	74.75	2.15	.35
Clarified quebracho	82.45	81.72	81.40	1.20	.10
Duplicate			81.53		.08
Chestnut ext., solid[1]		89.77	89.92	1.30	.15
Spent tan	9.37	8.76	8.75	4.00	.35

	Clearness		Insolubles	
	Official	Asb.-kao.	Official	Asb.-kao.
Ordinary quebracho[1]	Opaque	Opaque	5.18	4.67
	Opaque	Clear	5.37	6.31
	Opaque	Clear	3.36	4.51
Clarified quebracho	Brilliant		.73	1.05
Duplicate	Brilliant			.92
Chestnut ext., solid[1]	Brilliant			
Spent tan	Clear		.61	.62

[1] Using 1½ grams asbestos and 1½ grams kaolin. All separate samples.

MR. FOX:—Can't say that I think very much of the method.

MR. HUTCHINS:—Prefer the asbestos-kaolin method.

MR. KERR:—At the present status of the method, I would not care to vote for it.

MR. MANUEL:—It was found impossible by two different operators to use kaolin at all. A Hirsch funnel with a 1¼" solid plate on top of which was placed a 60 mesh brass gauze and then a layer of asbestos was finally used. A linen cloth was used to hold the asbestos in place. Attempt was made in many different ways to filter the quebracho extract but without success. The filtrate was always cloudy and kaolin when used to obtain a clearer filtrate always came through. This difficulty was possibly caused in part by slightly uneven suction. A few experiments were conducted on tan liquors and the results were such that the method gives promise of furnishing a quick method of filtration.

MR. OBERFELL:—As far as I am concerned must say that the asbestos-kaolin method of filtration is impracticable. I think the apparatus recommended this year is not as good as the one last year and is simply inadequate. I would oppose vigorously any move to have it included in the A. L. C. A. methods, either as an official, provisional or alternative method.

MR. ROGERS:—I am very much in favor of the asbestos-kaolin method.

MR. SHIELDS:—It seems to me that the prescribed amount of asbestos is hardly sufficient to secure a good mat.

MR. SMOOT:—I have found the method to give uniformly good clear filtrates if the mat was properly prepared. In preparing the mat, however, I had considerable trouble. When a small amount of suction was employed I could not get clear filtrates and if the suction was too great it clogged up entirely.

MR. HILBERT:—Provided the mechanical details for making a large number of soluble solids determinations can be successfully worked out, I prefer the asbestos-kaolin method.

1. The filtrates are clearer and more brilliant.
2. There is a great saving of time.
3. The chance of loss by evaporation is lessened.
4. The actual process of filtration is carried on throughout nearer to 20° than with the official method.
5. Duplicate determinations agree better especially with liquors of high insoluble content.

In sending samples to several of the members of the A. L. C. A. living outside the United States and whose interests are primarily in the I. A. L. T. C., the author had in mind conversations with these men in which he had urged the desirability of the adoption of the asbestos-kaolin method of filtration by both Associations as at least an alternative method of soluble solids filtration. The growing international commerce in tanning materials and the increasing tendency to make the tannin content the measure of value, call for a universal method of tannin analysis. In the matter of soluble solids filtration the methods in use by the two Associations of leather chemists lead to different values and neither Association seems ready to adopt the method of the other. The author was of the opinion that the asbestos-kaolin method of filtration had more merit than either of the methods in use and might well serve as a compromise method which could form part of a universal method. This side of the subject was further presented to the foreign members of the Association by letter and several interesting replies received, as shown herewith.

MR. TURNBULL:—The present I. A. L. T. C. method by use of the candle filter is satisfying both buyer and seller in this country. It would be exceedingly foolish of us to make any change.

MR. PAESSLER:—When solutions of solid quebracho in which the difficultly soluble tannins are in a very minute state of division were filtered, the asbestos-kaolin and the candle-filter gave brilliantly clear filtrates and concordant results. As, however, we are having no difficulties with the candle filtration there would seem no reason for our abandoning it, especially for a method which shows no advantages over the candle method.

MR. PARKER:—Undoubtedly the asbestos-kaolin method is quicker and with some materials gives a clearer result. I did not use the apparatus exactly as on your chart but fitted up a similar apparatus using a Hirsch porcelain funnel of 2″ diameter which I covered with asbestos. I would suggest that if this system be used that the Bruhl apparatus for fractional distillation in vacuum be used; this contains five or six vessels so that if the first portion did not come clear, it would be unnecessary to disconnect but that a fresh vessel could be put under as soon as brilliant clearness was obtained. I used a long fibre asbestos, especially prepared.

I am anxious to be perfectly fair and unbiased in this matter but I must confess that I cannot see any advantage of the asbestos-kaolin method over properly constructed Berkefeld filter candles. I consider, however, that if the American Association adopts the asbestos-kaolin method, the I. A. L. T. C. at their next conference in Paris would most likely make the method permissible to members of the I. A. L. T. C., but I do not think you will get the I. A. L. T. C. to give up the filter-candle method, with which they are perfectly satisfied and with which absolutely concordant results can be and are obtained.

MR. PROCTER:—I think very well of the method, though it absorbs a little more tannin than the candle does in cases where the latter will give a sufficiently good filtration. I am proposing to bring the subject before our International Commission, so that before the meeting in Paris next year it may have been thoroughly examined. Certainly if we were starting afresh the asbestos method would have much to recommend it. We have found that the absorption of tannin is in some cases slightly lessened by boiling the asbestos first with a little of the liquor, but I do not think that the advantage gained as compared with rejecting a fair quantity of the liquor is sufficient to justify the extra trouble.

Material	I. A. L. T. C. method. Candle		Reed's method. Asbestos-kaolin		
Natal Mimosa Bark	45.30	45.16	43.96	44.66	(C)
Mixed Extract	38.48	38.42	38.11	38.34	(C)
Sicilian Sumac	44.08	44.00	43.30	43.68	(C)
"Mimosa D." Extract	48.25	48.29	48.03	48.03	(C)
"Mimosa D." Extract	48.25	48.29	48.00	47.89	(AC)
Oakwood Extract	42.95	42.00	42.35	42.63	
Fir Bark Extract	40.52	40.72	39.12B	40.70	
Oakwood Extract	41.00	41.12	40.84B	40.84	(B)
Quebracho Extract	45.04	45.04	45.38	46.68	(C)
Pistachio	33.09	33.18	33.13	33.07	(C)
Sicilian Sumach	45.71	45.84	45.87	45.74	(C)
Sicilian Sumach	45.71	45.84	45.54A	45.52	(AC)

A—Small's asbestos.
B—Short fiber asbestos. Long fiber asbestos unmarked.
C—Boiled with a small quantity of the infusion before use.

From the replies it would seem probable that the I. A. L. T. C. might be willing to meet us half way in this matter and that our Association might have the honor of proposing the first acceptable item in the universal method. Unfortunately and much to the author's regret our own Association has apparently ceased to take any violent interest in the asbestos-kaolin method—(judging by the number of those willing to do any work with the method)—and of those expressing an opinion regarding the method a majority are not in favor of it. Whatever recommendations the author might make as voicing the sentiments of the collaborators must needs be unfavorable to the method. Based, however, on his own personal convictions any adverse recommendations would be wholly out of order. A careful study of the table of results is distinctly encouraging when one considers that many of the collaborators were working with the asbestos-kaolin method for the first time. Some of the collaborators evidently failed to appreciate the vital points in the conduct of the method; some apparently allowed the suction pump to work on the liquor being collected for evaporation, one used no kaolin, etc. Nevertheless, leaving out of consideration some wild results, which by the way are found as well in the reports of work by the official method, the agreement is good and the author still hopes that the sentiment of the Association may change and that the members may learn to appreciate the merits of the method and urge its adoption as vigorously as they now indifferently pass it by.

Perhaps the author may be pardoned for summarizing the faults and merits of the method as he sees them on the understanding that what he says is purely a personal opinion and not a statement in behalf of the collaborators in the work.

The criticisms have been, first, absorption by the asbestos and kaolin. Now a certain amount of absorption undoubtedly occurs, but this is largely satisfied by the preliminary digestion with the liquor and the rejection of the early portions of the filtrate. The resultant error is undoubtedly negligible as shown by work done on clear solutions and by a comparison of results obtained by other methods of filtration. The error from this source may be far from negligible, however, if the asbestos is not properly prepared. A thorough digestion with acid till the soluble bases are removed and then a complete washing are essential. With this precaution any asbestos may be used. For instance sample B. used by Hilbert was asbestos wicking such as is used for packing steam valves and bought at a steam fitter's supply house.

Objection two, is the difficulty of securing a proper mat. The author has had no difficulty of this sort with a properly prepared asbestos and with the amounts recommended. Several of the collaborators seem to think the amounts recommended too small and for general use this may be the case. It was the author's purpose to keep the amounts as small as possible in order to reduce the absorption effect to a minimum. A more probable explanation of the lack of success in securing proper mats is the use of filter plates with too large holes and failure to pull the asbestos down to a firm hard mat before throwing on the kaolin. Some of the men got around the difficulty of too large holes by using 100 mesh brass wire gauze as a cover for the filter plate, and with much success. It seems most surprising to the author, however, that these simple mechanical details should have proved such insurmountable obstacles to some of the men.

The third objection is the cumbersomeness of the apparatus and the difficulty of conducting more than a few filtrations at one time. It must be admitted at once that more apparatus and less common is required for the asbestos-kaolin method. But this objection is really not of much force. It is entirely possible to set up apparatus so that many filtrations can be run at one time. The main requisite is a large central reservoir exhausted by a mechanical vacuum pump and connected to a line of pipe with outlets at intervals which may be connected by cocks to the individual filters. Such an apparatus is certainly not prohibitive of attainment in these days of abundant electrical power.

The fourth objection is the opportunity for wild results. It must be admitted that the slovenly or careless worker can hit wider of the work by the asbestos-kaolin method than by the official method, but this is certainly a feeble objection on which to turn down a method.

As against these objections we have two certain advantages: first a great saving of time. This is too obvious to need further comment. Secondly, a gain in accuracy. Any one who has had much experience in the filtration of ordinary quebracho or hemlock extract solutions knows how impossible it is to obtain by the official method filtrates which will be brilliantly clear by both reflected and transmitted light; he knows also how difficult it is to make duplicate determinations which are in agreement, especially if the determinations are made on two different days. The causes are several, first, variation in the filter paper; second, variation in the rate of filtration; third, evaporation during the process; fourth, change of temperature of the solution. In all these respects the asbestos-kaolin method makes toward accuracy and concordance. It yields a filtrate, brilliantly clear by both transmitted and reflected light so that there is no question of more or less of cloudiness or opalescence; the time of filtration is so shortened that errors from evaporation or change of temperature of the solution are reduced to a minimum. Comparatively wide variations in room temperature will have little effect on the soluble solids filtration.

In conclusion the author can but express his personal belief that the method is too valuable to be turned down.

DISCUSSION.

PRESIDENT WILSON:—You have heard Mr. Small's report on the filtration subject, and I would call for a very prompt discussion of this matter. It will probably incite quite considerable discussion as there seem to be about as many opinions on the subject as there are collaborators.

MR. REED:—I might suggest, that any difficulties that occur with the preparation of the asbestos might be overcome in some such way as was suggested yesterday for the cloth, coming from a central source; also the same way that we obtain our hide powder. All the collaborators could obtain exactly the same preparation in that way and errors from that source would be eliminated.

PRESIDENT WILSON:—So far as the chairman can see, there is no objection to the principle of the thing, and the main fault so far is in designing a proper apparatus. The special apparatus which Mr. Small recommended for the final work, with all due respect to Mr. Small, is, I think, by far the worst which has ever been designed. We have at the bottom of that apparatus a long rubber tube, about a foot long, which cannot help accumulating the kaolin which always goes through when the filtration is started, and we cannot begin to say that kaolin is all washed out by the 150 or 200 cc. of solution which are run through. I think that it is a wise thing for us to try to get away from filter paper, and we have been striving for years to get some sort of material which will be non-absorptive of tannin, and I think, as I said before, the main feature is to design the perfect apparatus.

MR. SMALL:—With regard to the criticism, I cannot say anything more than I said in my report. I have used this apparatus extensively in the laboratory and have had *absolutely* no trouble of the sort that Mr. Wilson mentions. The stream is sufficiently rapid in the early stages of the filtration so that any finely divided kaolin which comes through, is carried out of the tube and out of the collection reservoir. The only proof I could adduce in support of that statement, is the fact that the solutions which I obtained were *brilliantly* clear. There was no suggestion of deposit on standing. I am perfectly willing to concede that some one may get up an apparatus that is better. I merely state that this particular apparatus can be used and give satisfactory results.

MR. TEAS:—I would like to ask what is the limit as to strength of liquors that can be advantageously filtered by this method—barkometer strength?

MR. SMALL:—I never have tried any experiments to see. So far as I can make a guess I should say that the limit would be very much higher than by the official method. You have the advantage of increased suction, and that will carry through a much heavier body of liquor. Moreover, I do not think the filter will clog as rapidly as filter paper will. Not in this connection but in another, I had occasion to filter some heavy solutions, and filtering them with suction I was able to get a reasonable amount through in a very much less time than I could by using filter paper.

MR. HALEY:—I would like to ask Mr. Small if this system will admit of a filtration of a 20 to 25 degree barkometer liquor?

MR. REED:—(Aside) Yes.

MR. SMALL:—So far as I know, it will. I cannot tell you from practical experience because I have not tried it, but I see no reason why it should not.

MR. TEAS:—I have always advocated a stronger dilution for analysis of extracts, and if this device will permit of filtration of stronger liquors I think it is a step in the right direction. Now we all know that the strength of liquor used in analysis is very much weaker than what is used in actual tannery work, and on certain classes of extracts the insolubles represented in the analyses are just a fraction of what they really are when you get liquor of the strength used in the tannery. Now, leaving the question as to which is the proper strength of liquor for analysis out of it entirely,—of course if we use a stronger liquor for analysis the price would probably be adjusted on that basis—don't you think it would be a good thing to provide for the filtration of the ordinary strength and then for the filtration of say 20 to 30 degree liquor of an extract, in order that the insolubles might be compared at the two strengths? It would not make much difference in a chestnut extract, but it would in a quebracho or a hemlock.

Mr. Haley:—I think Mr. Teas' suggestion is a very practical one. As I understand the straight analysis of a tanning extract, it is for the purpose of establishing the value of the product that is being tested. Now, does your system of analysis for the determination of soluble matter, and consequently the percentage of tannin, give the consumer the correct relative values of different tanning products? There are some tanning materials that in the liquor that the chemists analyze, show a higher percentage of insoluble matter than they do in a more dense liquor, but that is the exception. I think that refers to only one product so far as I know, and a product to-day not in very general usage in extract form; but you take an untreated solid quebracho extract—in glancing over these reports I see there is quite a difference of opinion concerning the presence of insoluble matter present in it, there always has been and I believe there always will be a great difference. In Europe, having so-called treated quebracho extract, the eye of the chemist is his guide for the insoluble matter. In other words, he does not filter when his eye tells him that his solution is clear enough not to filter. I could show hundreds of analyses of quebracho extracts that according to the English system of analysis show absolutely no insoluble matter, for the reason that they were never filtered, and it is the eye of the chemist that determines whether or not the solution should be filtered. On the other hand, I have gone to the trouble of having in the last six or eight months analyses made of different materials in extract on a 20, 30 and 40 degree barkometer basis, because in our opinion that is the basis upon which relative values should be established; for it is the density of liquor that the tanner uses in his tannery. He makes that density of liquor in his tannery by the combination of extracts with his base tanning liquors. Now, if a method can be devised—and that was my reason for asking Mr. Small if the method would admit of the filtration of a 25 degree barkometer liquor—if a method can be devised whereby a 25 to 30 degree barkometer liquor can be filtered, I think you can get just as important results as these sheets would indicate you are getting to-day upon a much weaker liquor, and certainly it would give the tanner a better commercial relationship between the different extracts that are tendered him for usage.

If this association is going to continue to be a factor in commercial trade, it must place its analyses upon a commercial basis, and that basis is to establish between different products relative values in the condition in which those products are used by the consumer; not the theoretical relationship that may exist between them according to the chemist's analysis. As you increase the density of your liquor in practically all extracts, you will increase the insoluble matter present in that extract, and at the expense of the tannin. Your total solids remain the same; your soluble solids will decrease; your non-tannins are the same, but the insoluble matter increases at the expense alone of the tannin. And since commercial value is placed to-day upon extracts largely on account of the percentage of tannin, you should place yourselves upon the same basis in your analyses. As Mr. Teas has truly said, it does not matter what percentage of tannin you report, the value will be placed upon the extract accordingly.

MR. ALSOP:—I think that in this matter an excellent plan would be to report the analysis as it is made now, and the insoluble solids in a 20 or 30 degree liquor. I think a good deal of information can be obtained from that, and I think it would be a start in the right direction.

ABSTRACTS.

Injury to Hide by Unsuitable Preservation. J. PAESSLER. *Ledertechn. Rundschau,* 1909, No. 51, pp. 401-3.—The frequency of publications on this subject shows its importance in leather industry at the present time. The defects in much of the imperfect leather sent in to the Freiberg Station for examination could be attributed to the above origin. The effects are the most serious economically in those grades of leather which are required to look well. Hide is very susceptible to fermentation and the original mischief may not be perceptible until the leather process is well advanced, dull matt grain being one of the usual defects. To prevent these, the animals should be skinned soon after slaughtering and the hides after cooling should be immediately dried or salted and not stored green even in winter. Blood is the most putrefiable substance known and should be let soil the hide as little as possible. If the hides are to be dried, this must be done quickly in a good draught. Too high temperature should however be avoided, else resoftening is difficult, also the interior of the hide does not dry and fermentation ensues, resulting in splitting in the finished leather. Antiseptic treatment before drying with salt, carbolic acid, lysol, creoline, etc., is to be recommended; formaldehyde however ought not to be used. For salted hides only fresh salt should be used and never that which has already been used on hide. The action of the salt is two-fold; one part dehydrates the hide and flows off, here the draining should be thorough; the other penetrates the hide, acting as antiseptic. Alumina salts should be excluded as denaturing materials for the salt used; petroleum or soda are suitable.

Brittle Grain in Chrome Leather. *Ledertechn. Rundschau,* No. 52, pp. 409-11.—A certain manufacturer of box calf met with frequent complaints of his product that had hitherto been of superior reputation. The writer on investigation found that the most defective pieces resulted from hides showing local irregularities in deliming, and these could finally be traced back to the original hides which were of foreign origin. A remedy was found in altering the method of soaking, which had formerly been carried out in old and tepid water, on account of the great hardness of the skins. In the new soaks, fresh cold water was used containing some caustic soda. Here the hides swelled considerably and were the next day turned, stretched and given fresh water. Next they went into a lime which had been little used and was sharpened with sodium sulphide; the hair yielded in 4 days. Next followed milling in warm water, then a fresh white lime for 3 days. After each strengthening of the white limes, they were used 3 times and were then sharpened with sulphide for dehairing. The former defects in the finished product no longer appeared and the leather was fuller and of a firmer grain. The feel was too hard, but this was finally bettered by making the pickle stronger and the liquor fatter. For improving the feel of chrome leather a decoction of linseed is recommended. The crushed seed is boiled over a water bath with twice its quantity of water, strained and extracted again. A neutral fat soap (olive oil or the like) is added and boiled. Finally to the luke-warm decoction, 20% whole milk is added. This luster is best applied to the leather luke-warm.

Marine Oils and Their Production. V. Bogh. *Ledertechn. Rundschau.* 1910, No. 1, pp. 1-2.—The writer, who directs the experimental station of the Dänish Tanners' Union, comments upon O. A. Jacobsen's recent article upon Norwegian cod-liver oil (abstract, ante, p. 144). He is astonished that any proposition for the employment of foreign capital should emanate from Norway, considering the restrictions imposed upon outsiders by home protective legislation. He further does not admit that blubber oil is inferior to cod-liver oil for leather dressing purposes. The chemical constants, iodine and saponification numbers, etc., of cod-liver and seal oil are about the same. The commercial products may vary according to the amount of degrasine contained, which is a secondary product of oxidation, especially at high temperatures. The objectionable mucous ingredients of pressed cod-liver oil give rise to fermentation when applied in leather manufacture; by boiling the oil, these are made harmless. Blubber oil (in Denmark the Greenland seal oil is used) is by nature free from these nitrogenous ingredients, even in the light colored oils. The brown or boiled blubber oil is not dearer than the corresponding cod-liver oil.

Mangrove Bark and Its Decolorization. J. PAESSLER. *Ledertechn. Rundschau,* 1910, No. 2, p. 9.—The chief merits of this material are its high tannin content and ready solubility of the tannin. Above all, it is the cheapest material known reckoned on actual tannin. It is not true, as some have maintained, that mangrove tans are only loosely fixed by the hide or that the rendement is low. Mangrove possesses one defect, however, the objectionable red color imparted to leather. This has hitherto been overcome by combination with light colored materials like myrabolams, producing brown. Dr. Arnoldi has worked out a process for decolorizing mangrove so that it may be used alone and give leather a brown color similar to oak without any pronounced red. The process is patented and the property of the Freiberg Station, to which those interested may apply.

The De-liming of White Hide. ETTOR GUISIANA. *Collegium,* 1910, No. 391, pp. 14-16.—De-liming with mineral acids must be conducted with caution and organic acids do not give very satisfactory results, and are expensive. The writer has devised a process which has given good results in various tanneries. After thorough washing the hides are treated in the drum with a sufficient amount of bisulphite of soda of 35° B. This expels H_2S from any sulphide present and neutralizes free lime, the end products being neutral sulphites of soda and lime, together with free caustic soda. After ½ hour a sufficient amount of dilute HCl free from iron is added, which liberates SO_2, forming harmless salt and easily soluble $CaCl_2$. The SO_2 plumps and bleaches the hide; the process is complete in ½ hour and no rinsing is needed. A temperature of 18-20° C. accelerates the reaction.

Determination of Tannin by the Zeiss Immersion Refractometer. P. FALCIOLA AND M. CORRIDI. *Collegium,* 1910, No. 392, pp. 21-5.—The authors, like Sager (abstract, this JOURNAL, 1909. [4], p. 107.) report comparative analyses by the above method as proposed by Zwick (*Ibid,* 1908, [3], p. 355). The gravimetric control was made by the filter method. Results similar to those of Zwick and Sager were obtained. Unlike Zwick, the authors do not think this a promising method for distinguishing tanstuffs, since the differences in equivalents are too slight. The figures in the concluding table which we quote represent percentage tans to one degree of scale.

			Falciola-Corridi	
	Zwick	Sager	limits	mean
Myrabolams	0.1945	0.184	0.160-0.179	0.171
Valonia	......	.....	0.175-0.193	0.181
Mimosa	......	0.162	0.166-0.173	0.170
Quebracho, wood	0.168	0.167	....	.....
Quebracho, ext.	......	0.180	0.161-0.171	0.168
Quercitron	......	.....	0.176-0.178	0.177
Chestnut	......	.....	0.179-0.176	0.177
Tuscan pine, ext.	0.193	0.187	....	0.170
Jaune de Cube	......	.....	....	0.160
Sumac	0.181	0.180	....	0.172

Materials for Loading Leather. W. EITNER. *Der Gerber,* 1910, [36], No. 848, pp. 1-3.—This practice began 40 years ago in England with the employment of starch products for stiffening buffalo sole leather, and the same materials soon began to be used for merely weighting purposes. On warming starch with very dilute sulphuric acid as a final product the so-called starch sugar is obtained. This is solid, being a variable mixture of maltose, dextrose and dextrine. As used in the leather industry it contains 10-30% water, 40-70% sugar and 10-40% dextrine. Its solution penetrates leather with great ease, especially when rich in sugar. An objectionable feature is the hygroscopic character of the sugar. Fermentation may ensue on storage of the leather with production of mold and discolorization. Glucose syrup has on this account largely displaced starch sugar. This product contains more dextrine which hinders the crystallization of the sugar. The average composition is 16-23% water, 30-49% sugar, 32-52% dextrine. The penetrating power is lessened, but the leather is less sensitive to moisture. Epsom and Glauber salts and barium chloride greatly increase the penetration of glucose and are much used. Glucose alone gives a more brittle leather. For moderate amounts, these salts are also used alone, but in excess may crystallize on the surface when barium chloride and Glauber salts are used together, the sodium chloride produced makes the leather hygroscopic and the deposited barium sulphate interferes with the blackening of sole edges and the wax takes no polish. Brilliantine, another starch product, averages 23.7% water, 5.3% maltose sugar, 62.4% dextrine, 8.6% soluble starch (amiduline). It is an opaque, thick mass, which in solution even with salts, does not penetrate the leather, and milling is resorted to. Too much of this material makes the leather brittle. Although sulphuric acid is used in the manufacture of the above products, it is never retained in sufficient amounts to injure leather. The brittleness results from excessive use of the filler.

PATENTS.

Leather Splitting Machine. U. S. Patent No. 946,819. J. BUSFIELD, Haverhill, Mass.

Process of Manufacturing Lactic Acid. U. S. Patent No. 947,078. W. KLAPPROTH, Niederingelheim, Germany.

Art of Tanning. U. S. Patent No. 947,169. F. VAN VOORHIS, Finleyville, Pa. A compound for tanning leather comprising the following ingredients in approximately the proportions named, namely—gambier, 25 pounds; ground canaigre, 10 pounds; ground Sicilian sumach, 10 pounds; soda ash, 12½ ounces; water, 50 gallons.

Process of Tanning. U. S. Patent No. 947,433. J. M. BROWN, Austin, Ark. The method of tanning a hide which consists in rendering the same soft and absorbent, then rubbing it on the flesh side with pulverized alum, then rolling it and allowing it to stand for a sufficient length of time to permit the alum to perform its function, then immersing it in an ooze consisting only of Terra Japonica and water, then washing it, and finally working and oiling it.

Pressure Roll for Skiving Machines. U. S. Patent No. 948,031. F. L. ALLEY, Lynn, Mass.

Skiving Machine. U. S. Patent No. 948,032. F. L. ALLEY, Lynn, Mass.

Machine for Treating Hides and Skins. U. S. Patent No. 948,208. D. P. CUMMINGS, Newton Center, Mass.

Artificial Leather. U. S. Patent No. 948,383. J. J. C. SMITH, Passaic, N. J. The process of producing artificial leather which consists in saturating fibrous sheet material in a composition of glue, glycerine, molasses and water, evaporating the water, superposing upon said sheet a composition of glue, glycerine, molasses and a fibrous filler, impressing said layer with a reproduction of the grain of any leather, and treating the product with dilute formalin.

Evaporator. U. S. Patent No. 948,322. J. F. HANRAHAN AND H. A. WENDE, Buffalo, N. Y.

Multiple Effect Evaporting Apparatus. U. S. Patent No. 948,376. S. M. LILLIE, Philadelphia, Pa.

Skiving Machine. U. S. Patent No. 949,062. G. H. DIEHL, JR., New York, N. Y.

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The Secretary would request that each member of the Association make an effort to obtain the signature of a candidate for membership, upon the application blank which he has received.

H. C. REED,
Secretary.

SOME CONSTANTS FOR COD LIVER OIL AND MENHADEN OIL.

By W. K. Alsop.

The leather chemist is frequently called upon to test cod liver oils used by the tanner, especially as to the presence of menhaden fish oil. It is not an easy matter to determine certainly whether menhaden oil has been added to the brown cod oils usually used by the leather trade if the amount added is less than 30 per cent.

Several years ago a number of tests were made to determine whether the specific gravity, acid value, bromine addition and substitution values, Mauméne test, unsaponifiable matter and color tests would give data useful for this purpose. Some experiments were also made with the fatty acids from these oils. This data was accidentally destroyed, but as it may be of some interest, I have tabulated certain results obtained from some of the samples tested since then and will simply add that the constants shown are about as found in the other tests; the other determinations being of no especial help in the matter.

The "constants" shown for cod oils are believed to be from "pure" samples as the term is generally understood for this class of oils. Just what is meant by pure as applied to some of the so-called "domestic" oils is somewhat problematical, but it may be assumed that they should at least contain no mineral or menmaden oil. It will be noted that the specific gravity varies from .922 to .9279 and the acid values from 11.9 to 39.4. It is necessary to discriminate between the white or light colored and the brown oils if these determinations are to be of any assistance whatever in detecting the presence of menhaden oil. The gravity of light oils is usually higher and acid value lower than for the brown oils. In the great majority of cases the gravity of the brown oil is from .9235 to .9255. As a general rule the darker oils have low gravity and high acid value. I have found the saponification value to range from 180 to 195, in most instances from 184 to 190. The iodine value (Hull)[1] has been from 132 to 160; in the great majority of samples from 135 to 145.

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[1] Lewkowitsch, Vol. I, p. 311-313.

The constants for menhaden oil, except where indicated, are from samples of northern winter pressed or cold pressed oil; the color being from light to medium brown. The lowest gravity ever found for this oil was .928 and the highest .9349. Fully 90 per cent. of all samples range from .929 to .931. The lowest acid value obtained was 3.53 and the highest 11.74. In at least 90 per cent. of all samples it is from 5 to 8.

The iodine values have been from 145 to 170, usually 150 to 160. The saponification value is generally 190 to 195, very seldom lower and occasionally somewhat higher.

The usual color tests are of no value in testing these oils, except the sulphuric acid test. Upon adding a drop of acid, diluted as in the Liebermann-Storch test, to two or three drops of the oil on a porcelain test plate and mixing with a stirring rod, cod oils give a bluish-violet color varying very much in shade in different samples. Newfoundland oil usually gives the least color and the domestic oil the most intense. Menhaden oil gives a brown color under similar circumstances. This test is of practically no value in detecting fish oil in cod oil owing to the different shades of color shown by the cod oil.

The unsaponifiable matter is of no assistance in detecting mixtures. I have found rather less unsaponifiable than the figures given for oils of this character, in fact, have never found as much as 1 per cent. unless unsaponifiable oil had been added.

It will be noted that the specific gravity, saponification value and iodine value all average lower, and the acid value much higher, in cod oil than menhaden fish oil. Also that the variations of these constants in samples of the same kind of oil render it impossible to quantitatively determine, or even to certainly detect the presence of menhaden oil, unless added in considerable quantity.

If one has experience in testing oils of this character and can take into consideration the characteristics of the sample being tested, these tests have considerable value, and useful deductions can be drawn from them, sometimes causing the "constants" of oil that is being purchased to change somewhat in certain respects.

I.—COD OILS.

Kind		Specific gravity	Acid value	Saponification value	Iodine value	Unsaponifiable matter	Cold test °F.
New Foundland		.925	25.5	190.	..	..	23
		.923	22.	189.	..	..	17.6
		.9255	25.4	191.5	..	..	..
		.923	31.8	..	..	..	..
		.925	29.6	..	..	..	..
		.9235	35.4	..	..	..	..
	light "bleached"	.927	19.2	..	..	..	..
	"white" "	.9279	14.8	..	..	..	..
	"	.9267	15.8	..	..	..	..
	"	.9263	12.2	..	..	..	..
	"	.9254	15.8	184.1	150.9	..	..
	"	.9261	11.90	..	..	..	..
		.9249	27.93	..	..	..	..
		.9252	28.40	..	..	..	..
		.9243	31.43	..	..	..	..
		.926	22.34	..	..	..	..
		.9248	28.4	..	..	..	..
		.9246	22.5	..	..	..	..
		.9257	19.13	..	..	..	..
		.924	38.11	..	..	..	..
	white	.9264	19.7	182.7	139.8	..	..
		.9245	28.6	189.	139.8	..	..
		.9249	28.16	185.9	139.6	..	..
		.9249	24.42	186.2	137.2	..	..
	light	.927	20.00	189.6	147.2	..	..
		.925	23.90	..	..	..	..
		.9242	22.26	..	..	..	..
		.926	26.39	..	..	..	..
		.9245	19.84	188.8	..	..	..
		.9243	33.09	..	..	..	..
"Domestic"		.925	38.5	..	..	..	..
		.9242	22.0	..	..	.35	28
		.9252	36.7	..	..	..	..
		.9257	23.67	..	..	..	..
		.9243	19.34	188.5	..	..	..
		.9233	16.52	..	..	.24	..
		.9238	25.67	190.2	136.7	..	..
		.924	33.01	..	..	.24	..
		.9235	22.62	..	..	.65	..
		.9224	29.7	184.	..	..	23
		.923	26.2	..	..	..	22
		.924	21.5	189.	..	..	23
		.926	20.2	185.7	..	..	25
		.925	19.6	194.	..	..	25
		.9252	19.3	189.7	..	..	25
		.922	39.4	..	..	..	..
		.9242	26.2	..	..	..	..
		.9237	34.4	..	..	..	..
		.924	19.4	182.7	142.7	..	..
		.9243	22.4	184.4	143.9	..	..
		.9241	23.7	183.5	144.5	..	..
	[1]crude	.9239	27.50	..	..	..	..
	[1]refined	.9244	25.64	..	..	..	..

[1] N. F.

II.—MENHADEN OILS.

Kind	Specific gravity 15.5° C.	Acid value	Saponification value	Iodine value	Unsaponifiable matter	Cold test °F.
Crude	.929	6.39	190.3	..	..	..
Refined	.9295	5.04	190.3	153.4	..	..
	.9292	6.08	190.3	148.1	..	..
	.9293	7.28	189.7	150.5	..	..
	.9292	..	190.7	..	..	..
	.9302	11.74	190.5	..	..	..
	.9329	8.60	191.8	166.3	..	..
	.929	7.24	189.6	151.6	..	30
	.931	7.57	194.5	..	..	..
	.9293	7.56	189.6	..	..	..
	.9286	6.61	191.6	..	..	..
	.929	7.62	192.3	..	..	..
	.9295	5.83	190.1	..	..	..
	.929	7.62	190.7	..	..	..
	.9304	11.39	194.	..	..	..
	.928	7.00	198.	..	..	28.5
	.9317	7.00	..	..	.29	25
	.931	6.6	..	..	..	27
	.9296	5.21	..	..	..	27
	.9304	4.38	..	..	..	..
Crude	.9306	5.41	..	..	..	..
Refined	.9314	6.38	..	..	..	..
	.9312	4.50	..	..	..	..
	.9295	7.34	..	..	..	..
	.9298	6.06	..	..	..	..
	.9308	6.98	..	..	..	..
	.9317	6.7	..	..	..	..
	.9315	3.53	..	..	..	..
	.9313	7.40	..	..	..	..
	.931	5.91	..	..	..	..
	.930	8.01	..	..	..	..
	.9305	9.22	..	..	..	..
	.9303	5.3	..	..	..	28.5
	.9322	6.06	..	..	..	..
	.9291	9.26	..	..	..	..
	.928	9.55	..	..	..	32
	.9349	4.58	..	..	..	..
	.9344	6.29	..	..	..	..
	.9331	6.06	..	..	..	..
	.9305	4.41	..	..	..	27
	.9305	6.44	..	..	..	32
Southern	.9369	..	..	..	.30	..

III.—SIMILAR VALUES ON MISCELLANEOUS OILS.

Kind	Specific gravity	Acid value	Saponification value	Iodine value	Unsaponifiable matter	Cold test °F.
Neats Foot	.9124	..	198.	63.8	..	47
	.9145	..	187.	75.7	..	32
Lard	.918	..	..	68.9	..	..
Whale	.920	17.11	195.2	108.3	..	..
"crude"	.9194	16.76	193.8	..	..	..
"natural"	.920	3.64	192.7	101.	..	..
Herring, California	.9254	5.22	190.1	132.	..	..
	.9227	10.08	..	124.4	..	..
	.924	12.09	..	109.3	..	..
Corn	.9236	1.54	..	115.9	.41	..
Peanut	.9156	.10	..	80.	.17	..
"Cod oil," mineral oil	.907	19.8	..	..	25.6	..
75% Menhaden	.928	10.72	..	..	..	..
"medicinal," mineral oil	.920	10.4	..	..	14.0	..
"Boston," mineral oil	.9226	24.1	..	..	5.60	..
"Menhaden," mineral oil	.9228	6.65	..	..	11.50	..
50% cod	.9274	16.41	188.4	..	..	..
mineral	.9273	6.63	184.1	..	3.18	..
mineral, sp.gr. .868	.9277	7.29	187.2	..	1.44	..

PICKLING.[1]

By M. C. Lamb.

Pickling is an operation which is becoming increasingly important. Whereas the process was at one time entirely confined to the treatment of skins intended for export, it is now largely employed as an intermediary process, after puering or drenching, previous to tanning with mineral salts or vegetable tanning materials.

The process of "pickling" consists in immersing the previously delimed or puered skins in a dilute solution of some suitable acid, to which has been added a sufficiency of common salt; the swelling effect of the acid being counteracted by the salt. The acid most commonly employed for the purpose is sulphuric acid (the ordinary vitriol of commerce).

---

[1] From *Leather.*

The various processes of pickling may be tabulated according to the specific requirements, namely:

1. Pickling skins for export.
2. Pickling sheep grains and sheep skins to be vegetable tanned.
3. Pickling sheep, goat and calf skins to be chrome tanned.

PICKLING FOR EXPORT.

The pickling of skins intended for export is a very large industry, particularly in the Antipodes; the number of skins exported in the pickled state from Australia and New Zealand amounting in value to many thousands of pounds annually.

The primary object of the operation in this particular case is to preserve the goods for some indefinite period.

The method most commonly employed in this particular case consists in placing the goods, after being puered, in a solution of vitriol to which a small quantity of common salt has been added in order to restrain the swelling action of the acid; this solution is commonly termed the "rising liquor." The goods being finally transferred to a saturated solution of common salt, called the "falling liquor."

The strength of solution and proportion of acid and salt vary very considerably in different works. Considerable care ought to be taken in this particular, as there is a great liability of doing much damage to the pelts under treatment; damage that may not be apparent at the moment but which will show itself when the goods come to be tanned. It might be mentioned *en passant* that this is the cause why many New Zealand and Australian pickled pelts turn out so badly when put into work in the tannery.

As is indicated by the term "rising liquor" the goods when placed in this solution swell somewhat; the amount of swelling being controlled by the quantity of salt present in the solution. If the amount of salt present is insufficient the goods will become greatly swollen, and though to outward appearance they may appear quite satisfactory when removed from the "falling liquor" irremediable damage will have been done by the destructive action of the acid on the fiber of the skin.

The following proportions of sulphuric acid and salt have been found to give good results when this the two-solution method is employed:—

(*a*) *Rising liquor.*
1½ lbs. sulphuric acid.
10 lbs. common salt.
100 gals. water.

(*b*) *Falling liquor.*
3 to 4 cwt. common salt.
100 gals. water.

The pelts should preferably be paddled in the solution, thereby ensuring, to a much greater degree, that each individual skin is thoroughly agitated in the solution, than is possible when the operation is performed in tubs and the goods simply stirred in the solution by hand. It is important that the goods should be kept in the "rising liquor" for at least 30 minutes before being transferred to the "falling liquor," in which latter solution they may be kept any desired length of time without liability of damage, providing they have been immersed and kept in constant agitation for at least 45 minutes.

Some three or four years ago the writer when carrying out some experiments with formic acid in deliming skins preparatory to tanning,[1] tried some experiments with this acid for pickling for which purpose it seemed to offer advantages.

Mr. A. Seymour-Jones also did some experimental work on the same lines[2] and obtained very satisfactory results; skins which he pickled with this acid and sent on a voyage of 1,000 miles, up the Amazon and back to England, crossing the Equator twice, arriving back in perfect condition.

Further experience with formic acid during the past three or four years has confirmed the opinion then formed of the superiority of this acid over sulphuric acid for pickling pelts for export.

Skins pickled with vitriol are liable to fungoid growths or mildew, particularly when very weak vitriol solutions are employed;

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[1] "Formic Acid for Deliming and Other Processes of Leather Manufacture," by M. C. Lamb, *Leather Trades Review*, Feb. 10, 1904.

[2] "A New Pickling Agent," by A. Seymour-Jones, *Leather Trades Review*, June, 1904.

formic acid being a strong germicide, preserves the skins in a perfectly antiseptic condition practically for any desired period, and there is little liability of injury to the fibers of the skin when this acid is employed as is the case with the corrosive sulphuric acid.

Considerable saving both of time, labor and plant can be effected when pickling goods by performing the operation, which can be satisfactorily done, by the use of one solution only. The goods being paddled or stirred in a tub or vat, or with advantage drummed, in the solution of salt and acid; the amount of salt necessary when the "one-solution method" is employed naturally being much greater than that required in the "rising liquor."

It has been pointed out by Eitner & Stiasny[1] that when using a one-solution process for pickling that the leather ultimately produced is increasingly softer when, within certain limits, the amount of acid used is increased. The recommendations of these workers as the result of their investigations are:—

(1) When naturally soft skins, *e.g.* sheep, are to be pickled, and the resulting leather is desired to possess a certain amount of firmness, the best results are obtained by using:

2 lbs. (by weight) sulphuric acid,
20 lbs. common salt,
200 lbs. (*i. e.* 20 gallons) water,
For each 100 lbs. drained pelt.

(2) For skins which are naturally hard, *e.g.* goat, and when a soft leather is required:

4 lbs. (by weight) sulphuric acid,
20 lbs. common salt,
200 lbs. (20 gallons) water,
For each 100 lbs. drained pelt.

In carrying out the one-solution method considerable care should be taken in the matter of the concentration of the solution as this is extremely important: therefore the amount of water employed should be very accurately measured.

The pickling is best performed in the drum. Having drained and weighed the skins to be pickled, three-quarters of the requisite quantity of water needed is placed in the drum and the

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[1] "Study of the Pickling Progress," by W. Eitner and Stiasny, *Der Gerber*, 1905.

goods are entered. In the remaining quarter of the water the salt has in the meantime been dissolved and the vitriol added thereto. Drumming is commenced, and the vitriol solution is carefully poured into the vessel through a copper pipe inserted in the hollow axle, during the rotation of the drum; the goods being drummed for a period of one hour when they may be removed, horsed up, and allowed to drain.

When using formic acid in pickling by this method the following are the quantities recommended, being the result of many experiments made by the writer:—

(1) For sheep skins and skivers:
7½ lbs. formic acid (40 per cent.),
25 lbs. common salt,
20 gallons water,
For each 100 lbs. drained pelt.

(2) For calf and goat skins:
10 lbs. formic acid (40 per cent.),
25 lbs. common salt,
20 gallons water,
For each 100 lbs. of drained pelt.

The operation being carried out in identically similar manner to that mentioned above.

PICKLING SHEEP GRAINS, SHEEP SKINS, CALF, ETC., TO BE VEGETABLE TANNED.

Mention has been made above to the fact that pickling is a process now largely employed in the preparation of goods for vegetable tanning, the process being most commonly used upon sheep grains to be eventually tanned with sumac for skivers, and upon sheep skins to be tanned for basils or roans.

The advantage to be gained by pickling goods to be immediately afterwards tanned is the saving of tanning material. The amount of tanning material required to convert a pickled skin into satisfactory soft leather is only about 50 to 60 per cent. of the amount that would be necessary if the goods had not previously been pickled; it has therefore, on this account been largely adopted. Moreover, a pickled skin when tanned has usually a softer and finer grain than is the case when the goods have not been so "processed"—a great advantage when the goods are to be finished in plain finish, *e.g.*, hatters' leathers. The skins having usually been through the processes of liming, puering and drenching are generally pickled in the paddle. Some manufacturers employ the two-solution method for the process, whilst others use the one-solution process; the latter, in the opinion of the writer, being preferable.

When pickling skins for tanning, and not for export, the amount of acid and salt to be employed can be reduced somewhat. The following will be found to be a reliable formula for the purpose:—

1½ lbs. sulphuric acid,
15 lbs. common salt,
20 gallons water,
For each 100 lbs. weight of pelt.

The goods being paddled or drummed for three-quarters of an hour in the solution, when they are removed and are ready for the tanning which must be done in liquors containing a sufficiency of common salt to prevent any liability of swelling.

A fact that is not generally realized by many tanners who pickle their goods, is that great danger exists of the goods when pickled with sulphuric acid possessing after tanning that *bete noir* of the leather dyer, "lime-blast."

Should the skins not have been sufficiently delimed during the preparatory processes of puering and drenching, the action of the sulphuric acid is to convert the lime salts present in the goods into calcium sulphate, a comparatively insoluble salt. The simple equation given below shows the chemical reaction which takes place:—

$$\underset{\text{Lime water}}{Ca(OH)_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Water}}{2H_2O.}$$

The insoluble calcium sulphate is converted into tannate of lime, during the vegetable tanning, thereby producing a similar effect to what occurs when the goods are lime or "wind-blasted;" the goods in the affected portions refusing to dye the same shade of color when placed in the dye-bath as the rest of the skin, thereby producing an uneven result.

Some classes of French Roans have of late years been particularly liable to this defect. In this particular case and also with some Australian basils the defect has been brought about by the careless manner in which the depilation has been performed; the skins after liming and unhairing having been simply washed to remove surplus lime, and then placed in the pickling solution without puering or drenching.

Formic acid is particularly suitable for use in pickling goods previous to tanning; the acid producing a soluble salt with lime, thereby preventing any liability of the "lime blast" defect. The acid can be used in exactly similar manner as described above in the case of pickling for export.

A method which the writer has used most successfully is carried out as follows:—

The goods after washing free from surplus lime in the paddle in water at 35° C. for 30 minutes are then ready for deliming. The deliming is best done in the paddle wheel: the goods are placed in the vessel together with a sufficiency of water at 30-35° C., paddling is commenced, and then the following solution previously prepared is slowly and carefully added:—

2 lbs. formic acid (40 per cent.),
5 lbs. common salt,
For each 100 lbs. weight of lime pelt.

The goods are paddled until flaccid and fallen which will generally require about 30 minutes, when they are removed and are ready for pickling. The pickling is best performed in the drum, but if this vessel is not obtainable it may be done in the paddle.

The proportions of acid and salt to be recommended in this instance are:—

10 lbs. formic acid,
20 lbs. common salt.
20 gallons water,
For each 100 lbs. weight of (limed) pelt.

Having been drummed or paddled in the pickling solution for one hour the goods are removed, allowed to drain and may then be immediately transferred to the tanning paddle or drum. Skins treated in this way require, as in the case of those pickled with sulphuric acid, to be tanned in salted liquors. Basils are best tanned in the drum, using for each 100 lbs. pelt an addition of 5 lbs. common salt.

Goods that have been treated in this way tan a beautiful light color and the tan liquor quickly strikes through; stout basils can be completely leathered in 8 to 10 hours, though a slightly longer period is to be recommended when weight is a consideration. Any tanning material may, of course, be used for the purpose; quebracho extract, particularly the sulphited quebracho extract is however particularly suitable, either used alone or in conjunction with chestnut extract. It will be noted that the method dispenses with the objectionable puer, and the goods require no drenching. In the case of greasy sheep skins, the goods are generally sufficiently tanned to allow of them being removed from the drum or paddle for hydraulic pressing at the end of two or three hours' tanning. Further, when this method is employed, there is practically no liability of the goods becoming "cased" or "crusted" on the grain by the use of too strong liquors in the early stages of tanning.

PICKLING FOR CHROME TANNING.

Many manufacturers, particularly in America, of Glacè Kid pickle the skins preparatory to tanning by the double-bath or Schultz process. The advantage claimed in this particular instance being that the process conduces to softness and fine grain in the finished leather.

The method usually employed is the "one-solution method;" the operation being invariably performed in the drum. As in other pickling operations, considerable variation exists in the formula employed. The following may be taken to be typical, through any of the above-mentioned may be used with equal advantage, providing that the amount of acid used in the first bath of the tanning process is regulated according to the amount of acid used in the pickling:

3 lbs. sulphuric acid,
15 lbs. common salt,
20 gallons water,
For 100 lbs. drained weight of puered pelt.

It is important when pickling goods to be vegetable tanned to take particular notice that the salt employed is of good quality and practically free from iron contamination, otherwise staining that cannot afterwards be removed is likely to ensue during the tanning process.

One particular advantage that the pickling process possesses when employed upon skins that have been puered is the cleansing effect that the process has upon the goods, removing the dirt and iron stains which would otherwise be found on the tanned goods.

Goods that have been pickled with formic acid never possess the "lime or wind-blast" defect brought about by goods having been left lying exposed to the air in the limed condition, or by washing in a water that is temporary hard. The acid used in pickling being sufficient to convert the insoluble calcium carbonate, which in this case is responsible for the "blasting," into calcium formate, a soluble salt.

A NEW CHROMOGENIC ORGANISM.[1]

By S. R. Trotman.

I recently had occasion to examine some skivers which had developed a discoloration during drying. This varied from pinkish brown to a distinct pink. An analysis of the skivers showed a slight excess of lime and a preponderance of soluble extractive matter in the damaged goods. As excess of lime is liable to produce harshness and brownish discoloration, there was some reason for supposing that this might be the cause, but this would not account for the increased extractive matter. This suggested a decomposition possibly resulting from bacterial growth. Cultures made from the pink skin showed the presence of two chromogenic organisms; one of these proved to be a variety of pink torula which produces a reddish brown growth on gelatine media, but not identical with the ordinary pink torula. The second was a mould which forms a bright scarlet mycelium, and when sown on sound skins produces a color which is identical with that observed on the damaged ones. On gelatine the colonies start as colorless or faintly pink spots, which gradually be-

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[1] From *Journal S. C. I.*

come darker till they have a bright red color. After growing for about a week a number of colorless aereal hyphæ are thrown up, the color being confined to the mycelium, which forms a skin-like growth on the surface of the gelatine and gradually causes its liquefaction. I believe that no instance of such an organism has been hitherto recorded.

COMMERCIAL ANALYSIS OF OIL IN EGG YOLK BY MEANS OF DIFFERENT SOLVENTS.[1]

By Dr. J. Gordon Parker and M. Paul.

In the analysis of Egg Yolk for use in the Leather Trade, the all important constituent is the percentage of egg oil or in other words, the percentage of fatty matter contained, which can be used in the manufacture of gloving or other leathers. Ferdinand Jean[2] has given the differences obtained by extracting egg yolk with various volatile solvents, and the results published by other authors since Jean's paper are as follows:

Upon dry egg yolk	**Petroleum ether**	**48.24 oil per cent.**
	Ethyl ether	**50.83 oil per cent.**
	Carbon disulphide	**50.45 oil per cent.**
	Carbon tetrachloride	**50.30 oil per cent.**
	Chloroform	**57.66 oil per cent.**

It has been claimed that the differences in the amount of oil obtained by various methods of extraction are due to the solubility of the lecithin and albuminous matter in the solvents. More recently this important question has been studied by Kathreiner and Schorlemmer[3] and also by Vignon and Meunier[4] who have proposed that chloroform should be adopted as the standard or official solvent for the chemical analysis of oil in Egg Yolk, giving as their reason that the lecithin is soluble in chloroform and secondly that it is important to have a solvent of definite chemical constitution. These authors found on analyzing various samples of Egg Yolk that by extracting with chloroform, the figures obtained for the percentage of phosphorus and nitrogen were con-

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[1] From *Collegium*.

[2] F. Jean, *Congrès de Ch. Appliq.*, 1900, p. 482; *Collegium*, 1903, p. 71.

[3] Kathreiner et Schorlemmer, *Collegium*, 1903, p. 134, 137.

[4] Vignon et Meunier, *Collegium*, 1904, p. 325 and 335.

cordant and therefore, concluded that the lecithin was completely extracted. Schorlemmer and Sichling[1] on the other hand, have shown that with a commercial Egg Yolk containing boracic acid as an antiseptic that the solvents also dissolved the boracic acid. It is generally admitted that the high results obtained by extraction with chloroform or carbon tetrachloride are due to a solution of the albuminoid matter and the lecithin. It was therefore, our desire, first to confirm this fact and secondly on confirmation to explain this analytically and thirdly to find the best solvent which would give results which would be the most correct from the consumers standpoint, in the sense that the percentage of oil found would not be influenced by the percentage of antiseptic used, by any adulteration or impurity which are frequently estimated as egg oil by the use of one or other of the common solvents. This question is one of no mean importance and to be completely dealt with requires a large number of analyses of egg yolk from different sources, not only egg yolk specially prepared but various samples of commercial egg yolk preserved with various preservatives and also adulterated in various proportions. The figures that we give are only obtained from one authentic sample of Siberian Egg Yolk. This sample, however, we know to be pure Egg Yolk from hen's eggs, the only addition being boracic acid added as an antiseptic. The sample of Egg Yolk was carefully dried in vacuum, a sufficient quantity of sand was added to split up the material so that the mixture could be dried rapidly in a vacuum oven thus avoiding a prolonged heating in the air which would be liable to oxidize the fatty matters and thus cause an error in the results. In order to estimate the percentage of egg oil, the following solvents were then used—petroleum ether, chloroform and carbon tetrachloride. The petroleum ether used was redistilled and only that portion boiling between 70 and 75 was used. The chloroform and carbon tetrachloride were pure by redistillation. The extractions were carried out in an ordinary soxhlet apparatus fitted with a condenser and the extraction was continued until the whole of the soluble matter was extracted. The results are the mean of four separate extractions and the analysis carried out upon the total oil thus

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[1] Schorlemmer and Sichling, *Collegium*, 1906, p. 90.

extracted. The percentage of boracic acid present in the sample may be taken at 2 per cent.; the acidity is simply stated in cubic centimeters of normal acid, the figures being obtained volumetrically; the percentage of nitrogen is determined by kjeldahl method; phosphorus determined as pyrophosphate of uranium by Moreau's method, which consists of oxidizing the phosphorus contained in the material by fusing with the following mixture:

One part	Potassium carbonate
One part	Sodium carbonate
Two parts	Potassium nitrate

the fusion being carried out in a platinum crucible at as low a temperature as possible. The fused mass is then dissolved in hydrochloric acid neutralized by ammonia and precipitated in an acetic acid solution by means of acetate of uranium.

For the determination of unsaponifiable matter the oil was saponified by means of an alcoholic solution of metallic sodium which has the advantage of producing an anhydrous soap with extreme rapidity. Some soaps retain a considerable percentage of moisture with the result that the percentage of matter extracted is frequently increased especially when chloroform or carbon tetrachloride are used as these solvents mix easily with water with the result that a considerable quantity of soap is removed and estimated as unsaponifiable matter. Chloroform containing only 2 per cent. of water will frequently dissolve as much as 10 per cent. of soap. From an examination of the figures in the table, it will be noted that the percentage of unsaponifiable matter obtained by extraction with ethyl ether and petroleum ether are very low. Ethylic ether gives 2.1 per cent. of unsaponifiable matter and the percentage of oil obtained, places this extractive agent midway between petroleum ether and carbon tetrachloride. We do not give the figures obtained by the use of this solvent as it is well-known that chloroform and carbon tetrachloride mix fairly rapidly with considerable quantities of water; any moist product, therefore, becomes easily dissolved and it was found that the unsaponifiable matter dissolved by chloroform and carbon tetrachloride was largely made up of soaps of a weak alkaline nature. The use of these materials, therefore, as extraction agents would permit of considerable adulteration by reason of the great capacity of egg yolk for emulsifying with soap; soap can therefore be introduced in commercial samples and if, as recommended by Kathreiner, Schorlemmer and Vignon, chloroform or carbon tetrachloride be used then this soap would be estimated as egg yolk. As the molecule of the fatty acid is extremely heavy by comparison with sodium or potassium, the increase in weight of the mineral ash is, therefore, very small, otherwise the difficulty of the detecting of these materials would be obviated by the production of ammonia soap.

The proportion of phosphorus and nitrogen contained in the extracted oil is to all intents the same by the three means of extraction and further the relative proportion of phosphorus to nitrogen is remarkable; it appears to us, therefore, that it is to neither the albuminous nor the lecithin that the increase of yield is due (in lecithin the relation of phosphorus to nitrogen is 2.22). It seems that comparing the differences in the amount of saponifiable matter that there is an appreciable difference in the oil extracted. The difference in the amount of ash and also the acidity partly explains this, as the ash may be the residue of more or less complex solids contained in the water. From the figures obtained, therefore, we concur with previous workers that chloroform and tetrachloride have the advantage of being solvents of definite chemical constitution, but we consider that petroleum ether specially distilled and only that portion boiling between 74 and 76 centigrade should be used, that it would be easier to obtain this than to obtain carbon tetrachloride or chloroform either sufficiently pure or anhydrous. In the event of chloroform and carbon tetrachloride being used it is absolutely necessary to have the condenser perfectly dry and water tight in order to prevent the introduction of any moisture which would rapidly mix with the carbon tetrachloride or chloroform and falsify the figures. If the distillation is carried out by heating in an air oven instead of over a water bath this difficulty is overcome.

We simply desire to show by the above results that this question requires further study and state our opinion that the determination of egg oil in egg yolk by means of ether, chloroform, or carbon tetrachloride gives results in percentage of egg oil which are not borne out by practical work.

EGG YOLK.

	Original egg-yolk per cent. upon the original matter	Extraction by		
		Petroleum ether (75° C.)	$CHCl_3$	CCl_4
		Per cent. upon the original matter		
Water	50.75	..	..	..
Oil	..	28.55	32.96	30.59
Color	..	clear	intermediate	deep dark
Unsaponifiable	..	0.26	7.49 (soap)	3.78 (soap)
		Per cent. upon the oil extract		
Upon the ashes: Mineral matter	2.2	1.42	2.37	2.43
Upon the ashes: Insoluble ashes	..	0.64	1.77	1.84
Upon the ashes: Soluble ashes	..	0.78	0.60	0.59
Upon the ashes: Phosphorus	..	0.490	0.57	0.53
Upon the ashes: Chlorine	..	traces	traces	traces
Upon the ashes: Boracic acid	present	?	present	present
Phosphorus	0.412	0.791	0.783	0.705
Nitrogen	2.44	0.512	0.518	0.465
Relation P/N	..	1.54	1.51	1.51
Acidity (cc. of normal acid)	32.7	10.1	30.6	26.2
Chlorine	0.38	0.015	0.19	0.35
Saponification value (without acidity)	..	206	177	185
S. G. at 75° C	..	0.917	0.937	0.952
Dilatation (15 at 75° C.)	..	0.494	0.0507	0.0492
Coefficient of exp. by °C.	..	0.00082	0.00084	0.00082
Fusion	..	28.29	34	31

After extraction of the oils analysis of the soluble in water.

	Per cent. upon the original matter		
	Petroleum ether	$CHCl_3$	$CHCl_4$
Extract dry	2.48	2.3	1.91
Chlorine	0.18	0.126	0.14
Nitrogen	0.19	0.134	0.14
Phosphorus	0	0	0
Acidity (cc. of normal acid)	cc. 10.6	4.6	4.0
Ashes	0.8	0.71	0.64
Boracic acid	present	present	present

We purpose continuing this subject with a view to determining the amount of saline matters dissolved in the soxhlet by the different solvents either in their anhydrous condition or in the condition in which they usually exist containing a certain quantity of moisture, in which condition they usually reach the analyst. Unless the egg yolk is perfectly dried in vacuum it is extremely difficult to obtain perfect desiccation; sufficient sand must be added to obtain a perfect state of division, otherwise the prolonged heating in the air is liable to oxidize the fatty matters and thus cause the introduction of a further error of no mean proportion.

The above must only be considered as a note on this subject, further work is already in hand on standard samples obtained from different parts of the world.

A NEW DEVELOPMENT IN CHROME TANNING.[1]

By Robert W. Griffith.

The present development in the art of chrome tanning has been achieved, not by reason of the solution of the difficulties which were early encountered, but rather by avoiding the dangers which brought disaster, and which, as experience has taught, arose from a too close adherence to the older practice of tanning.

But the old order has changed and given place to the new to an extent little dreamed of but a few years ago, and the question whether chrome tanned leather is but a passing fad is open to discussion no longer.

New tricks have been learned and progress has resulted which has kept pace with modern demands.

Now that the solution of the early difficulties in chrome tanning is no longer vital or essential to the attainment of a satisfactory commercial product, nevertheless it is desirable that those difficulties should be examined and considered in the hope that their solution will, as it were, blaze a new trail to the desired goal of perfection.

The difficulty which caused more trouble, perhaps, than any other was due to the fact that any chrome tanned leather would, if permitted to dry out immediately after tanning (the usual custom with vegetable tanned leather), obstinately refuse to absorb moisture, in order that the processes of dyeing and fatliquoring could be proceeded with.

This then was the first lesson which experience taught in tanning chrome leather—that the tanned hide or skin had to be kept

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[1] From the *Shoe and Leather Reporter.*

wet from the tan bath until fatliquored, and failure to observe this rule was attended with disaster, so far as the production of good leather was concerned.

But before the operation of fatliquoring could be proceeded with, the free mineral acids consequent to the fixation of chromic hydrate upon the fibre, had first to be neutralized and the stock subjected to a thorough washing with water.

It was soon discovered that if this operation of neutralizing and washing took place too quickly after tanning, that is, before the chromium base had "fixed" itself on the fibre, a large portion of the tanning salts which otherwise would have become absorbed by the fibre were washed out with the result that the leather subsequently had the appearance of being undertanned.

Consequently, the usual practice has been to allow the goods to be placed in pile on a "horse" several hours after tanning and before neutralizing and washing.

It is apparent that the length of time during which the goods are "horsed," and the condition of the goods, must affect the "fixation" of the chromium base on the fibre and this in turn reflects itself on the quality of the leather.

In alum and vegetable tannages the drying out or "crusting" of the goods immediately after tanning is recognized as having a most important bearing on the quality of the finished leather.

Now, if it were possible to "crust" chrome tanned leather out of the tar bath exactly as alum or vegetable tanned leathers are treated, it is clear that it must bring about a uniformity in the fixation of the chromium base which has not hitherto been attained and because of this better absorption and fixation of the chromium base and its accompanying salts by the fibre, the quality of the leather is thereby considerably improved.

A process recently invented by the writer permits of chrome tanned hides and skins being dried out after tanning, and may be allowed to remain in the "crust" condition as long as it is desired to do so.

The following is a description of the method employed:

The goods on being taken out of the tan bath are horsed up over night without being washed, and the next day are set out and shaved.

The wet or shaved weight of the stock is taken approximately. A bath is prepared in a drum with four pounds of standard lactic acid (22°) for every 100 pounds of wet leather, and sufficient water to diffuse the acid so that the liquor will come in contact with the goods immediately after they are thrown in and the drum revolves.

The goods are run in this bath for ten minutes, after which they are taken out and are sent to the drying loft immediately and allowed to dry out.

After drying the goods can be stored away until wanted and can then be sorted into suitable grades and weights as required.

The dry leather when treated in the manner described absorbs water readily and assumes its original wet condition as it was when it came from the tan bath.

At this stage, the leather can be washed thoroughly without any fear of removing desirable tanning salts or of interfering with the character of the leather.

The operation of dyeing and fatliquoring can be immediately proceeded with and because of the even absorption of moisture by the leather, these processes proceed very uniformly and are consequently facilitated.

After the goods are "set out" from the fatliquor, they can be tacked out at once, a process which yields a considerable gain in measurement and is accomplished without affecting the character of the leather.

Where it is desired to experiment with this process on a small scale, it is recommended that the bath in which the goods are treated be made up by volume rather than by the weight of the wet leather.

A suitable strength is one-third of standard lactic acid and two-thirds water.

In combination tannages of chrome and vegetable tannin, the fixation of the latter is brought about more intimately by treating the stock after the chrome bath, with a bath of lactic acid.

The development of the chromium tannage for the heavier leathers, such as sole, harness and belting leathers, will, in all probability, proceed along the lines of a compromise, and result in the production of a combination tannage of chromium and a vegetable tannin.

In order that the fixation of the combined tannages on the fibre shall be so intimate as to permit of the vegetable tannin acting jointly as a tanning agent and a "filler," and that the result will produce a leather superior to either of the tannages employed independently—a bath of lactic acid after the chrome bath, and before treatment with the tannin liquor, ensures the fixation of an organic acid on the fibre which is in sympathy, as it were, with the organic tannins and brings about a more complete assimilation of them.

PETROLEUM OILS IN LEATHER MANUFACTURE.[1]

By Roland A. Earp.

Since the discovery of petroleum in the last century, there has been an almost uninterrupted increase in the extent and variety of its applications. At first looked upon with some suspicion, it has now become recognized as one of nature's most useful productions. Primarily it finds use as an illuminant, a lubricant, and a fuel; whilst there are many applications of minor importance to petroleum is put.

As regards leather manufacture, the amount of petroleum involved is at present quite of secondary importance. Petroleum can scarcely be said to be in very great favor with tanners: with reason too, for instead of being produced in a form suitable for leather manufacture, and sold on its own merits, much of the petroleum used by tanners has consisted as an adulterant of cod, or some other oil. Consequently tanners, in many cases, associate petroleum with a bad sample of oil, and thus have but a poor opinion of its merits.

There is not much doubt but that petroleum, as produced by the refiners, has a very limited use in leather manufacture. Indeed, the fact that tanners still prefer to buy cod or linseed oil or tallow, rather than mineral oils at half the price, fully shows this. The present article, therefore, deals with the question whether

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[1] From *Leather*.

it is possible to produce tanners' oils from petroleum suitable for the many processes where oil is used.

Let us first compare the properties of petroleum with an oil such as cod oil, which for generations has proved its entire suitability for the trade. As a sample of petroleum, we will take a de-bloomed oil of about the same density and body as cod oil. The two oils are very similar in outward appearance, yet one is suitable for leather manufacture and the other is not. Why is this so?

No doubt tanners will be able to answer this question for themselves to a great extent. In the first place the mineral oil will not "take" in the same manner that the cod will. Again, chamois leather manufacturers would find it impossible to make their leather from the mineral sample.

These two comparisons really indicate the vital differences between the two oils. Cod oil penetrates far more quickly and completely than mineral oil. Not only so; but once cod oil has penetrated, it will remain in a firmer state of combination with the leather fibre. Again, cod oil is capable of actually tanning raw hide, whilst mineral oil has no tanning properties. But although these differences are very apparent, the cause of the difference may not be so easy to fathom, so before entering upon methods for dealing with petroleum so as to produce an oil of combining or tanning power, I will first indicate what I consider to be the reasons of the incapacity of mineral oil.

Cod oil belongs to that class of bodies known as fixed oils. Fixed, because they cannot be distilled without decomposition. Mineral oils distill without suffering any change. Cod oil also consists chiefly of saponifiable fats: that is, fats which first emulsify and then dissolve up, on boiling them with a solution of alkali such as soda or potash. Mineral oil has no such power to combine, and upon boiling with alkali, it remains upon the surface of the liquid, totally unacted upon; it consists entirely of unsaponifiable matter.

But this difference, which is the most important from some points of view, may not make very clear the reason why the two oils should have such different leather-producing properties. The clue is to be found in following the difference in behavior of the two oils when taken internally.

As a food, mineral oil passes through the system nearly unchanged; whereas cod oil is nearly all assimilated.

Now the nature of the mechanism of the assimilation of food is fairly well understood. There are three main classes of foods, namely fats, carbohydrates, and albuminoids, and they all have their own peculiar method of being assimilated. Carbohydrates and albuminoids we have nothing to do with, so we will follow the fats through their process of assimilation, which is the simplest of the three.

Fats, in their progress through the alimentary canal into the system, are not required to become chemically changed before they can be absorbed. It is only necessary that they should be emulsified, that is to say, broken up into particles of an extremely minute size. Once emulsified, the fats are in a condition to be taken up by the living cells of the intestinal wall and conveyed into the system. No chemical change is involved, for the nature of edible fats is the same as that of the fatty tissues of the body; but to get there they have to be packed in very tiny parcels.

In order to aid the emulsification of the fats, the digestive organs in a healthy individual provide a slightly alkaline fluid, which is capable of emulsifying any edible fat. But where the digestion is weak this fluid is wanting, and most fats pass through the system unchanged. In such cases medical men prescribe for their patients those fats which are most readily emulsifiable, or in other words, those which are most digestible. Cod oil is the most digestible, as it is the most emulsifiable of the edible fats, and hence this oil has a large use as a food for invalids. It is also a common practice to emulsify this oil by shaking up with a trace of alkali, in order to make it still more easily digested. Milk is an example of an oil naturally emulsified previous to being taken as a food.

It is worthy of note that cod oil, which is the most suitable leather oil, is also the most digestible oil known. The unique position of this oil is, in both instances, attributable mainly to its readiness to emulsify.

Turning now to mineral oil, this is not at all emulsifiable.

Whereas with the slightest trace of alkali, cod oil at once forms an emulsion, it is quite impossible to emulsify mineral oil at all. This is the main difference in properties which determines their relative suitability for leather. Cod oil is capable of becoming atomized, and in this state of penetrating into each individual of the numberless cells which constitute leather fibre, just in the same manner that it penetrates into the cellular lining of the alimentary canal. Mineral oil, on the other hand, cannot do this. It soaks into leather, certainly, but remains there as an interfibriary uncombined constituent of the leather, instead of participating in the structure of each minute leather cell, as does cod oil. For heavy sole leather it is almost useless. For light leathers, where interfibriary lubrication is desirable, its inutility is not so pronounced.

Take now the second main difference in characteristics between cod oil and mineral oil. Cod oil can tan leather by itself, whereas mineral oil cannot. What is the reason of this?

Here again I think that the cause is to be found mainly, if not entirely, in the power possessed by cod oil of becoming atomized or emulsified. Perhaps also the fact that cod oil largely consists of fatty acids, or glycerides of fatty acids, enables some slight chemical union to take place between hide-substance and the oil; just as there may be a slight chemical action between tannic acids, and glucosides of tannic acids, and hide-substance in the ordinary process of tanning with vegetable tannins. Perhaps also there may be something in oil tannages similar in nature to the well-known aldehyde tannages. Whatever theory is adopted, the difference in tanning power between cod oil and mineral oil is accounted for. Mineral oil cannot be emulsified, it contains no fatty acids nor glycerides, and it contains no aldehyde.

The question remains as to whether mineral oil is capable of being converted by practical methods into an oil suitable for leather manufacture. To be of use, it must be brought into a physical state comparable with that of cod oil, or more precisely, the same physical reactions must take place between hide or leather and the oil that take place in the case of cod oil. Namely, the oil must be intimately assimilable, and it must have tanning properties. These two properties are, I think, synonymous, though it is not necessary to consider them so for the purposes of this article.

Consider first the production of an oil suitable for tanned leather. In dealing with emulsification I have so far confined my remarks to emulsification with water. In wet leather we have not only water, but a solution of tannin in water. Why I mention tanned leather first is because the first successful treatment of mineral oil that I am acquainted with was based upon a method of rendering it emulsifiable with tannin solutions. It was hoped that such an oil would penetrate and become assimilated as completely as cod oil, or any other oil, for the reason that tanned leather was thoroughly impermeated with tannin solution, and atomization would consequently follow. Experience has fully justified this anticipation, and this oil seems to be quite as suitable as cod oil for tanned leather. It has, moreover, advantages of another nature over cod oil.

This oil is manufactured by dissolving in mineral oil some of the insoluble-in-water vegetable tannins. The resulting oil is emulsifiable in greater or less degree, or may be made entirely soluble in a solution of tannin, according to the amount of material dissolved in it, and according to the strength of tannin solution it is mixed with. The fact that these insoluble-in-water tannins have a very high combining power for leather makes a very heavily tanned leather possible by means of them, when brought into contact with the leather in this form.

To make a mineral oil that will emulsify with water is a more difficult matter, and I am not prepared to make known the process, having spent a great deal of time and trouble over it. But it is interesting to note that this emulsifiable mineral oil acts as a tannin upon untanned hide, and there seems to be no reason to doubt but that it will not only supersede cod oil in its application in the finishing and currying of tanned leather, but also in the manufacture of oil tannages.

The antagonism with which petroleum was met when first it was brought upon the market as a lubricant, and illuminant, is now a matter of history. At the present time, practically all the oil used for these purposes is petroleum. But notwithstanding this enormous use the supply of saponifiable oils, which, before the advent of petroleum, had to satisfy all demands, is scarcely sufficient for the industries of soap-making and others, where, so far, it has been found impossible to utilize petroleum. All saponifiable oils, including cod oil, are consequently hardened, and will probably still further advance in price.

It is therefore to be hoped that petroleum will extend its application to our industry, and so relieve leather manufacturers of the burden of buying an oil which is kept up in value by the great demand for it in other branches of manufacture.

ABSTRACTS.

Annual Report of the Freiberg Experimental Station. J. Paessler. *Ledertechn. Rundschau,* 1910, Nos. 5-6, pp. 33-5, 41-3.—The samples received were largely tanning materials, about 75% more than in 1908. Both the filter and shake methods were used according to wish of sender and average results by each method are reported. These are *not comparable* directly, however, for the same samples were not in general analyzed by both methods. The figures for less tans found by the shake method were derived from combining the results of previous years with some comparative analyses made the past year. In the table, F = filter method, S = shake method, the numbers in parentheses giving the numbers of samples analyzed.

	Oak bark		Pine bark		Mimosa bark		Mangrove bark	
	F(41)	S(95)	F(50)	S(30)	F(29)	S(12)	F(26)	S(20)
Tans	10.9	10.1	13.0	10.1	35.0	33.2	32.8	29.2
Non-tans	6.7	6.9	9.0	9.2	11.0	12.1	7.5	7.3
Insol.	71.9	71.6	65.2	67.9	42.9	43.6	45.8	49.4
Less tans		0.8		1.8		1.5		1.5

	Mallet bark		Valonia		Trillo		Myrabolams	
	F(9)	S(3)	F(12)	S(25)	F(146)	S(25)	F(9)	S(5)
Tans	42.7	33.9	33.2	28.7	42.5	39.8	35.8	30.7
Non-tans	7.9	11.8	11.7	13.7	13.7	16.4	12.3	17.2
Insol.	37.3	42.2	44.5	46.4	32.5	32.5	42.9	42.5
Less tans		4.0		2.5		3.0		4.5

	Myrab. hulls		Dividivi		Quebracho wood		Sumac	
	F(12)	S(4)	F(13)	S(15)	F(9)	S(8)	F(128)	S(87)
Tans	50.1	46.5	44.2	38.9	18.7	20.1	24.6	23.6
Non-tans	17.2	22.5	17.7	22.4	1.5	2.3	15.6	18.0
Insol.	23.1	21.0	29.1	29.8	66.0	63.3	51.0	49.5
Less tans		6.0		4.0		1.0		2.2

Of the extracts analyzed, oakwood was generally normal, a few samples giving abnormal non-tans 17 to 19%, with 21 to 23% tans indicating improper extraction or adulteration. One sample gave 33.1% tans (filter), 27.7° B. It is astonishing that such extracts are not manufactured universally, saving duty and freight. Chestnut wood extracts formerly came of 25 or 30° B., but this year samples often showed 27 to 28°, generally 32 to 33% tans (filter).

Degras and moellon showed at times adulteration with mineral oils. Some samples of neats-foot oil did not resist chilling and were unsuited for chrome leather because of liability to spew. Some samples of marine oil showed a high iodine number and the senders were advised to heat to 140-160° to avoid resinifying. One linseed oil used in manufacturing patent leather darkened greatly on boiling. This was found due to albuminous substance which had not settled out. Only well settled oil should be used for light colored lacquered leathers. A sample of degras giving an objectionable dark sediment was found to be very rich in oxy-acids; oxidation had evidently been pushed too far in the manufacture. Leather samples frequently showed loading with sugar, salts and extractable tannin. A leather for sabre sheaths which had been long stored could be crumbled by the hand and contained 1.5% free H_2SO_4.

Lactic Acid and Its Anhydride. A. Besson. *Collegium,* 1910, No. 397, pp. 73-9.—Generally lactic acid is sold by its weight in total acid, but English tanners stipulate free acid only to be reckoned, claiming that the anhydride is inoperative in de-liming. The writer has found that in the detemination of anhydride by Philip's method (*Collegium,* 1906, p. 88) that his results were always lower than those of other analysts, and as he shows, more correct: 25 cc. of a technical lactic acid were diluted to 250 cc. and 10 cc. of this required 6.68 cc. 0.1 N alkali. To 10 cc. samples thus neutralized varying excesses of alkali were added and boiled for varying periods, and then titrated back. The total consumption of 0.1 N alkali was.

Excess of alkali	2.00	1.00	0.50cc.
Boiled for 3 minutes	7.52	7.24	7.02
Boiled for 1½ minutes	7.44	7.17	6.96
Just boiled	7.22	7.00	6.93

This computed to a total aicd of 53.5% for the shortest period and 58.9% for the highest. The explanation is that the commercial acid contains foreign substances which by prolonged boiling consume alkali, which is erroneously charged to anhydride. On repetition of these experiments with a c.p. lactic acid selected of maximum anhydride content, 10 cc. of diluted acid required 5.00 cc. 0.1 N alkali. The same amounts also required:

Excess of alkali	0.2	0.5	1.0	2.0 cc.
Boiled 3 minutes	..	..	..	6.10
Boiled 1½ minutes	..	..	6.10	...
Just boiled	6.07	6.07	6.09	6.10

These results correspond to 74.75% free acid and 90.75 to 91.19% total acid. The differences with varying excess of alkali or prolonged boiling are slight and may be attributed to slight impurities. To judge whether these results were really correct, 10 cc. portions of the same acid were then treated with varying excesses of alkali for varying times at ordinary temperature and then titrated back. The total consumption of alkali rose regularly according to excess and time from 5.96 to 6.21 cc. This increase was proved due to absorption of CO_2 from the air (phenolphthalein indicator was used) for on repeating the last experiments, adding excess of acid, boiling and then titrating back, the consumption of alkali was found to be nearly constant, the corresponding figures being 6.01 to 6.04 cc.

The author's final conclusion is that boiling should be avoided while free alkali is present. His new method for the analysis of lactic acid is:

To an aliquot part of the acid solution taken, a few drops of phenolphthalein are added, titrated to red with alkali, then 1 to 3 cc. excess added according to concentration of sample and left stand cold 10 minutes. An excess of acid is then added, boiled and titrated back with alkali.

On substituting lime water for the alkali in titration of the total lactic acid precisely the same results were obtained showing that $Ca(OH)_2$ will completely fix lactic anhydride in the cold in less than 10 minutes and that the English tanners are in error in not crediting lactic anhydride as deliming reagent. This opinion was probably based upon over-estimation of total acid by the old boiling process.

Leather Analysis. U. J. THUAU. *Le Cuir,* 1909, [2], Nos. 22, 24, pp. 507-10, 555-7; 1910, [3], No. 2, pp. 17-20.—The article opens with a discussion of the methods of inspection of leather used in the armies of various European governments. In Germany, Dr. Paessler gives a special course in leather chemistry at Freiberg to officers of the army detailed to this branch of the service and their training is supplemented by visits to practical tanneries. In France the officials having these matters in charge are far behind the times. The methods of leather analysis in vogue would appear absurd to the members of the International Association. High praise is given to the methods followed in the laboratories of M. Godfrind, chemist to the magazine of apparel for the Belgian army. All the leather goods are manufactured by the State in the prisons or by the troops and the materials are purchased and delivered by the magazine. In the analysis of leather, moisture is determined by drying at 105°, fats are extracted with petroleum ether or CCl_4, and the extracted fats saponified and subjected to complete analysis if necessary. Extracted matter is examined by I. A. L. T. C. methods. Hide substance is computed from N by Kjeldahl, 1% of which corresponds to 5.62% hide of kine and 5.75% in goat-skins. Requirements are: Ash, below 1%, water extractable, 8% in heavy leather, 6% in all others; hide substance for collars, over 44%, for heavy leather 48-50%, for upper leather and saddler's leather 49-51%. These figures are based upon the conditions of tanning and currying. Heavy leather includes the entire hide, while in split leather the grain is richer in N than the flesh.

The writer goes on to specify what in his judgment leather analysis should show in the reception of leather for the French army. The detailed report should specify:—

Water
Mineral matter
Fatty matter
Organic solubles:
  uncombined tan
  non-tans
Leather substance:
  dermal matter
  combined tannin

100 per cent.

Deductions:
  Soluble organic matter
  Total tannin (combined and free)
  Per cent. N in leather
  Per cent. N in leather substance

Coefficient of rendement.
Degree of tannage

Sugar (glucose), per cent.
Total SO_3, per cent.
Free SO_3, per cent.
CaO, per cent.

100 parts of leather substance
  contain:
    combined tannin
    dermal substance

Specific gravity
Minimum, maximum, mean
Thickness of leather

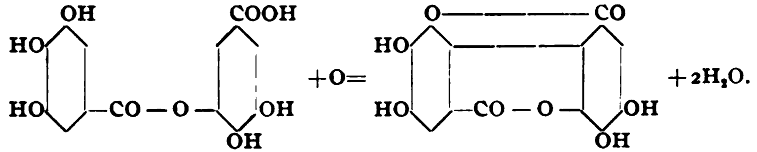
The coefficient of rendement, established by von Schroeder, is the amount air dried leather (containing 18% H_2O) furnished by 100 parts of dermal substance, for example the coefficient R of a leather containing 40% dermal substance would be 250. The degree of tannage D represents the amount of tannin combined with 100 parts of dermal substance.

Sampling.—Small uniform pieces are cut from the back, neck and flank; these are chopped up, powdered in a mill and thoroughly mixed. When a mill is lacking a small circular saw is useful. If only one sample be taken, the neck represents the best average. For a complete analysis, 100 gms. are sufficient.

Water Determination.—With non-greased leather, 10 gms. are dried at 100-105° C, 1 to 2 days. For greased leather, Procter first extracts the fat and then dries for water. This method is used by Capt. Nicolardot of the Technical Section of the Artillery. He distinguishes and lays stress upon 3 forms of water in leather, (1) of soaking (imbibition), (2) of hydration or absorption, (3) of constitution. These affect the mechanical strength of the leather. The writer does not think such exact conclusions can be drawn from the water determination. Leather is not a definite substance, but extremely variable. The chief factors are the ratios of combined and free tannin to the dermal substance.

(*To be continued.*)

Ellagic Acid. P. SISLEY. *Bull. Soc. Chim.*, [4], 1909, 727-30.—A good yield (50% of the tannin) of ellagic acid free from gall of lavin was obtained by treatment of tannin in alcoholic solution with 2 mols. KOH and exposure to the air. The separated potassium salt was decomposed with HCl. Graebe's formula is confirmed.



Gallotannic acid Ellagic acid

Researches on Sulphite Cellulose Lye. A. STUTZER. *Zeit. Anorgan. Chem.*, 1909, [22], pp. 1999-2005.—Average analyses by the author show that 1 liter of the lye contains 120 gms. organic and 10 to 15 gms. mineral matter. It is more concentrated than formerly and the dry residue represents in fuel energy 580 calories to the original liter. The lye contains no red tannins, but decomposition products of such which can precipitate gelatine. The main theme is the possible utilization of this waste for fodder.

School of the Tanner; Irregularities in the Liquor. A. SCHMIDT. *Le Cuir*, 1910, [3], Nos. 2, 4; pp. 20-22, 69-71.—The great fluctuations in liquors are rarely due to improper preparation but as a result of many complex elements while in use. Not only does the leather remove the tannin, but at the same time some hide dissolves, especially in weak solutions, and this sets up fermentation according to temperature, proportion of antiseptics, etc. The saccharine components of the tanning materials in any case may decompose yielding acids and this is accelerated by the microbic action of the dissolved hide. With tans like those of quebracho containing little sugar no acid is formed in this way, and it is necessary to add artificial acids. The diminishing of tannin by the absorption by hide is regular and may be adjusted for in a rational regular system of liquors. The most important factor is then to so prepare the liquor that the decomposition during tanning is reduced to a minimum. In the preparing of liquors in the tannery, the most important element is naturally the full utilization of the material. The old-fashioned tanner seldom attained this, but reckoned so much bark, so much liquor. The modern tanner takes account of the actual tannin content of the material. Moreover he has abandoned the old process of extracting new bark with expended liquors. Another modern improvement is the extraction with hot water; only in this way can all the tans be utilized and the result is a more concentrated liquor as well. In adopting this process, some have erred in extracting at too high a temperature. There is a critical temperature for each particular material above which the readily soluble, cold dissolved tans are liable to decompose. It may be said in general, that most materials contain both easily soluble and hot soluble tans, and that these differ among themselves in solubility. It is best to extract these separately and not successively in one liquor.

(To be continued.)

The Soaking of Dried Hides. By a practician. *La Halle aux Cuirs*, 1910, [54], Nos. 2, 3, pp. 21, 39.—For light leather there is danger of fermentation which attacks and removes hide substance (coriine), enveloping the fibres, resulting in a hard stiff leather which will not take up degras in currying; the mischief is often not apparent until this last stage is reached. With sole leather over-soaking need not be feared so much, as a supple leather is not required; the sweating method, which is itself a fermentation process, yields a satisfactory product. To shorten the time of soaking, the use of luke-warm water in winter is admissible; 25° should not be passed. Mechanical beating shortens the process, the fibers being opened for reception of water, but there is danger of weakening the leather, and this device should not be employed until softening is well advanced, and more particularly to even up local irregularities; milling fails in this last respect. A third excellent method is the addition of caustic alkali or sulphide to the soaking liquors; the amount however should not be sufficient to start depilation. The writer has seen in foreign tanneries dried hides successfully treated direct in the limes without pre-soaking; the liquors, however, become soon loaded with impurities.

Effect of Desiccation upon Crude Hides. By a practician. *La Halle aux Cuirs,* 1910, [54], No. 7, p. 105.—Every tanner knows that a hide once dried will not yield as supple a leather as a corresponding fresh hide. The writer attributes this to the action of lime and other salts in the soaking water, which partially tan and protect the fiber, giving a permanent rigidity. Experiment shows that with repeated alternating soaking and drying, the ash of the hide steadily increases. Green hides do not take up salts in the same way, being already filled with natural juices. With Oriental hides which have been treated with preservatives before drying, the hardening originates in a similar way, but previous to soaking.

Beam House Work on Hides for Chrome Upper Leather. By a practician. *La Halle aux Cuirs,* 1909, [53], Nos. 42-3, pp. 683-4, 700:

The Sulphide Bath.—Crystallized sodium sulphide is used and it is unadvisable to use different supplies after becoming used to the results produced by one special brand, for there is much variation in causticity. Also a sulphide containing much iron should be shunned. The sulphide bath is made up to 2° B., and this is raised to 2½° with slaked lime. In taking this gravity the test sample should not be let settle, but the lime kept in suspension. Except with fresh skins, the hides are left 2 to 3 days in the de-hairing bath, even 4 days in winter. After that, although not strictly economical, it is better to throw the bath away, and know what one is working with. Although the hair may yield the first day, the full treatment is desirable to obtain suppleness and fine grain. The hide may lose weight, but this does not matter if we sell by surface measure. After the liming, the hides are milled an hour, giving up their hair, being washed meanwhile. The washing is however not finished until after fleshing and should then be thorough, else the useful fermentation of the bate will be prevented or retarded by retained alkali. For calf skins, bran bate is generally used. The lactic acid restores the swelling lost in washing and neutralizes any trace of lime left. 7 kilos of bran are used to 100 kilos of white hide, which is covered with water in a tub at 40-45° C.; the tub is covered and left stand according to season. One-third or fourth of the residual liquor is saved for preparing the bate for the next lot, when 5 kilos bran are used.

Dehairing Sheep and Goat Skins.—In the usual process softened and well-cleaned sheep skins are piled flat, flesh up in graded sizes, the largest at the bottom. With a broom each hide is coated on the flesh with a paste of slaked lime. The skins are then placed flesh to flesh and rolled up so that the wool does not come in contact with lime. These bundles are packed close in vats, which are then filled with water and left stand until the wool is loose. In this process the water and lime solution each gradually diffuse through the hide and the wool is little affected.

Sulphide of Arsenic Process.—Three limes are used successively and then discarded. The first contains 1 to 1½ kilos sulphide of arsenic to 100 kilos hide with sufficient lime, and used 4 days. The second contains one-third of the used preceding lime, together with 20 kilos quicklime (slaked); 4 days. The third is prepared similarly and here the hides remain 6 days for sheep, 10 days for goat (winter).

Manufacture of Pigskin Leather. *Technische Briefe* through *LeCuir,* 1909, [2], No. 22, pp. 517-8.—This is one of those leathers which require careful attention to the quality of the materials and every detail of the tannage to insure a product of good appearance. Pigskin is distinguished from most crude hides in its containing considerable deposits of fat, and by its peculiar grain. The river work should be very thorough accompanied by careful mechanical working to relax the fiber. An old lime is used at first 2 to 3 days, then a new lime for 14 to 16 days, until the bristles may be easily removed. The grain of untanned pigskin out of the lime is very sensitive and the dehairing is best effected with a soft stone. Pigeon or dog dung is used for bating. Thorough working of the flesh is needed because of the greasy nature of the hide. For tanning, the old pit process is the best with an after-tannage. Pine bark liquor is used at the start, which maintains the plumping and fixes the grain; later oakbark liquor is used. On leaving the after-tannage, the hides are well evened, then treated with sumac, which improves the color. Very little grease should be used in currying, nor should the currying be depended on to render the leather supple. Ordinarily before finishing, a bleaching with alternating solutions of sugar of lead and H_2SO_4 is used.

New Processes for Brightening the Color of Leather. MAGYAR BÖRIPAR, through *LeCuir,* 1910, [3], No. 2, pp. 25-6.—The dull color of extract tanned leather is due chiefly to surface deposit of tanning materials. Bleaching reagents are not very effective as a remedy for when applied sufficiently to produce the desired effect the leather is injured. It is better to prevent the original formation of the undesirable color, which is done by using the best decolorized extracts. Failing this, a superficial washing of the grain may be resorted to, removing the excess of extract. The leather is placed in a weakly acid tan liquor for one or several days and the grain is then washed with pure water, using a brush. By another more recent process, the dried leather is soaked a short time and the grain is then cleared by brushing with pure water. This is followed by bleaching, the grain being soaked in a solution of antichlor (sodium hyposulphite) followed by dilute HCl. A device for overcoming the dark color is to subject the tanned leather to milling with solutions of sumac, myrabolams and other light tanning materials. Bleaching as above may follow if desired. If all other means fail in lightening the color, the leather may be surfaced with the following mixture: 2 lbs. Marseilles soap, and ½ lb. stearine are boiled in 10 liters water. A second mixture is boiled, avoiding lumps, of 10 lbs. kaolin, 15 lbs. talc, 1 lb. sodium fluoride and 40 liters water. These two are finally mixed together with 20 liters of clear fish oil. The whole is shaken in a drum with 50 liters of strong myrabolams or valonia liquor to a perfect mixture. A simpler receipe is 12 liters of water boiled with 1.5 kilos ground valonia; this is strained and ½ kilo soft soap dissolved, then 1.5 liters old linseed oil stirred in. After softening the leather and treatment of antichlor as before, the above dressings are applied with a hand broom, let dry, lightly re-moistened, the leather piled and finally cylindered.

Colored Splits. FERDINAND KOHL. *Ledertechnic. Rundschau*, 1910, No. 4, pp. 25-6.—If split after liming, the hides should be well de-limed and go to the tannage clean. If split after the complete or partial tanning, contact with iron should be avoided and the splits returned from the machine to the tannage quickly. For chrome tanning, the single bath is generally used. The best results are obtained by a combination tannage. Straight chrome tanned splits are apt to show a hairy or woolly surface, which may be made smooth by an after tannage with vegetable material. Vegetable tanned splits, especially when not well de-limed, are apt to have a hard feel and an after tannage by the semi-chrome process is beneficial. For this the hides are milled with luke-warm soda or borax, rinsed and then put in the single bath. A dye like Cyanol extra, Fast Brown D (Cassella) may be applied at the same time if it is desired to color the leather through. It is important to secure as smooth a surface as possible. Shaving follows the splitting directly or at least before the after-tannage, which is best in a warm sumac bath. With semi-chrome, the shaving is done before the borax treatment and with straight chromed splits before the neutralizing. The greasing generally follows the after-tannage and with an emulsion as neutral as possible. If the split is only to be dyed on one side, the flesh is treated with a mixture of tallow and marine oil. The split side is then rubbed with a stiff brush and cold water and dried. The flesh side is then whitened and rubbed with a decoction of sea-moss, mixed with talc or China clay, aired, glassed and dried. If no regard need be paid to the flesh, it is easiest to dye in the drum. In all cases it is desirable to secure a good penetration of the dye to imitate grain leather. Acid dyes are the best, such as naphthol yellow, Indian yellow, G. & R., Havana Brown S. conc., Acid Phosphine JO, New Red B, Fast Blue R, Naphthylamine Blue Black 5B, Neutral Black B., etc. (Cassella). These are applied 1 to 2 hours at 40° C., with the addition of a little ammonia. When dyed completely, sulphuric acid is added for fixing, about ¼ the weight of dye. This can be followed by a solution of basic dyes such as Diamond Phosphine GG, PG, R and D, Manchester Brown GG & PS, Leather Brown A, Jute Red G, Oxblood A, Leather Black JBB, etc. (Cassella). These are used in about ½ the amounts of the acid colors, milling ½ to ¾ hour at 40 to 45° C. After rinsing, a dilute casein solution is applied. This is prepared by stirring with water to a paste and adding ammonia or borax equal to 1/10 the casein. This is gradually thinned and before use colored with an acid dye to correspond to the leather. The leather is then aired, flattened and dried, next moistened with dilute formaldehyde and well rubbed with a decoction of sea moss which has been colored and is applied cold. After airing, this is repeated and finally the leather is glazed and dried. Then a colored gelatine solution is applied and the grain impressed. Finally a light coating of shellac or a wax glaze may be given.

PATENTS.

Leather-Treating Machine. U. S. Patent No. 950,430. W. P. BOAK, Koshkonong, Mo.

Hide-Working Machine. U. S. Patent No. 950,618. E. A. FISHER, and J. W. STEINHAUSER, Bethel, Vt.

Leaching Vat. U. S. Patent No. 951,206. W. H. TEAS, Ridgway, Pa.

Process of Evaporating Solutions. U. S. Patent No. 951,322. OTTO MANTIUS, Chicago, Ill.

Manufacture of Caoutchouc Leather. French Patent No. 404,021. ALBERT NUNES.—Vegetable or mineral tannage is pushed to complete transformation of the gelatine by the tanning agent, with partial removal of the gelatine, if desired, and this product is then impregnated with a caoutchouc solution.

Tanning Process. French Patent No. 404,318. HENRI MORIN.—A combination process; formaldehyde alone gives a hard, brittle leather. By combining the ordinary tanning agents or the nourishment used in tawing, the fibers are prevented from adhering.

Process for Decolorizing Tannin Extracts. French Patent No. 406,362. Soc. Deutsch. Versuchsanstalt f. Lederindustrie et H. ARNOLDI.—The treatment is with active (amalgamated) aluminum, prepared by action of mercuric chloride on the cleaned metal.

Process for Deliming Hides. French Patent No. 406,646. GUSTAV EBERLE, Germany.—Weak acids are known to give the best results, hence the patentee uses anhydrides and lactones of fatty and oxy-acids, such as acetic anhydride, lactide, etc.

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D. L. Tucker to Box 304, Gary, Indiana.

NOTICE.

Attention is again called to the notice appearing in the March JOURNAL in which the members of the Association are requested to communicate with the Secretary expressing their views for or against the reporting of analyses to the first place in the decimal. By analyses, is understood all Official and Provisional Methods of the Association.

It is urged that every member of the Association send in his views on this subject.

H. C. REED, *Secretary.*

Stamford, Ct., April 13, 1910.

COMMITTEE APPOINTMENTS.

The Committee on the Preservation, Cure, and Disinfection of Hides, which is co-operating with a Committee of the I. A. L. T. C. is as follows:

Mr. Van A. Wallin, Chairman, Grand Rapids, Mich.
Dr. Louis E. Levi, care of Pfister & Vogel Leather Co., Milwaukee, Wis.
Mr. Aaron Weil, Alphonse Weil & Bros., New York City.
Mr. M. F. Nichols, 697 Cherry St., Grand Rapids, Mich.
Dr. Allen Rogers, Pratt Institute, Brooklyn, N. Y.
Mr. Frank L. Howes, Howes Bros. Co., Boston, Mass.
Mr. Henry W. Boyd, Armour Leather Co., Chicago, Ill.
Mr. F. P. Veitch, Department of Agriculture, Washington, D. C.

THE ANALYSIS OF GLUE GREASE.

By S. S. Sadtler.

The analysis of glue grease will vary somewhat according to different requirements. The determinations the writer has generally made are: Ash, water, free acid and non-saponifiable oil. In three out of four of these determinations it was found desirable to carry out the determinations somewhat differently from what seemed to have been customary heretofore. The methods adopted in our laboratory are herewith described.

1. *Water.*—This is given by difference according to Trotman (*Leather Trades Chemistry*, S. R. Trotman). We determine it.

however, by distillation of 200 grams in a cylindrical copper retort, using 100 cc. of benzine distillate such as a grade known as "Tesene," or a cut from 62° benzine. To carry over the water and to prevent superheating of the oil and possible breaking up of some of the oxygenated constituents, thus forming water, 50 cc. of the "solvent" are distilled for 200 grams of grease taken. This carries over all the water. This distilled solvent and the water carried over are caught in a burette. Each cubic centimeter should measure linearly at least ½ inch on the tube and better 1 inch. If made specially it might be graduated for 10 cc. and then have a bulb that would hold about 200 cc. (Article by the writer on the Determination of Moisture by Distillation, in a recent number of *The Journal of Industrial Chemistry.*) The writer has used xylol as means of driving over water but the mixed solvent is preferable to any constant boiling-point fraction.

2. *Ash.*—This is carried out by incinerating about 5 grams at a moderate heat until fully carbonized, lixiviating three or four times with warm water. The carbonaceous residue is then burned in a platinum crucible until the carbon is consumed and the aqueous extract evaporated to dryness in the crucible and weighed with the insoluble portion of the ash.

3. *Free Acids.*—As the free acid in this grease is sometimes over 50% and as the composition of the acids is not fixed, it is not accurate to calculate them from an amount of caustic potash used in the titration. The method employed by us is that found by the writer to be useful for the separation of fatty acids from the neutral oil, so that emulsions are avoided. It is briefly as follows: About 2 grams of the fat are taken and dissolved in ether, an equal volume of alcohol is then added, a little phenolphthalein solution and alcoholic potash or ½ normal caustic potash until just distinctly alkaline. It is then transferred to a separatory funnel by means of ether, and water is slowly added with regular rotation until no more oil is separated from the lower layer. The aqueous layer is washed with ether to remove any traces of oil, and the ether layer is added to this main ether extract. The combined ether solution of oil is washed with two changes of water to free it of alcohol and soap. This residue from the ether extract contains the neutral oil, both saponifiable and non-saponifiable. The fatty acids are obtained by difference from

the combined percentage of ash, water, neutral, non-saponifiable and 100 per cent.

4. *Non-saponifiable.*—The neutral oil from (3) is boiled a half hour with 25 cc. alcoholic potash, then cooled without driving off more than about ½ the alcohol, about 40 cc. of ether is added and the whole transferred to a separatory funnel by washing with a little more ether. Water is now added slowly and the ether and aqueous layers are washed as in (3), and the combined washed ether layers are evaporated. The residue consists of the non-saponifiable matter.

The following analyses show the variation in composition from the same glue works. All the analyses were made by this method.

Lot	Water	Ash	Free acid	titration	Non-saponifiable	Neutral oil
25	1.25	1.53	41.5	..	3.1	42.2
78	1.00	0.07	42.3	..	4.08	52.55
79	1.00	0.06	49.2	..	3.24	47.56
80	0.75	0.025	39.69	..	5.25	54.30
A	..	..	20.65	18.22	..	..
B	..	..	60.40	65.86	..	..

As A and B seem to be abnormal results it was thought well to check up by titration. This showed what the writer believed would be the case where the free acid was such a large percentage of the total fat that a calculation to oleic acid would not be accurate and reporting in terms of KOH would not signify anything very definite.

In conclusion it might be said that, particularly in the case of the non-saponifiable, that a procedure in the ordinary way of shaking out with ether after saponification is likely to result in hopeless emulsions, while all emulsions are avoided by this method.

PROBLEMS OF THE LEATHER INDUSTRY.[1]

By Prof. H. R. Procter.

Though the technology of leather manufacture is one of the most ancient, and has been highly developed by the accumulated experience of ages, it is as yet less influenced by scientific know-

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[1] From the *Journal S. C. I.*

ledge than many other industries. This is less due to any special ignorance or unwillingness of tanners than to the extraordinary difficulties of the problems it presents, and the risk and costliness of experiment. Much has, however, been accomplished in recent years towards clearing up the prevailing darkness, and this has been hastened by the introduction of new tanning agents, such as chrome salts and aldehydes, which are so far removed from the older methods as to render much of the previous experience valueless, and to compel the adoption of new methods and a study of their underlying principles.

The skins of animals naturally presented themselves to our forefathers as valuable for clothing and other purposes; but, wet, they were subject to rapid and offensive decay, while, dried, they became hard and horny, and therefore ill adapted to most uses. To retain softness while preserving the skins by drying was the first problem which presented itself, and it was solved in a variety of ways in pre-historic times, rather, probably, by accident than by any reasoned experiment. Thus skins which were oiled and stretched while drying remained soft and flexible, and became resistant to moisture and decay. Wood smoke, which must always have been present during drying in primitive dwellings, was found to assist this preservation, and certain barks and fruits, possibly first used as dyes, had a still more marked effect. Alum, which in some countries is a natural efflorescence from shales containing alumina and pyrites, was possibly first applied as a substitute for salt, the preservative qualities of which had long been known. The hair, first loosened accidentally by putrefaction, was more conveniently removed by liming, and improvements in dyeing and finishing were gradually introduced, so that even in ancient Egypt the "Art and Mystery" of the tanner had reached a high stage of development in detail, though the principles then, and almost to the present date, were those of the primitive savage: and even during the past century the improvements consisted rather in the substitution of machinery for hand-labor than in any more radical departure from earlier ideas.

While discussing the problems of the trade as they present themselves to-day, it will be well, as I am addressing myself, not only to the specialist but to the general chemist, to give some slight sketch of the methods of the present. While the earliest users of the skin probably aimed at retaining the hair and wool, these are no longer needed for most of the purposes to which leather is now applied, and the first stages of the modern process are usually devoted to their removal. In a few cases, and especially in the removal of wool from sheepskins, where the wool is of more value than the pelt, the primitive method of putrefaction is still employed, though under better conditions, the skins being hung in rooms of carefully regulated dampness and temperature, and the progress of the operation being closely watched. Wool and hair, though apparently growing from the true skin (*corium*) are really the product of a thin outer layer of cellular tissue (*epidermis*) which not only covers the entire surface, but surrounds and forms a sheath to the hair-bulb. The soft and growing cells of the layer are readily disintegrated by putrefaction, and thus the hair is loosened. While the skin itself is composed of white fibers of collagen, a material which passes at once into gelatine on heating with water, the epidermis and hair consist of keratin, which is nearly related to coagulated albumen. Thus the effect of chemical reagents on the two layers differs widely. While the gelatinous fiber is merely swollen and split into finer filaments by the action of alkalies, the epidermis is softened and ultimately dissolved. Lime is generally used for this purpose, not merely on account of its cheapness, but because its limited solubility allows it to be added in excess without forming a dangerously concentrated solution, while, as it is consumed by the hide it is instantly replaced from the undissolved portion. Practically the process is conducted in pits in which the hides or skins are laid in milk of lime, from which they are withdrawn at intervals of one or two days, and the liquor is mixed, and if necessary more lime is added before they are replaced. One to three weeks is required for the operation, according to the character of the hides or skins, and the purpose for which they are intended. Suspension and mechanical agitation in the lime liquor hastens the process by insuring rapid renewal of the saturated solution, but is more frequently used on the Continent than in England.

Though lime is the agent principally used, its action is frequently quickened by the addition of sodium sulphide, or occasionally of other alkaline salts. The action of soluble sulphydrates is peculiar and completely different from that of hydrates, swelling the *corium* very little, and dissolving the keratin structures rapidly. It has, however, been shown by Stiasny[1] that in complete absence of hydroxyl ions, this solvent action does not take place, and the most favorable condition is when SH and OH ions are present in equal concentration. This condition is fulfilled when sodium sulphide is dissolved in water, of which it takes up one equivalent, forming an equi-molecular solution of sodium hydroxide and sulphydrate; but much smaller proportions of sulphydrate materially quicken the liming process, while retaining the value of the hair, which is completely pulped and destroyed in concentrated solutions. Fresh lime solutions are practically sterile, but as they get charged with dissolved organic matters they become capable of supporting a variety of bacterial life, though from the presence of excess of lime, their alkalinity except from ammonia remains unaltered. While sterile limes have little solvent but powerful plumping effect on the hide fiber, the bacteria or their products increase the former and lessen the latter, and at the same time increase the solvent action on the epidermis and consequently hasten the unhairing. Thus it is an axiom in sole-leather tanning, where the utmost weight and solidity is desired together with plumpness, to use new rather than old limes, but as absolutely new limes unhair very slowly, if at all, it is usual to begin the process in liquors which have already been used for one or two packs, finishing in a quite fresh lime. In the case of skins and dressing leathers, where some solution of the interfibrillary substance is desired, advantage is usually taken of the somewhat more solvent effect of older limes. The theory of the process is by no means completely elucidated, and till this is done, complete chemical control is impossible, as the effect of the various constituents is not fully known. Even the determination of the valuable dissolved hide-substance is difficult since it is as yet impossible to distinguish the epidermis-products from those of the corium.

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[1] Gerber, 1906, this J. (Abst.), 1907, p. 25.

On the completion of the liming process the hair is removed and mechanically either by hand with a blunt two-handled knife, or by machine, or sometimes where it has been treated with sulphides, by mere friction in a revolving drum. The fat and loose cellular tissue is also pared or scraped from the flesh side, and, in the case of sole leather, the hide is "rounded" into butts and offal, which are tanned separately.

Before actual tannage, it is necessary to remove the lime, of which the skin retains perhaps three per cent. of its wet weight, and which would cause discoloration and destroy tannin, or at least neutralize their acidity if introduced into the liquors. In the case of sole leather it is desired to retain the hide in plump condition, and in earlier times it was frequently taken to the liquors after only a slight washing with water, which removes but little of the absorbed lime, as alkalies are obstinately retained by hide-substance, possibly in a state of chemical combination, which is slowly hydrolyzed. At present, even in sole leather tannage, a part at least of the lime is usually removed by acid treatment, as with the tanning materials now in use, and especially with extracts and rapid tannage, but little acid is produced by fermentation. The use of acids for deliming is not, however, so simple as at first sight might be supposed, since the affinity of hide for acids is not less than for alkalies, and the swelling which they produce has an even more injurious effect on the leather since it is not neutralized by the liquors, which themselves must have an acid reaction. It is therefore essential, if strong acids are used, that there should be no excess beyond that needed for neutralizing the lime, since acid is absorbed by the hide to saturation even from very dilute solutions. With weak acids the operation is easier, as their feeble hydrion concentration prevents excessive swelling, owing to the hydrolysis of the acid compound with the hide, and so weak an acid as boric acid can be used in large excess without injurious results, while acetic, lactic, and even formic acid require much less precaution than the stronger mineral acids.

In the case of the lighter leathers used for the upper part of boots and other purposes where softness and pliability are required, it is essential that the tannage should be begun with the skin in an absolutely unswollen condition, and hence, while even the strong mineral acids in great dilution are frequently employed to remove the greater part of the lime, the process is usually completed by one or other of the fermentation processes which have been used from immemorial time. The simplest of these is the bran drench, for which bran is infused in warm water and allowed to ferment with the production of lactic and acetic acids from glucoses formed by the action of an unorganized ferment, cerealin, which is present in the bran, on the starch which it contains. The glucoses are then fermented by bacteria, which are always present in the vats, and of which the action is inhibited by a small excess of acidity, so that the process is really a simple acid "pulling down," in which so long as only the right bacteria are present, the acidity is automatically self-regulating. At the same time, considerable quantities of hydrogen and carbon dioxide are evolved, which cause the skins to float in the liquor.[1] Unfortunately, it is impossible to work under accurate bacterial conditions, and putrefactive and butyric bacteria are always present which may get the upper hand with disastrous effects. This risk can only be lessened by careful attention to temperature and the other conditions, such as the amount of glucose, the acidity and the age of the liquors which favor the development of the right organisms; and the provision when necessary of a plentiful supply of ferment organisms from a sound working drench. Frequent cleansing of the vessels with hot water and the maintenance of a constant temperature of about 70° F. are useful precautions. Putrefactive bacteria will not thrive so long as the drench remains acid, and the greatest danger arises from organisms which form butyric acid, which by its powerful and solvent swelling action may completely destroy skins in a few hours.

Though from its simplicity I have first mentioned the "drenching process," it is rarely used alone, bnt generally only to complete the removal of lime after "puering" or "bating," which are fermentative methods of quite a different character, in liquids containing nitrogenous matters and usually alkaline in reaction.

The chemical effects caused by bacterial fermentations, are due

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[1] Compare Wood, this J., 1890, p. 27; 1893, tp. 422, 1897, p. 510. Brit. Ass. Rep., 1893, p. 723.

not merely to direct changes produced inside the organisms, but even more generally to the action of the digestive ferments or zymases which they secrete into the liquid. These unorganized ferments, like the pepsin of our own stomachs, are not living things, but have the power of causing chemical change in the substances they act on, without themselves being destroyed. They are in fact catalytic agents.

The "bate" is a fermenting infusion of pigeon- or hen-dung, and is usually employed for the heavier dressing leathers, while the "puer," similarly made with dog-dung, is employed for the finer and thinner skins used for light shoes, glove leathers, and moroccos. Though these differ both in effect and mode of use, they depend on the common principle of making use of nitrogenous and largely anœrobic fermentation and its products; but in the two cases the active organisms differ, and it is uncertain whether, in either case, they are really derived from the intestinal bacteria or are accidental and extraneous ferments, for the growth of which the diluted excrement forms a suitable medium. The case of puer has been very fully investigated by J. T. Wood,[1] and also by Popp and Becker. Wood found that the filtered bacterium-free puer liquor had considerable puering effect, and that the presence of actual living organisms was not essential. Even after boiling, which not only destroyed life, but coagulated the zymases present, this effect, though greatly diminished, was not entirely absent: and he traced what remained to the salts of amines and the amino-acids formed by the decomposition of the skin. On substituting phenylamine hydrochloride for the natural amine salts, and adding zymases precipitated by alcohol from the puer liquor, satisfactory puering was obtained in the absence of life, but of course at a cost too high for technical use. Practically, Wood, in conjunction with Popp and Becker, produced the puer-substitute "erodin," which consists of a culture-medium of peptonized gelatinous tissue, with a special mixed culture of selected bacteria, capable of attacking the keratin-structures but not of liquefying gelatine: and this has been largely and successfully employed in some branches of leather manufacture, though in

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[1] This J., 1894, p. 218; 1895, p. 449; 1898, pp. 856, 1010; 1899, pp. 117, 990.

others, and especially in the manufacture of chrome-kid, it has not taken the place of the natural product. While it is much safer and more certain in its action than the latter, from the definite character of the ferments employed, and sentimentally less disgusting, it is practically not less odorous than the original, which no doubt derives its name from an old French verb, *puer*, which still survives in the participle *puant*, stinking; and it is a little more complicated in use. It has been suggested that the special action of excrement was caused by the excess of digestive ferments which it contained. Wood pointed out that this could not be due to pepsin, which only acts in acid solution, but that the pancreatic ferment trypsin possessed many of the required qualities, acting in alkaline solution, and not merely dissolving albuminoids, but emulsifying fats; and on experiment he found that it actually had marked puering properties, though the fact that it is itself an excellent nutriment for bacteria renders it highly improbable that any can exist unchanged in the dog-dung, which is always allowed to undergo a fermentation of some weeks before use. The idea has, however, been developed by Röhm and Haas in Germany, who have produced an artificial puer under the name of "Oropon," containing pancreas-products and ammonium chloride, which acts at once on the skin without previous fermentation, and which both experimentally and practically gives very promising results, while at the same time it effectively removes lime and renders drenching unnecessary.

It cannot, however, yet be said that the problem of puering has received its definite chemical solution. The properties required are not merely that of removing lime, which is only imperfectly accomplished by puering unless supplemented by drenching, but of removal of fat by emulsification, and solution of the cellular epidermis-structures still remaining in the skin. Some solution of the hide fiber itself, or at least of the interfibrillary substance, is also usually required in order to soften the leather, but this must be controllable and very moderate in amount.

The puer liquor is always used warm (80°—90° F.), and its action is very rapid, thin skins being completely reduced within the hour. This rapid action renders it quite unsuitable for the thicker sorts of leather, of which the surfaces would be digested and dissolved before the center was properly penetrated, and hence recourse is had to the milder action of the "bate," made with bird-dung and used cold for four or five days. Not only is the medium here much less nitrogenous, but the bacteria are quite different, apparently rosary-like chains of small spherical cells (*streptococcus*), which thrive at low temperatures, while the puer bacteria require nearly blood-heat for their development. It is also pointed out by Wood that bird-dung contains the urinary constituents which in animals are separately secreted. Less scientific study has been devoted to the bating than to the puering process, but there is no doubt that a bate-substitute on the same lines as erodin could be made by the selection of suitable bacteria and an appropriate culture-medium. There is, however, no reason that all the necessary effects, both of puering and bating, should not ultimately be attained by purely chemical treatment without the risk and uncertainty which must always attach to bacterial and ferment action.

The actual conversion of the prepared skin into leather is not less rich in unsolved problems than the processes which have preceded it. At the point which we have reached we have the more or less purified gelatigenous fibrous structure before us, really an organized jelly, still readily capable of destructive putrefaction, and becoming on drying a translucent horny sheet. We may fairly ask what is the general character of the change into an imputrescible and pliable dry material which we can bring about by agents so different in chemical character as chrome salts, vegetable tannins, and aldehydes? In general terms the question was answered by Knapp in 1858,[1] though his answer only suggests further inquiries as to the actual change. Knapp in effect tells us that the raw skin consists of water-swollen gelatinous fibers, which on mere drying adhere and contract into an almost homogeneous horny mass, and that the essence of tanning is so to treat these fibers that they dry and contract without adhering, and that they are rendered incapable of absorbing water and again becoming adhesive. In the main the explanation which he gives of the change is the somewhat crude one that

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[1] "Natur und Wesen der Gerberei," Braunschweig, 1858.

the fibers become superficially coated with the tanning substance, and so isolated and water-proof. The supposition is in no case very convincing, and is incapable of direct proof or actual observation of the protecting layer, in the case of formaldehyde is obviously untenable, and with regard to chrome is improbable from the minimal quantities of chrome hydrate which suffice to effect the change. No less difficulties meet the still earlier hypothesis of Sir Humphrey Davy that the leather is a direct chemical compound of the nature of a salt between the gelatine and the vegetable tannin; among which may be cited the very variable composition, not only of actual leather, but of the directly precipitated tanno-gelatine. In the light of modern knowledge it seems safest to conclude that in the various methods many different causes—chemical, physical, and mechanical—are at work to produce the isolation and non-absorbence of the gelatinous fibers; and that it is not necessary to assume unity of cause because of apparent similarities in the final result. Thus Knapp was able to produce a white leather (which, however, returned to the pelt state on soaking in water), by mere dehydration of the skin with alcohol, which first isolated the fibers by replacing the water between them, and then dehydrated them so that they were no longer capable of adhesion. By the employment of alcohol containing a trace of stearic acid in solution, the isolated fibers were mechanically coated with a minute quantity of this substance, by which the pliability of the leather and its resistance to water were greatly increased. A somewhat more complex instance of leather production is afforded by the "pickling" process, in which the raw prepared skin is first slightly swollen by sulphuric acid, usually with addition of salt to control the swelling, and then treated with saturated common salt solution, in which it becomes thin, white, and imputrescible, and if dried forms a very perfect white leather, which is permanent so long as it remains dry. This case has been very fully investigated by the writer, who has brought strong evidence to show that the hide-fiber, which is amphoteric (or at the same time acid and basic from the presence both of amino- and carboxyl-groups), actually forms a chemical compound with the acid, which is semipermeable to the salt and is dehydrated by its osmotic pressure.

From this process it is an easy step to the alum and chrome tannages. Both aluminium and chromium are weak bases, the salts of which have a strongly acid reaction in consequence of their partial hydrolysis on solution in water into free acid and a basic salt. In presence of the hide-fiber the free acid is absorbed and fixed, and the hydrolysis is carried so far that the basic salt becomes colloidal and insoluble in water, and in this state forms a coating or possibly an adsorptive or chemical compound with the fiber, which is also dehydrated by the addition of salt, and thus prevented from swelling or adhesion. In the modern single-bath basic chrome process, the hydrolysis of the normal chrome salt is already carried in the liquor as far as possible without the precipitation of an insoluble basic salt, so that the fixation of small quantities of acid by the hide causes also the fixation of comparatively large quantities of basic chrome salt, and the residual acid is removed and the chrome salt rendered still more basic and insoluble by subsequent washing and the treatment with borax or some other alkaline salt, generally known as "neutralization." Exactly in what condition the chrome exists in the hide, whether as oxide, hydrate, or very basic salt, is as yet not definitely determined, but though the quantity of acid can be reduced almost indefinitely in the leather without injuring its quality, an actually alkaline condition at once renders it horny and apparently undertanned. The two-bath method of chrome tannage only differs from that just described in that the basic salt, instead of being ready formed in the liquor, is produced in the skin itself by the reduction of chromic acid with thiosulphate. Whether the tanning effect of chrome, which is shared in degree with iron, alumina, and other metals forming basic salts, is due to the absorption and coating of the fiber with colloidal chrome oxide in an insoluble irreversible condition, or to some more intimate sort of combination is yet unknown.

Tannage with aldehydes, and especially with formaldehyde, seems still more definitely one of chemical change. Aldehydes have peculiar powers of uniting with a great variety of substances to form new compounds, often insoluble; but apart from this, it is difficult to see how a volatile substance like formaldehyde can form a resistant coating on fibers which prevents their adhesion and renders them water-proof and imputrescible by mechanical means, especially when present only in the very minute quantity which is necessary to complete an aldehyde tannage; and the conclusion is almost irresistible that at least the surfaces of the fibers are so altered by the action of the aldehyde as to become themselves insoluble and non-adhesive. The suggestion that in a practical aldehyde tannage the surfaces only are affected is somewhat supported by the facts that over-tannage renders the whole fiber brittle and tender, and that even with very small quantities of aldehyde this effect will ultimately occur, unless means are taken to destroy all surplus and uncombined formaldehyde (usually by its reaction with ammonia), as soon as the tannage is completed.

The ordinary oil tannage or "chamoising" of "wash leather" and buff leather has been a puzzle to chemists. For wash leather the "lining" or inner split of sheepskins, after suitable preparation to free it from excess of lime, is "stocked" or beaten with fish oil till the water is replaced by oil, which is then allowed to oxidize by spontaneous heating in piles after exposure to air. Only oils with more than one pair of unsaturated bonds are capable of producing this effect, and though marine oils are invariably employed in practice, it has been shown by Fahrion[1] that similar effects may be produced by linseed, or even in a lesser degree by rape oil, and it is known that the latter is employed in the manufacture of the Japanese white leather, so much used for brace tabs. The most obvious explanation of the chamoising process would be that of the mechanical coating of the fibers by the varnish-like products of oxidized oils, but this is apparently excluded by the fact that oil leathers can be, and habitually are, washed without injury with alkaline solutions, in which these oil products are freely soluble, and by which they are readily removed from vegetable fibers. It is pretty clear that the union of the leather-fiber with the oil, whether physical or chemical, must be more intimate than that of a mere surface-coating; and Fahrion (*loc. cit.*) has shown that by saponification a portion of oil can be extracted from the leather which cannot be removed by any solvent. The present writer at one time suggested the theory that the oil

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[1] "Ueber die Vorgänge bei Lederbildung," Zeits. Angew. Chem., 1909, Hefte 43-45.

tannage was actually an aldehyde one, produced by the acryl aldehyde which is freely evolved from the glycerine during the heating process; but this idea, though perhaps partially correct, seems to be negatived as a complete explanation by Fahrion's observation that the fatty acids themselves are capable of producing oil-tannage, since in this case acryl aldehyde is of course absent, but aldehydes arise from the oxidation and breaking up of the acid-chain itself, and it is quite possible that these combine chemically with the hide-fiber.

Though the use of vegetable tannins is even yet probably the most important means of leather production, the actual nature of its action is still a subject of dispute. The advance of colloidal chemistry has proved that many apparent solutions are really only extremely fine emulsions or suspensions in which the presence of separate particles can actually be shown by means of the ultra-microscope, though no defined line can be drawn between actual solutions like that of sugar in water, and obvious suspensions like butter-fat in milk or clay in turbid water. In all these cases of colloidal suspension it is known that the particles possess electrical charges somewhat similar to those of the ions in electrolytic solution, and that if these charges are removed or neutralized, the suspension immediately settles. These charges, like those of the ions, may be positive or negative as compared to the liquid, and if a suspension with+particles be mixed with another with— particles, the two neutralize each other, and are precipitated together in a way which closely resembles the formation of a chemical compound, such as barium sulphate, by the union of + Ba′ with — (SO_4):

It is known that gelatine and tannin both form solutions containing ultramicroscopic particles, which in the gelatine-solution are + and in the tannin —, and it is now generally believed that their mutual precipitation is a colloidal and not a truly chemical (ionic) reaction, though it must be remarked that the progress of scientific thought at present tends to break down any clear line of demarcation between the two ideas. Whether chemical or not, the actual precipitate is not definitely quantitative, and there seems no limit to the extent to which tannin can be removed from it by washing with hot water.[1] On the other hand, Knapp's view that the action is confined to a mere surface-coating of the fibers is not supported by any clear evidence, but it is quite probable that the action is at first a surface one, even if it ultimately extends throughout the fibers. When a solid is brought into a solution (either ionic or colloidal) in which the solid and the dissolved bodies have relatively opposite electric potentials, the dissolved body is attracted by the solid and becomes concentrated on its surface, and this surface-condensation (known as adsorption) in some cases leads ultimately to true chemical action or close physical union which renders the combination permanent and irreversible. In ordinary cases, the surface of a solid is so limited in relation to the surrounding liquid that the quantity fixed is relatively a small one, but where the surface is almost infinitely extended by the division of the solid into a fine emulsion or suspension, or by a porous or fibrous structure, it may be very considerable. This latter, it may be pointed out, is the condition of the hide with regard to the tanning liquor or any other solution from which adsorption can take place, and it is obvious that the splitting up of comparatively coarse fibers into microscopic fibrils which is caused by liming must be of great importance, not only as regards rapidity of tannage, but in respect of the weight of tanning substance adsorbed and ultimately fixed. As a matter of experience, unswollen hide always gives a thin and hungry leather, and though in this respect swelling by acids may take the place of that by lime, it remains an axiom that in some stage of the process the fibers must be split up, if well tanned and satisfactory leather is to result. A point of importance with regard to adsorption, at least so long as it remains reversible, is that the amount adsorbed bears a definite relation to the concentration of the solution; so that, regarded as an adsorption process, the heaviest tannage will be given by the strongest liquors, a statement also in accord with practical experience.

Before adsorption can take place on the internal surfaces of the skin, the tanning solution must reach them, and this, in the ordinary method of laying in liquor, it can only do by diffusion through the outer portions. While all crystalloid or "true" so-

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[1] J. T. Wood, this J., 1908, p. 384.

lutions diffuse with comparative rapidity, colloidal solutions, and tannin solutions among the rest, diffuse extremely slowly, an obvious explanation of the well-known fact that while alum or (not too basic) chrome solutions will penetrate the thickest hide in a few hours or at most a few days, vegetable tanning solutions may take months to produce a similar effect. Diffusion can only occur from a more to a less concentrated solution, and tannage must cease when the concentration inside the hide is equal to that without, and hence the axiom that the strength of tanning liquors must be constantly increased as the tannage proceeds. The further rule that it must be begun in weak liquors is partly a corollary of the first, but also depends on the fact that much time must be allowed for diffusion if the effect is to be uniform, and not to result in too rapid tannage of the surface before the interior is penetrated, since the tanned surface is more or less impermeable to further passage of tannin.

It may be asked whether it is not possible to employ physical or mechanical means to hasten the diffusion and shorten the very considerable time required for tanning the heavier leathers. Diffusion is quickened by heat, but this can only be employed to a limited extent, though it undoubtedly hastens tanning. Some years ago electricity was largely boomed as an effective means, but any hastening of the process which was observed was shown to be due much more to mechanical motion than to the current employed. It is, however, possible that electricity may ultimately have some practical value, and the process of Mr. L. A. Groth, in particular, is not entirely without scientific basis. He suspended the hides in pits between two electrodes connected with an alternating current generator. This arrangement gets over the troubles arising from the electrolysis of salts contained in the liquor, the products of which would destroy tannins, though these are probably not themselves electrolytes. It can be shown that when an electric current is passed through a porous diaphragm, it also causes flow of the liquid in one or the other direction according to the positive or negative charge of the diaphragm in relation to the liquid, an effect known as electric cataphoresis; and some experiments by S. Rideal (this J., 1891,

p. 942) seemed to show increase of absorption during the time the current was passed. It is, however, doubtful whether under such conditions the current would go through or round the hides, and still more so whether the gain of rapidity, if any, would be of sufficient commercial value to pay for the increased cost. One of the electric processes was carried out in closed rotating drums, and it was observed that either with or without current extremely rapid tanning was effected, even thick hides being completely tanned through in three or four days. This observation has been the basis of several successful processes of quick tannage, which are carried out in drums with concentrated liquors, but without electricity.

One of the most important questions in modern vegetable tannage, and also the most puzzling, is that of the influence of acids on the process. In sole leather tannage a considerable acidity of the tanning liquors is essential to the production of a firm and plump leather, for which a swollen pelt is necessary, and even in dressing leather a distinct acid reaction is required, since the hide is usually brought in in an alkaline condition, and alkaline liquors do not tan. The natural acids are principally derived from the fermentation of sugars contained in the tanning materials; but the modern process is carried out with concentrated materials, and is so comparatively rapid that litttle fermentation occurs, and artificial acidification is often required. From a research now being carried out by one of my students, it seems that small traces of acid at first slow the absorption of tannin, but a minimum is soon reached, after which additional quantities increase absorption. Apparently the acid contained in swollen pelt is partially but not entirely displaced by tannin as the tannage progresses. In the ordinary process of sole leather tannage, the butts (trimmed hides) are first suspended in weak and nearly exhausted liquors of sufficient acidity to remove any traces of lime, and to replace the previous alkaline swelling by an acid one. These liquors are gradually strengthened in tannin, and usually also in acid, by moving the goods forward through a series of pits through which liquors are circulated in the reverse direction; and the suspension generally lasts about ten days, though it may be longer. During this short period, and in spite of the weak liquors, at least 25 per cent. of the total tannage is accomplished, since the green goods take up tannins with great avidity. Great care is required to secure the complete removal of lime and a uniform swelling without irregular contraction or "drawing of the grain," which would result from too astringent liquors, and the color which is here set has generally a determining influence on that of the finished goods. The use of old and used liquors is not only prescribed at this stage from reasons of economy, but because their previous use has removed the more astringent tannins, leaving only those of lesser affinity for the hide, together with neutral salts and other non-tanning bodies which conduce to a milder action. If it becomes necessary to add fresh tanning materials at this stage, naturally mild materials, such as gambier and myrabolams, are selected.

The tannins are broadly divided chemically into derivatives of the dihydric phenol catechol, and those of the trihydric phenol pyrogallol. Each of these classes contains at least several individuals differing in practical character and constitution, and probably in some cases by the added presence of other phenols as, for instance, phloroglucol in the molecule. It is by no means certain that any tannins are really acids, though they combine with alkalies, possibly on account of lactone or phenolic structure. One principal cause of the practical differences of tannins in use depends on the extent and character of the solid products to which they give rise on slow decomposition in the liquors; most catechol tannins yielding more or less of insoluble "reds" or phlobaphenes, while many pyrogallol tannins are associated with some body which deposits pale yellow and very insoluble ellagic acid. While these solid products play an important part in the later stages of the process in giving weight and solidity, they are not desirable in the earlier or true tanning stage; and one reason for using old liquors is that most of these insolubles are already deposited.

After the suspension, the goods are laid flat in liquors of gradually increasing strength, in which at first they are moved daily, but finally are brought into much stronger liquors with intermediate layers of solid tanning material. Of these they receive three or four of a duration increasing from one to three or four weeks, the final liquor being often a gravity as high as 1.100 (100° Bkr.), and largely composed of oakwood and other extracts concentrated in the vacuum pan. These liquors not only ensure the absolutely saturated tannage of the leather, but materially add to its weight by the solid contents of the liquor mechanically absorbed and finally dried into the leather. Before this last stage of the process, the actual tannage may be assumed to be nearly complete, and what goes on is mainly the mechanical coating of the fibers and the filling of their interstices with insoluble reds and ellagic acid in accordance with Knapp's ideas. This is not merely profitable to the tanner in the sense of gain of weight, but increases the durability and water-resistance of the leather.

The principles of dressing leather tannage do not differ from what has just been described, but the goods are brought into the tanyard in an unswollen condition, and the liquors are so low in acidity as to avoid swelling. The deposition of solid matter is also much less, owing to the weaker and generally older liquors employed. the different selection of materials, and the shorter duration of the process.

Such is a brief sketch of a few of the more important problems presented by the industry. Many points have been entirely neglected, and I have thought it best to devote the limited time at my disposal to matters of salient interest in the general theory, leaving it to others to deal with the more detailed and practical questions of actual manufacture.

THE GERMICIDAL EFFECT OF WATER FROM COAL MINES AND TANNERY WHEELS UPON BACILLUS TYPHOSUS, BACILLUS COLI AND BACILLUS ANTHRACIS.[1]

At the headwaters of several of the main tributaries of the large river basins in Pennsylvania may be found extensive coal operations, either in the anthracite or the bituminous fields; notably in Carbon county, in the Lehigh River basin; in Schuylkill county, in the upper Schuylkill River basin; in the Lackawanna and Luzerne districts of the Susquehanna River basin, North

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[1] From *Pennsylvania Health Bulletin.*

Branch; in the bituminous fields in the Allegheny Mountains of the Susquehanna River, West Branch; in Dauphin county on the lower Susquehanna basin; also in the lower Monongahela basin; and the lower Allegheny River basin. It so happens that on the main streams, below these extensive coal fields, have been built the cities in which reside a large percentage of the entire population of the Commonwealth. The source of supply to the public in these places are without exception the rivers at their doors. It has been observed that these waters are remarkably free, comparatively speaking, from bacterial life, although the streams are used as repositories for sewage by the settlements strung along their banks, even up to the summits of the watersheds. Especially notable is the absence of sewage organisms from these streams, before the waters—mingling with fresh waters coming from districts outside the coal regions—have become alkaline; that is, while they still contain sulphur waters in sufficient quantities to characterize the streams. It is only during high stages of the rivers, when the mountain brooks are sending down floods in torrents to the main valleys, that the sewage from the mining settlements and the culm dust may be transported by water from the coal regions even to the sea. At such times the volumes of fresh water overcome the acidity of the mine waters and, the dilution being sufficient, preclude any germicidal effect of the acid mine drainage. Were it not for this disinfecting, germicidal action of waters drained from mines, the streams emerging from the coal fields would be large factors as polluting agents of the water supplies of Philadelphia, Pittsburg, Harrisburg and other cities. This power to destroy sewage organisms in natural water courses has been recognized by the State Department of Health in the decrees relative to sewage issued in conformity with law, upon unanimous agreement of the Governor, Attorney General and Commissioner of Health. The spent tan-liquors from tanneries are known to exert a somewhat similar influence on sewage organisms. The experiments with these two wastes hereinafter described were made in order to determine what effect mine waters of a certain quality and spent tan-liquors of a certain quality would have on certain micro-organisms.

The waters on which these experiments were carried out were sent to the State Department of Health Laboratories from one colliery and from two tanneries in different parts of the State.

The samples are described as follows by the parties furnishing them:

THE MINE WATER.

"The mining is about the ordinary class of anthracite mining where the veins have a dip of about 30°. The colliery has been opened by a shaft of 590 feet in depth and from the foot thereof gangways and tunnels have been opened eastward probably 2,500 feet and westward for about 8,000 feet in the Mammoth Skidmore Seven Ft. and Buck Mountain veins (all in the White Ash group) and with two to four lifts of about 100 yards each, where four lifts are worked, the extra two being mostly in the Buck Mountain and Seven Ft. veins.

The water is that which is constantly flowing from the coal and surrounding strata and collected in ditches at one side of the gangways and tunnels and flowing to the lowest point in the mines, or, in this case, the foot of the shaft, from which point it is pumped to the surface and either wasted or used in washing the coal in preparing it for market. At this colliery all the water that is pumped during the daytime or working hours is used in washing the coal. The sample of water sent had not been used for any purpose, having simply been collected and pumped in the usual manner and in this case collected by holding the jar under the discharge at the upper end of the column pipe.

This colliery prepares the coal by washing and uses the mine water exclusively for doing so. Some collieries use a proportion of fresh water for washing coal at times when fresh water is plentiful. At some collieries the mine water can be used for generating steam after having been in a measure 'purified,' but is never used when it is possible to get fresh, clean water for that purpose.

The water of this colliery has, so far as is known, never been used for generating steam.

I might add that what we sent is what may be considered a sample of the average water, but at the same time I wish to say that you would probably find no two samples of water sent from different collieries to be exactly similar."

THE SPENT TANNERY LIQUOR.

"One of the tanneries is a sole leather tannery, using no bark, but extracts for tanning. The principal tanning extract is quebracho—an extract made from a South American tree. Dry and salt hides are used and hair is removed by the lime process, not by sweating. The hides are soaked in water vats to soften them, then the fleshings, etc., are removed. The hair is then loosened by lime and removed by a de-hairing machine. Then the hides are placed in water vats and washed and then put in what is called a color wheel. This color wheel contains a very weak solution of tannic acid made by using the spent tanning liquors from the regular tanning process. After passing the color wheel, the hides are passed through acid vats to neutralize the lime and then through the regular tanning process. The color wheel from which the sample sent you was obtained contains the only tannic acid that is wasted. The sample was collected immediately before the wheel was emptied and shows the part of the tannery waste containing tannic acid. Two wheels are used each day and both deliver about 6,000 gallons per day to the total waste of about 100,000 gallons. The other part of the waste is from the soak vats, wash-wheels and vats, lime vats, acid vats and de-hairing machine.

The sample of the waste sent you causes but little trouble until the total waste reaches the creek, where the tannic acid combines with the iron in the water and forms the usual dark inky color. The Stoneham tannery uses hemlock bark and no extract."

When the regular tan-liquor has become very weak, and the leather will no longer take tanning from it in the usual process, it is put into the color wheel. Then into the wheel is put the leather before starting in the regular tanning process, so that this new leather that has a great affinity for tannin will remove from this weak liquor all the tannin possible.

This wheel is drum-shaped and the sides composed of strips arranged to allow free entrance and exit of the liquor contained in the vat in which the wheel is partly immersed and rotates.

For a matter of convenience the source has been represented on the second report by the letters A, B, C, D, E and F, which represented the different sources, as follows:

FROM CORRY.

A—From color wheel.

B—From general waste and contains waste liquor after its entrance into the settling tank with all the other waste.

FROM WARREN.

C—From the general waste and contains some tannic acid waste as well, as all other waste.

D—From the color wheel. This wheel is similar to that at Corry, but the liquors when used in this wheel are stronger than those used at Corry and contain more tannic acid. After the liquor has been used in the color wheel it is not wasted, but is added to stronger liquors and again used in the regular tanning process, so that there is no waste from this wheel to the stream.

E—Is a sample from what is called "run away liquor." This liquor is from the vat in which the leather is first put in the regular tanning process; because the leather at this time is new, almost all of the tannic acid is removed. This liquor is not wasted, as is the usual case, but is shipped to Ridgway, where it is used in making dyes and other by-products.

F—Is a sample from what is called the bleaching process. This waste contains sulphuric acid, as well as tannic acid. After the leather has been tanned, it is passed through a series of vats containing different strengths of alkali and acid for the purpose of removing the dark color obtained in the regular process and thus allowing of a lighter finish. This waste is allowed to run directly into the stream.

The three experiments agreed very closely except that the germicidal effect of the waters seemed to decrease on keeping them under artificial conditions in the ice box. The first experiment in a dilution of 1-500 of typhoid bacilli in mine water showed that they were materially decreased in number when plated immediately after being suspended in the mine water, and that they were absent after one hour. After a lapse of 10 days, the typhoid culture in the same dilution was again ma-

I—EXPERIMENT ON THE GERMICIDAL ACTION OF MINE WATER AND TAN-LIQUOR ON B. TYPHOSUS AND B. COLI COMMUNIS.

		At once	15″	1′	3′	6′	24′	48′	72′	96′
1st										
Mine water	B. typhosus 0.2 cc. + 100 sterile tap water.....	190 000	..	150 000	200 000	..	600 000	1,000 000	..	..
	B. typhosus 0.2 cc. + 100 sterile mine water...	2,500	..	0	0	..	0	..	..	..
	B. coli. 0.2 cc. + 400 cc. sterile tap water......	1,400 000	..	1,400 000	1,600 000	..	1,400 000	..	..	..
	B. coli. 0.2 cc. + 400 cc. sterile mine water	580 000	..	150 000	60 000	..	1,500	..	100	0
Tan-liquors	B. typhosus 0.2 cc. + 100 cc. sterile tap water..	110 000	..	150 000	200 000	..	600 000	1,000 000	..	..
	B. typhosus 0.2 cc. + 100 cc. sterile tan-liquor.	160 000	..	135 000	400	..	0	0	..	..
	B. coli 0.2 cc. + 400 cc. sterile tap water.......	1,400 000	..	1,400 000	1,600 000	..	1,400 000	..	..	..
	B. coli 0.2 cc. + 400 cc. sterile tan-liquor......	600 000	..	420 000	420 000	..	200 000	..	600	0
2nd										
Mine water	B. typhosus 0.1 cc. + 100 cc. sterile tap water..	54 000,000	50 000,000	54 000,000	50 000,000	54 000,000	54 000,000	..	..	..
	B. typhosus 0.1 cc. + 100 cc. sterile mine water	400 000	3	0	0	0	0	..	..	..
	B. coli 0.1 cc. + 100 cc. sterile tap water.......	80 000,000	80 000,000	70 000,000	75 000,000	70 000,000	..	..	..	..
	B. coli 0.1 cc. + 100 cc. sterile mine water.....	500 000	120 000	17 000	200	24	0	0	..	..
Tan liquor	B. typhosus 0.1 cc. + 100 cc. sterile tap water..	600 000	700 000	400 000	500 000	.. ..	..	..	..	..
	B. typhosus 0.1 cc. + 100 cc. sterile tan liquor.	200 000	60 000	7,000	600	200	0	0	..	..
	B. coli 0.1 cc. + 100 cc. sterile tap water	800 000	600 000	10,000 000	400 000	..	..	..	..	..
	B. coli 0.1 cc. + 100 cc. sterile tan-liquor......	500 000	300 000	240 000	120 000	100 000	210	0	..	..

terially reduced at once, but showed the presence of three colonies of typhoid after fifteen minutes' suspension in the mine water.

In reference to the spent tan-liquor, the typhoid showed a slight reduction when plated at once and similar reduction after one hour's emulsion, and marked reduction after three hours. and a disappearance after 24 hours. In emulsion of the tan-liquor after a lapse of 10 days, the typhoid showed a slight decrease at once, progressive decrease up to the sixth hour, and did not grow after 24 hours' exposure. The controls were perfectly consistent and normal, gradual increase taking place after the emulsion was made in some preparations in sterile water.

In reference to the colon bacillus, the reduction is much less. There is still, however, a germicidal action. It showed a reduction in mine water after being plated at once, and continued to reduce, although still present up to the third day. The dilution in the first experiment was 1-2,000. The organisms failed to grow after the third day; in the second experiment ten days later a dilution of 1-1,000 the reduction is relatively greater than in the first experiment with a dilution of 1-2,000, for the colon bacillus only grew up to the sixth and one-half hour, and could not be found after 24 hours' exposure.

In reference to the tan-liquor, the reduction of the colon bacilli is comparable, but much slower. The controls were normal in sterile water. It is therefore evident that in fresh mine water, the typhoid organisms will disappear at once, and when mine water has been kept under artificial conditions they do not disappear until one hour has expired. In fresh mine water, the colon bacillus will disappear after the third day, but when it is kept under artificial conditions may live longer. In the dilution of 1-500 (which is very high), tan-liquor has a germicidal effect upon typhoid after the third hour in fresh solution and after 24 hours in old solutions under artificial conditions. Spent tan-liquor shows much less effect upon the colon bacillus both when it is fresh and under artificial conditions, and shows a lower germicidal activity than the mine water throughout.

A forty-eight hours' bouillon culture of B. coli and a very old culture of B. anthracis, containing numerous spores, were

II.—EXPERIMENT ON THE GERMICIDAL ACTION OF TAN-LIQUOR ON B. COLI, COMMUNIS AND B. ANTHRACIS.

Dec. 27-Jan. 7, 1909. Rivas.

	At once	After 1 hour	After 3 hours	After 24 hours	After 48 hours	After 3 days	After 6 days	After 7 days
B. coli								
0.1 B. coli culture in 100 cc. tan-liquor, A	20 000	2,000	0	0	0	0	0	0
0.1 B. coli culture in 100 cc. tan-liquor, B	130 000	120 000	120 000	300 000	350 000	401 000	380 000	500 000
0.1 B. coli culture in 100 cc. tan-liquor, C	170 000	90 000	90 000	30 000	200	2	0	0
0.1 B. coli culture in 100 cc. tan-liquor, D	100 000	60 000	60 000	1	0	0	0	0
0.1 B. coli culture in 100 cc. tan-liquor, E	1,000	0	0	0	0	0	0	0
0.1 B. coli culture in 100 cc. tan-liquor, F	8,000	0	0	0	0	0	0	0
0.1 B. coli culture in 100 cc. sterile tap water	1,200 000	1,500 000	1,100 000	6,000 000	..	..	..	..
B. anthracis								
0.1 B. anthracis culture in 100 cc. tan-liquor, A	30 000	10 000	8,000	12 000	6,000	7,000	4,000	10 000
0.1 B. anthracis culture in 100 cc. tan-liquor, B	30 000	26 000	5,400	5,400	7,000	8,000	10 000	8,000
0.1 B. anthracis culture in 100 cc. tan-liquor, C	42 200	25 000	4,000	4,500	2,500	4,000	6,000	5,000
0.1 B. anthracis culture in 100 cc. tan-liquor, D	14 000	10 000	8,000	10 000	6.500	7,000	3,000	3,000
0.1 B. anthracis culture in 100 cc. tan-liquor, E	50 000	20 000	10 000	8,400	3,000	5,000	4,200	3,800
0.1 B. anthracis culture in 100 cc. tan-liquor, F	40 000	28 000	16 000	7,700	8,000	14 000	9,000	6,000
0.1 B. anthracis in 100 cc. sterile tap-water	120 0,000	100 0,000	120 0,000	140 0,000	120 0,000	150 000	1,400 000	1,600 000
Sterile water control	0	0	0	0	0	0	0	0
Medium control	0	0	0	0	0	0	0	0

selected for the second experiment. One-tenth of a cc. of the above cultures was added to duplicate samples of the tan-liquor from the above sources (A, B, C, D, E and F). In one serial of each the B. coli was added and to the other the B. anthracis, respectively; likewise one-tenth of a cc. of the cultures of B. coli and one-tenth of the culture of B. anthracis was added to two bottles containing 100 cc. of sterile water as control.

After the addition of the culture to the tan-liquor and the sterile water controls, the samples were thoroughly shaken and plated at different intervals, the first plate being made at once after the addition (the operation taking about five minutes). They were plated again after one hour; after three hours; after 24 hours; after 48 hours; after three days; after six days and after seven days, respectively. The result was as follows:

The B. coli in the tan-liquor A disappeared after three hours. In tan-liquor B, no germicidal action was shown; in tan-liquor C, it took six days to disappear; in tan-liquor D, it took 48 hours to disappear. In tan-liquor E, the B. coli disappeared after one hour, and likewise in tan-liquor F.

The tan-liquor shows very slight germicidal action on the B. anthracis; in no case did the latter disappear up to the seventh day, which is as far as the experiment has been yet conducted.

The tan-liquor A, E and F produced a decidedly germicidal action on B. coli after one hour. This action was less marked in tan-liquor D, taking 24 hours to disappear, and still less marked in tan-liquor C. It was apparently without any effect in tan-liquor B up to the seventh day. In general, it may be said that the tan-liquor has a germicidal action as a whole, when it is compared with the control of sterile water, to which the same amount of bacteria (one-tenth of a cc. of the culture was added) because this latter shows the number of bacteria to be over 1,000,000 in contrast to the number found in the tan-liquid in which from the first plating at once, up to the seventh day, the number of bacteria has been gradually reduced and then to a complete disappearance, with the exception of tan-liquor B, in which the reduction was never over 50 per cent. up to the seventh day.

To put the conclusions in fewer words:

Mine water will prevent the growth of typhoid bacilli after the lapse of one hour. Mine water will markedly limit the growth of colon bacilli so that they die off progressively and cannot be cultivated after a lapse of 24 hours. The organisms lived for three days but could not be found on the fourth day, in one experiment in which the dilution was high. Spent tan-liquor limits the growth of the typhoid bacillus and causes it to disappear after the sixth hour. Tan-liquor permits the growth of the colon bacillus up to the twenty-fourth hour and in one experiment where the dilution was 1-4,000 it was found after three days.

As to B. anthracis, the same may be said as in the case of B. coli, the tan-liquor in general producing a decided diminution in the number of bacteria, in all cases from plating made at once, up to the seventh day, but in no case was there a complete elimination of these micro-organisms from any one of the waters, showing, therefore, that the spores are not especially affected by the tan-liquor in question.

The only inference that can be drawn from the above experiments is that, so far as the risk of the most serious of all water pollutions is concerned, that by the typhoid bacillus and its companion and index, the colon bacillus, and inferentially of the cholera bacillus, which is known to succumb readily to sulphuric acid, the attempt to exclude mine water and spent tan-liquor from the streams which may eventually become sources of drinking water would be a mistake. Evidently neither of these organisms can live for any considerable time in water containing these wastes in any appreciable quantity. Especially is this true of that most dangerous and elusive bacillus, that of typhoid fever. Data are not yet available to indicate to what distance from the mine or tannery the protective influence of these wastes will extend. That of the mine water will evidently continue effective to a much greater distance than that of the tannery waste. As the waste is occasionally infected with anthrax spores, it should never be discharged into the streams in an untreated condition.

There has long been an opinion prevalent among those who have studied the health conditions of Philadelphia that the acid condition of the head waters of the Schuylkill River, owing to mine drainage, was an important factor in holding in check the prevalence of typhoid fever in that city.

These results indicate that this opinion had a solid foundation.

FERMENTATION IN THE TANYARD.[1]

By Dr. L. A. Groth, K.G.V.

The unprecedented advance which has taken place during recent years in the many-sided development of bacteriology, the science which is devoted to the study of those low forms of life, which are grouped together under the name of micro-organisms, has opened up, so to say, a new world of study, which will bring forward results of incalculable importance.

The great discoveries made by Pasteur have been the foundation upon which subsequent investigators have based their researches, and which have already produced results, to some sections of the industrial world, the immense value of which it is impossible to over-estimate.

Pasteur has thus clearly distinguished between the bacterium, which causes the "acetic" or vinegar fermentation, which is a process of "oxidation," transforming alcohol into vinegar; the bacillus including the "lactic" fermentation, which is a process of "decomposition," in which sugar yields lactic acid; and that which brings about the "butyric" fermentation, a process of "reduction" in which butyric acid is formed.

All organic substances, particularly animal matter, attain with extreme rapidity putrid fermentation. The richer the material is in oxidizable substances, the greater the chance of infection, and consequently of destruction.

Hides, fresh from the slaughter house, soon ferment, and if tanning operations are delayed they undergo a very great change, which results in the liquefaction of a portion of the gelatinous matters they contain, which liquefaction is caused by the development of bacteria. Hence an inevitable loss of weight and tenacity,

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[1] From *The Leather Trades Review.*

since the gelatine thus transformed cannot be coagulated by the tannin.

This putrefaction continues even in the presence of the lime used in the unhairing process, and throughout the operations previous to the hides being immersed into the tanning liquor.

The decomposition of tannin has been attributed wrongly to the action of the oxygen of the air, as bacteriological investigations now prove it to be due to the action of micro-organisms, and that the tannin decomposes spontaneously, that is to say, without addition of fermenting matter, but solely under the influence of such micro-organisms, and is transformed into gallic, butyric, and ellagic acids, thus forming a solution entirely unfit for tanning purposes.

When the hides, therefore, are immersed in the tanning liquor, containing gallic acid, together with other compounds, such as mineral salts, resinous matters, and glucose, etc., matters which all, more or less, facilitate the destructive decomposition, the fermentation of the hides induces that of the material in which they are immersed, and two concomitant destructions are set up, that of the hides and that of the tannin and assimilable substances, which will result in a fictitious loss of tannin and a variable weight in the manufactured product, disproportionate to the quantity of raw material employed. A considerable loss of time will also occur by the weakening of the liquor, which cannot act with its full original strength, the tannin having been converted principally into gallic acid, which is also destroyed.

The rapidity of these destructive actions upon the hides and tanning materials alike may be judged from the enormous multiplication of these micro-organisms. One grain of finely ground oakbark has been found to contain 60 millions of bacteria. The loss produced during the tanning process is thus not only enormous, but very rapid.

Unfortunately, the fermentation does not stop with the leather being removed from the tanyard. The leather being a hygrometric substance, and besides containing, on leaving the drying sheds, more or less a quantity of water, is very susceptible of deterioration.

In tanned leather, placed in piles, according to the heat and surrounding humidity, a great change is produced. If the humidity is sufficient, the temperature of the pile increases, and may even reach 40° to 45° C. This increase of temperature is the result of an intense development of cryptogams, the leather deteriorates on both sides, grain and flesh alike, and at the places attacked stains appear, arising from the appearance of species of cryptogams, which germinate on the surface and penetrate the hide.

In leather almost dry, the fermentation is less intense, but, nevertheless, there is produced a prolification of micro-organisms which attack the leather, decrease its weight, and reduce its tenacity.

The cryptogams most frequently noticed is a mucor. Its appearance is manifested on the surface of the leather by the emission of a grey, silky powder puff (mycelium), which speedily becomes covered with a greenish dust. A microscopic examination reveals colorless segmented myceliums terminated by a head or bag of a circular form, filled with round spores of yellowish green. When the mucor is ripe the spores burst out, and from each spore, which falls on fertile soil, a mycelium is developed, which spreads out and bears at its extremity a cord of fresh spores On cutting the leather thus attacked, the mycelion filaments present numerous branches spreading through the grain and flesh cells. In numerous instances these myceliums penetrate the leather entirely, and the cryptogamic development appears on both the grain and flesh sides.

From the foregoing the following conclusions may be drawn:

1. That all fresh hides or skins placed in contact with tannin set up the fermentation of the latter, and, consequently, produces its destruction.

2. That whenever hides and skins in fermentation (which is always the case) come in contact with tannin, this body is transformed, principally, into gallic acid (which itself is destroyed), making the solution unfit for tanning purposes.

3. That all hides and skins fermenting lose their gelatine, which, liquefied by the action of the bacterian organism, cannot be coagulated by the tannin.

4. That pure tannin decomposes spontaneously, that is to say,

without addition of fermenting matter, but solely under the influence of micro-organisms, and is converted into gallic, butyric, and ellagic acids.

The destructive actions of the micro-organisms can, as is well known, be temporarily reduced and prevented by the employment of antiseptics, or by heating the tannin liquor, but a "permanent" preventive is thereby far from being obtained; besides, many of the antiseptics thus employed have an injurious action upon the tanning liquor, and consequently, upon the leather produced.

With a view of ascertaining if, and how far the application of electricity would act in preventing the fermentation and decomposition of the tanning liquor, I have made extensive experiments, the results of which seem to prove that the electricity, applied in a certain manner, not only entirely prevents the decomposition of the tannin, but there is also every reason to believe that the leather produced in a tanning liquor thus electrically treated is entirely protected from future deterioration by the destructive actions of the microorganisms. Electricity seems, therefore, even in this respect, to play an important part in the leather industry.

THE AMOUNT OF SKIN SUBSTANCE DISSOLVED IN FELLMONGERS' COLLECTING LIMES.[1]

By J. T. Wood and S. R. Trotman.

In the Leather Trades Review, of June 9, 1909, Mr. Seymour-Jones drew attention to various causes of looseness in sheep skins. By "looseness" is meant that condition of the skin fibers in which, instead of being compact and close like a piece of felt, they are loosely united like the texture of a blanket. In a short introduction, the editor remarks: "It is not too much to say, perhaps, that the matter of sheep pelt improvement is almost of national importance, for the demand existing today for high grade sheep pelts can hardly be met, whilst, on the other hand, common stock can hardly find a purchaser at remunerative prices."

Amongst the causes of looseness, a prominent place is given

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[1] From *Journal of the S. C. I.*

to the loss of skin substance caused by the condition of the lime liquor in which the pelts are collected in fellmongers' yards before being sent in to the leather dresser or tanner. The common practice is to throw the fellmongered pelts into an old lime, which is claimed to be a weak one. Some yards clean the lime-pits out after each lot of pelts and others after a few lots have been through, others every six or twelve months, and in one case they never remember cleaning out the limes, but they were freshened up from time to time. Here we have cases—and they are but too numerous—where fellmongers, not through carelessness, but through want of knowledge, keep the old limes for storing up the pelts pending sale.

Lime alone is capable of dissolving the interfibrillar substance of the skin, but in its fresh condition it will not attack the actual skin fibers. Out of each lot of pelts the lime dissolves a certain quantity of the interfibrillar substance, and this affords nutriment for bacteria, with which the pulled pelts are swarming. This bacterial lime is now capable of attacking the fibers of the skin, and thus taking out valuable substance, which should be made into leather. A new lime is antiseptic, and if pelts, after pulling, are washed in clean water and put into such a lime, they are practically sterilized for the time being, and will keep intact until the lime has dissolved out sufficient skin substance to act as nutriment for bacteria. It is these bacteria which produce the ammonia compounds, and which effect the solution of the skin substance.

The presence of dissolved skin substance in the limes may be demonstrated by placing 50 cc. of the filtered lime liquor in a 100 cc. cylinder, adding 10 cc. of glacial acetic acid, and filling up to 100 cc. with a saturated solution of common salt; the dissolved skin will be precipitated and float to the top. This method has been proposed by Gordon Parker and others, and has been in practical use in the tan-yard for many years.

In the Trent Bridge Laboratory, we have used hydrochloric acid in excess, and saturated the solution with salt. In this way somewhat more skin substance is precipitated than by the method mentioned by Seymour-Jones (*Leather Trades Review,* June 9, 1909,) in which the solution is made only slightly acid, and not completely saturated with salt. In the article referred to the number of cc. occupied by the skin in the tube after standing for one hour are termed "degrees," and for works use this is a convenient way of expressing it.

At Trent Bridge Works, Nottingham, we have made a number of analyses of fellmongers' collecting limes, and by permission of Sir John Turney, we are able to give the results of these analyses. The limes were obtained from districts as far separated as Scotland and Cornwall, and thus represent a fair sample of the condition of fellmongers' limes in this country.

The following are the details of the analytical methods employed. The liquors were filtered through a thick plug of cotton wool for analysis. The total alkalinity was determined by titrating 10 cc. of the filtered lime liquor with N/10 hydrochloric acid, using phenolphthalein as indicator. A portion of the filtered liquor was boiled in a Kjedahl apparatus, the expelled ammonia being collected in excess of decinormal acid and titrated (see foot note). The residue in the flask was titrated with phenolphthalein and decinormal acid, the acid used being calculated to lime. Soda, if present, was of course included in this figure, but there was in no case reason to suspect its presence.

The dissolved hide substance was obtained from the total nitrogen by multiplying by the factor 5.62. In determining the total nitrogen, the liquor was first acidified and concentrated, the ammonia already present being assumed to be derived from hide substance. This is undoubtedly the case, since the degradation of the skin under the influence of putrefactive bacteria rapidly passes the peptone stage with the production of amines and ammonia. A dilute solution of gelatine free from ammonia when incubated with a drop of lime liquor gave reactions for ammonia in three days.

The following is a further analysis of lime liquor 17[1] in which the nitrogen has been differentiated.

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[1] The more accurate method of estimating ammonia in lime liquors of Procter & McCandlish (J. S. C. I., 1906, p. 254), was not used, as we considered the distillation method sufficiently accurate for works control.

Percentage of nitrogen present as hide substance	35.5
Percentage of nitrogen present as ammonia and bodies capable of yielding ammonia when boiled with alkali	21.4
Percentage of nitrogen present as peptone	43.1

The nitrogen as albumose or hide substance after the first stage of hydrolysis was determined by precipitation with zinc sulphate. Ammonia and ammonia-yielding compounds were obtained by direct distillation, and the difference between the sum of these and the total nitrogen was assumed to be peptone nitrogen.

The results on the table are of interest, as we believe they show for the first time in what a bad condition many of these limes are. In general, the older the lime the more skin substance it contains in solution, but the factors of temperature and quantity of skins put through cause this to vary. If it can impress upon fellmongers, and those who have to deal with pelts, what waste is going on in this direction, it may be pointed out that an amount of skin substance equal to a good pelt, weighing 7 pounds, is dissolved in every 20 liters (about two buckets) of sample No. 4. For the mean of all the limes examined, such a pelt is contained in every 63 liters of liquor. The minimum shows one pelt in 300 liters (sample 8), but this is practically dirty water through which the skins have been drawn.

As to the nature of the skin substance dissolved in the limes, Van Lier (see this J., 1909, 1150,) has shown that the true interfibrillar substance of skin is totally extracted by means of weak lime solution (about 0.7 gram of lime per liter) in from 8 to 28 days, according to the nature of the skin (eight days for cow and horse; 28 days for calf), but this is for quite fresh lime solution renewed every 24 hours. The alkalinity of such a solution is 2.25 cc. N/1 per 100 cc. In the limes shown in the table it will be seen that the alkalinity in one case reached 12.8 cc. In addition to this excessive alkalinity, a microscopical examination shows the presence of numerous bacteria in these limes, which undoubtedly attack the actual fiber of the skin, and take out substance which should be made into leather.

In a paper entitled "Recent Progress of Tanning as a Chemical Industry" (J. S. C. I., Nov. 30, 1903, p. 1274,) one of us has already suggested that the role of bacteria in the liming process ought to be studied in our research laboratories in the same way that the bacteria in tan-liquors, bates, and drenches have been investigated by Andreasch, Becker and Wood. The various species growing in the liquors should be isolated and their life history and action on skin worked out. In such a way the process of liming as carried out in practice would be thoroughly illuminated.

Approximately 0.2 per cent. of nitrogen corresponding to 1.12 per cent. of skin substance is equivalent to 76 of Seymour-Jones' degrees, so that when the skin substance passes this amount it is no longer possible to distinguish between the limes, as the whole tube is filled with a mass of separated skin.

In conclusion, we recommend the following limits for a lime in which pelts are collected: Lime in solution not to be less than 0.1 gram of CaO per 100 cc. The alkalinity should not exceed 6 cc. N/1 per 100 cc. To attain this standard the pelts would

ANALYSIS OF FELLMONGERS' LIMES, USED FOR COLLECTING SHEEP PELTS (GRAMS PER 100 CC.).

No. of Analysis	Lime (CaO) in solution	Alkalinity as cc. normal acid per 100 cc.	Ammonia	Total nitrogen by Kjeldahl's method	Dissolved hide substance
1	0.030	6.08	0.039	0.230	1.292
2	0.100	6.80	0.022	0.148	0.832
3	0.034	6.40	0.065	0.165	0.971
4	0.061	12.80	0.090	0.600	3.370
5	0.039	6.56	0.033	0.224	1.260
6	0.076	6.04	0.025	0.126	0.708
7	0.112	5.32	0.035	0.161	0.905
8	0.088	3.88	0.008	0.023	0.129
9	0.039	4.90	0.023	0.187	1.050
10	0.072	10.60	0.041	0.196	1.102
11	0.117	8.84	0.038	0.406	2.280
12	0.090	4.20	0.014	0.134	0.753
13	0.109	5.90	0.028	0.117	0.657
14	0.103	6.00	0.031	0.157	0.882
15	0.086	6.06	0.026	0.098	0.550
16[1]	0.091	4.50	0.022	0.126	0.710
17[1]	0.100	8.40	0.029	0.168	0.940
18[1]	0.100	5.10	0.021	0.096	0.539
19[1]	0 140	7.12	0.036	0.168	0.944
Min.	0.030	3.88	0.008	0.023	0.129
Max.	0.140	12.80	0.090	0.600	3.370
Mean	0.083	6.50	0.033	0.105	1.043

[1] Nos. 16 and 19 are collecting pits for linings. Nos. 17 and 18 are the spent pits from pelts limed for splitting.

require to be well washed in clean water after pulling, and the lime pit cleaned out and renewed after two lots of pelts have been put through.

We would suggest that the Fellmongers' Association might advise fellmongers gratis as to these conditions, the ascertainment of which is of a very simple character.

ABSTRACTS.

The Diffusion of Vegetable Tan-stuff Solutions and Its Significance in Tanning. Franz Neuner. *Der Gerber,* 1910, [36], Nos. 850, 852; pp. 31-2, 61-3.—The author follows Stiasny in defining tanning as essentially an adsorption process of colloidal tannin, accompanied by secondary chemical reactions. Colloids such as glue, dextrine, albumin, etc., are distinguished from the crystalloids such as salts, sugar, etc., by the slow diffusion of their solutions through membranes; they do not form genuine solutions. Tannins are intermediate in character; they form colloidal solutions which diffuse to some extent. The penetration of tannin solutions into hide may proceed in two ways. When the fiber is loose, capillary action results and there is an infiltration; when the hide is well plumped, it is analogous to a jelly and diffusion phenomena prevail. The extent of tannin adsorption is generally less the greater the diffusibility of the solution. According to the theory of diffusion, the smaller the particles of tan-stuff, the easier they diffuse, approaching the crystalloids. On the contrary, the larger the particles, the easier they are precipitated or adsorbed, hence there is a certain contrast between diffusion and adsorption and the substances producing them.

The author next proceeds to describe some experimental studies on diffusion of tan-stuff solutions. An open cylinder of 10 cm. diameter was closed at the bottom by a membrane of parchment paper. In this cylinder were 150 cc. of the solution to be dialyzed and the whole placed in a concentric glass cylindrical basin of 15 cm. diameter containing 650 cc. pure water, both liquids at the same level. The liquids were made antiseptic with chloroform and the dialysis let proceed for 5 days at a temperature of 15 to 20°. The outer and inner solutions were then analyzed, as well as the membrane. The original extracts used were adjusted to contain 1.75% total solubles.

As a sample, the complete record of an experiment with mimosa is given:

	Total solids		Non-tans	Tans
	Gms.	Per cent.	Gms.	Gms.
I. Original solution	2.6448	100.00	0.7329	1.9119
II. Dialyzed solution	0.5551	20.99	0.3202	0.2349
III. Residual solution	2.0348	76.94	0.4244	1.6104
IV. Absorbed by membrane	0.0523	1.98		
II + III + IV (check) ..	2.6422	99.91	0.7446	1.8453

That is, 43.69% of the original non-tans diffused into the outer (dialyzed) solution and 12.29% of the original tans.

The following results were averaged from many determinations:

	Per cent. total solids diffused	Per cent. non-tans in total solids
Tannin	6.30	6.21
Malet	11.34	17.14
Mangrove	12.11	16.09
Quebracho	12.75	11.66
Mimosa	20.99	27.71
Valonia	21.27	31.29
Oakwood	21.49	36.30
Chestnut wood	23.10	34.31
Oak bark	25.70	46.59
Myrabolams	32.09	46.35
Pine bark	34.32	54.63
Sumac	45.78	67.69

The speed of diffusion of the total solids is seen to increase with the amount of non-tans, these being more crystalloid in character.

In the next table, showing the speed of diffusion of the tans, the order is similar, though there are some differences.

	Per cent. original tans diffused	Per cent. non-tans in total solids
Tannin	4.20	6.21
Mangrove	4.88	16.09
Malet	5.22	17.14
Oak bark	8.62	46.59
Quebracho	10.16	11.96
Oak wood	10.79	36.30
Mimosa	12.29	27.71
Valonia	14.19	31.29
Sumac	15.17	67.59
Chestnut wood	17.69	34.31
Myrabolams	19.18	46.35
Pine	20.11	54.63

An entirely different order was found on comparing the speed of diffusion of the original non-tans; of these there diffused in per cent.:

Quebracho	32.33	Oakwood	40.26	Myrabolams	47.02
Chestnut wood	33.47	Mimosa	43.69	Mangrove	49.97
Valonia	36.80	Oak bark	45.29	Sumac	60.46
Malet	40.91	Pine bark	46.13		

The relative diffusions of the non-tans are seen to be entirely independent of those of the tans. Neither are the differences so great among themselves.

In most cases during dialysis, there was an increase of total non-tans through decomposition of some tannin. After dialysis, the total percentages found based on 100 original were:

	Non-tans	Tans
Quebracho	107.58	98.05
Chestnut wood	96.37	99.81
Oak wood	110.57	91.51
Pine bark	100.82	98.71
Oak bark	108.71	91.05
Maletto	111.75	97.89
Mimosa	101.60	96.53
Mangrove	93.53	101.27
Myrabolams	103.37	96.35
Valonia	102.10	93.40
Tannin	94.71 (?)	96.54
Sumac	100.01	99.03

The decomposition was much more rapid than that resulting on mere standing of the solution without dialysis.

The above results correspond well with the conclusions drawn from practical experience. The rapidly diffusing tans of pine, chestnut and myrabolams are recognized as quick tanning agents. Mangrove and maletto are slow and likewise diffused slowly. Tannin (gall-nuts), however, is not considered a slow penetrating tan. The difference in diffusion between chestnut and oak is remarkable. Chemically, these tanstuffs cannot be distinguished, but practice shows that chestnut penetrates more rapidly than oak, which agrees with the diffusion ratio.

It is seen why pine, chestnut and sumac are best suited for a fore-tannage; they diffuse quickly and penetrate rapidly, while the slower diffusing maletto, oak and quebracho are better suited for the full tannage. If slow diffusing materials are to be used for the fore-tannage, they must be used dilute, which has the effect of increasing the diffusion, as shown later. For the later stages of the tannage, slow diffusing tans can act by infiltration, since the structure of the fiber has been modified by the fore-tannage.

The percentages of total solids (doubtless exclusively tans) absorbed by the parchment were:

Mangrove	0.40	Maletto	0.78	Quebracho	1.54
Oak wood	0.65	Oak bark	0.87	Myrabolams	1.65
Sumac	0.75	Chestnut	1.09	Mimosa	1.98
Valonia	0.75	Pine	1.52	Tannin	3.31

The order is much the same as in the relative yields from these materials in practical tanning, and the parchment seems to have undergone a sort of tannage. Valonia forms an exception, it ordinarily giving good rendement. Here the parchment seems to fail in holding the ellagic acid which is deposited on leather fiber.

(To be Continued.)

Comparative Experiments Upon the Tanning Effect of Cold Soluble Sulphited and Non-Sulphited Quebracho Extracts. H. FRANKE. *Der Gerber,* 1910, [36], No. 854, pp. 93-4.—It is sufficiently well known to every tanner that quebracho tan-stuff not only possesses to an eminent degree the power of giving weight to leather, but that it also has certain defects which are disagreeably manifest in practice. If boiling water be used to well extract the tanning substances from the quebracho wood a liquor is obtained which is extraordinarily turbid on cooling, having almost the appearance of thin mud. The substances which make the liquor so unsightly are already present in the wood. They are almost insoluble in cold water.

To avoid this inconvenience, the readiest means is apparently to extract the quebracho wood with cold water. One may expect in this way to obtain liquors which contain only the readily soluble portions of the quebracho, while the difficultly soluble part remains in the wood. But on making the extraction in this way, it is soon seen that by means of cold water only a minimum part of the easily soluble substance is obtained; this can only be extracted by the aid of boiling water.

It cannot be doubted that liquors so much fouled with insoluble matter may produce disagreeable consequences in the tannage. If the tanning for instance, is carried out by suspension, the slime readily deposits on certain parts of the leather. In this manner stains are formed. Further the tanning is retarded in the places covered with slime and the possibility of a uniform tanning through is questionable. These well known facts force the practician to always more or less clarify the liquors.

The simplest process consists in leaving them stand several days in clearing vats. It is indeed impossible in this way to obtain solutions which are really clear, but a considerable portion of the insoluble substances settle out. Liquors only partially thus clarified are tolerably usable for tanning. Such a clarification is unavoidably necessary, although even it has its disadvantages. Aside from the fact that this process, although simple, consumes time, there is a considerable loss of tanning substance during the settling. The gradually precipitating sediment has the property of absorbing considerable amounts of tannin, and thereby weakening the liquor. A very considerable loss of useful tans is therefore unavoidable.

It is therefore of the highest value to the tanner that the extract industry has succeeded in producing quebracho extracts completely free from insoluble substances. Until recently the "cold soluble quebracho extracts" which come into commerce owed their ready solubility to a radical chemical transformation by sulphiting the quebracho tan-stuff. The extracts recently manufactured at the factory of Dr. Albert Redlich at Wilsdorf, near Bodenbach-on-the-Elbe, are, on the contrary, pure products. These extracts are the product of liquors which have been freed by a rational clarification of all insoluble substances. Such a manufacturing process furnishes an extract which should especially possess the advantageous properties of the pure tanning substance of quebracho.

Laboratory experiments prove that the quebracho extracts manufactured by this clarification are far superior to sulphited extracts in weight-giving properties.

Comparative experiments were made at first with hide-powder. These experiments, made according to the method of Youle and Griffith, were intended to show what is the total increase of weight of a fixed amount of hide-powder subjected to the action of liquors of equal strengths from cold soluble sulphited and non-sulphited extracts. For these tanning experiments the commercial quebracho extracts were used.

As to the details, the following may be noted; the extracts employed were dissolved in so much water as to give liquors of about 6 per cent. tans. The analysis (filter method) gave:

	Sulphited extract	Non-sulphited extract, "Triumph"
Total extract	7.7	6.9%
Tans	5.9	5.9
Non-tans	1.8	1.0

Further, for each experiment 5.90 gms. hide-powder (5.00 gms. dry) were taken and agitated with 125 cc. of water in a shaking apparatus. Then 125 cc. of tan liquor were added in separate 25 cc. portions, agitating one-half hour after each addition. After the last addition agitation was maintained one hour, when the tannage was considered complete. The entire tannage therefore was made with 125 cc. of a 6 per cent. liquor, which at the close was diluted to 250 cc. This was separated from the hide-powder by filtration through gauze. In order to determine the increase of weight of the hide-powder, it was necessary to establish the amount of extractive matter still remaining in the liquor. The following figures were obtained:

	Sulphited extract	Non-sulphited extract
Total extract before tannage (250 cc.)	9.6463	8.5750 gms.
Total extract after tannage (850 cc.)	6.2200	3.7125 "
Total extract absorbed	3.4263	4.8625 "
Total extract absorbed	35.52	56.71%
Increase of weight	68.53	97.25 "

On comparing the numbers obtained, it is concluded that the non-sulphited extract gives a much more favorable increase of weight than the sulphited extract.

The same result is arrived at from experiments in tanning leather. In making these equal weights of white calf-skin were taken and care used in the parallel experiments to add the tan-stuff regularly in equal amounts. Laboratory experiments of this sort give the best representation of the tannage on comparing the compositions of the finished leather. This is shown below; the numbers are based upon an average moisture content of 18 per cent. Only the last numbers are comparable.

	Leather tanned with			
	Sulphited ext.		Non-sulphited ext. "Monopol"	
Moisture	14.47	18.00	18.00	14.75%
Ash	2.55	2.44	1.71	1.78
Fat	2.00	1.92	1.83	1.90
Loss by washing	6.85	6.57	6.13	6.38
Leather (hide) substance	48.00	46.02	42.38	44.06
Fixed tannin	26.13	25.05	29.95	31.13
Nitrogen in leather	8.5	8.2	7.5	7.8

From the leather analysis may be computed:

	Rendement number	Tannage number
Leather from sulphited extract	217.3	54.4
Leather from non-sulphited extract	235.9	70.8

The tannage number expresses how many parts of tannin are fixed by 100 parts of hide substance. It is seen to be considerably higher with the non-sulphited extract.

From the rendement numbers may be computed the approximate yields in leather that would be obtained with the tan-stuffs in question. Here also there is a striking difference in favor of the non-sulphited extract.

The leather rendement (reckoned on white weight) amounted to 41.48 per cent. with the sulphited extract and 45.05 per cent. when the non-sulphited extract was used for tanning.

The Building of the Freiberg Experiment Station for Leather Industry. *Ledertechn. Rundschau,* 1910, No. 9, pp. 68-70.—From the last annual report are reproduced four floor-plans with description. The basement contains storage room for glassware, a photographic dark-room, leather stock-room, a large room for experimental tanning, a packing room, etc. The main floor is occupied mainly by laboratory rooms. The second story contains the office and laboratory of the director; some other special laboratory rooms, a room for hide-powder, library and considerable space for collections. The third story contains lecture room, additional business offices, etc.

The Profitable Working of Colonial Sheep-skins. *Ledertechn. Rundschau,* 1910, Nos. 7-9, pp. 49-51, 57-9, 66-7.—Domestic sheep-raising has enormously fallen off in Germany and more or less in other European states, the soil being needed for more profitable returns. Foreign sources are now the chief supply, South America, Australia, the Cape and German colonies. Germany does not import much crude sheep-skin, but derives much of her wool from France. The greater part of the colonial sheep-skins are worked up in South France, which has long had a monopoly of this industry. The writer thinks Germany should produce more in this line; economical conditions are equally favorable for the most part and the supremacy of France is due to superiority in the manufacture itself. The French give especial attention to furnishing high grade wool and this enables them to manufacture the secondary product, leather, at a low figure.

Some account is given of the crude material. In the colonies sheep are bred exclusively for wool and the hides are derived from such beasts as are slaughtered for food and those which die from epidemic. Irregularities in drying, easily occurring in those primitive districts, affect the grain of the future leather. After arrival from the interior at the seaport, the skins are sorted and prepared for shipment, being first sprinkled with an arsenic solution mixed with a decoction of tobacco to prevent injury by insects. It is imperative that thorough drying follow. For economy of space during transport, the hides are compactly bundled under hydraulic pressure. In case they are not well dried, this imperils over-heating and fermentation, producing local damage during transport; hence it is well to unpack soon after delivery and sort out and air the damaged hides.

For softening, the hides are laid flat, wool up, in the empty vat until this is three-fourths full; they are then weighted and soft, cool water run in. An addition of 300 gms. caustic soda to the cubic meter is made. If a special reservoir cannot be used for preparing the soak liquor, the caustic soda solution is run in uniformly together with the water at proportionate rates with thorough mixing before striking the hides. The action of the alkali is antiseptic and it also swells and loosens the hide fiber and benefits the wool itself by partially saponifying the dried sweat: if too much alkali is used, however, the wool itself is attacked. After 24 hours the water is run off and the hides are worked on a machine not known in Germany, the "sapreuse." The hides here pass between two rollers, one of fluted iron, the other of rubber, which squeeze out the softened dirt. A spraying with water immediately follows, while at the same time a cylinder with hook-shaped ribs combs out the wool, removing the burrs, etc. This machine treatment dispenses with beam work. The hides go from the sapreuse back into the soak, which is strengthened with from one-half to the full amount of alkali first used. The softening is complete in another 24 hours.

The de-wooling is the most important part of the work. To produce good wool and high yield, the sweating process is only to be considered, which is quite different from the "Schwöden" (lime treatment) employed in German tanneries. This last ruins the wool and is only to be recommended for skins with poor wool: these by nature give the best leather. For fine wool then, the sweating process is to be chosen. This must be conducted very systematically, and with great regularity. The sweating chambers are best below ground or in any case guarded from changes of weather and temperature, which are of great influence. The uniform climate of South France greatly favors the process as carried out there. The chambers should be 2¾ m. high, with insulated walls and ceiling and tight closing ventilators. The hides are hung 15 cm apart from hooks set in beams in the ceiling, which are about 90 cm.

apart. The base of the room forms a reservoir containing water 40 cm. deep, covered by an open-work, removable flooring. The tight closing doors open into a common corridor and not into the free air. It is best that the room be entirely filled with hides, 200 to 300 hides being a good size. The water is warmed by steam to 23 to 26°, according to season, etc. The temperature is of great importance and is observed on a bent thermometer, with its scale outside the room. Before warming the water, about one-fourth liter ammonia water is added for each dozen skins. The action of the moist ammonia vapor is to dissolve the hair roots and open the pores of the hide. To control the process, the hide is examined at the back of the neck; if the wool yields here, the entire hide is ready. Any unfinished hides are sorted out and hung up together in another chamber and sweated again a few hours. In the normal process the wool may be pulled the next day. If the process be regular, there is little danger of the wool being loosened prematurally with damage to the hide as in the old-fashioned method. Should this threaten, the doors and ventilators are opened, the water drawn off and replaced by fresh, cold water. As a rule, however, airing of the chambers and corridors is avoided.

Wool-pulling in France is done by hand or with the aid of slickers made of rubber; women generally do the work. The wool is carefully laid away as it comes from the hide without disturbing the staple, and then commands the same price as shorn wool. On a large scale, the dewooling may be effected by machinery, the skins being first well sorted. This process gives clean hides and good leather. In France the wool-pulling and tanning of sheep-skins are carried out as separate industries. The dried "sweat pelts" are also sent to other states. They are not regarded as high grade ware in Germany, and moreover the best sorts are sent to America or kept by the French tanner. Pickling is also employed for the exported hides. The greater part of these sheep-skins, are however, tanned in France, producing leather which competes closely in foreign markets. Also chrome tannage has been introduced with success. If the German tanner hopes to substitute a home product, he must pay more attention to the wool.

Fundamental Rules for Practice. L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, Nos. 10-11, pp. 73-6, 81-3.—The writer (director of practical work in the Freiberg Tanning School) is the more convinced as his experience increases, that leather making, like everything else, proceeds according to fixed natural laws. The processes are complicated and unfortunately too little investigated, but there is abundance of material results for a profitable discussion. The practician himself recognizes the domination of laws unknown to him by rigidly adhering to empirical principles. It is emphasized that the young tanner who intends to specialize, should nevertheless acquire a thorough foundation in *all* the fundamental principles pertaining to the entire technology of leather manufacture.

1. *Preparation of Vegetable Tanning Liquors.*—In the leaching of the crude materials, the law of diffusion is prominently active. When two liquors of unlike concentration are separated by a membrane, they mutually pass through this and circulate until both are equalized to the same concentration. As an example, a tan-bark removed from a saturated liquor and placed in fresh water would diffuse its included concentrated liquor into the water and vice versa until equilibrium resulted and a uniform dilution was reached. What is not so often recognized, is that the process may be reversed. The following precept may be laid down: A thoroughly leached bark is unsuited for the filtration of good liquor, for it withdraws tannin from this and must be extracted again to avoid loss. For example, if a leach vat contains 6,000 K. of wet leached bark, two-thirds being water, and 4 cubic meters of a liquor containing 120 gms. tannin be slowly filtered through, the tannin will finally be equally distributed and the liquor naturally weakened one-half, and the bark enriched with the rest. If 8 cubic meters had been added the loss would have been one-third, with 12 cubic meters, one-fourth, and so on. In general, the greater the quantity filtered, the greater the absolute amount of tannin taken up by the bark, but the increase is slower as the liquor increases. Filtration is generally rapid and the dilution is not so complete as in the extreme case described above, but generally so much liquor is filtered that the bark becomes highly enriched and must be leached again.

Another principle is that the only method of increasing the extraction effect in a system at equilibrium is to elevate the temperature, thereby increasing the solvent power; new material goes into the solution and circulation ensues until again balanced. The end result is the same whether the balanced cold solutions be warmed or the original extraction be warmed at the start. Movement of the bark or liquors will not increase the final effect for any given temperature, but may *accelerate* the result, as is practically done by stirring or transferring the liquors by pumping. This situation is well realized in the "Automat" extraction apparatus; here the principle of opposing currents is applied. The bark as it is leached is continuously in contact with weak liquor; equilibrium is unbalanced and maximum action results. It is quite different in the so-called extraction battery, whether a series of open vats or closed copper vessels. Here the liquor remains for some time in contact with the wet bark until equilibrium is established, and only when the liquor is forwarded to stronger bark does the circulation begin anew.

Relatively few practicians in the writer's experience seem to have a clear grasp of the fact that in this method of successive extraction a bark is treated with nearly twice (minus 1) as many different liquors as there are vats before it is thrown away. He shows by schematic diagrams, that in a series of 6 vats, where the cycle is begun by leaching the nearly spent bark with fresh water and completed by leaching fresh bark with the last liquor, that 6+ 5 = 11 progressive shifts of the entire series of liquors are employed to completely leach one charge of bark.

(*To be Continued.*)

Wrinkled and Folded Grain. Wilh. Eitner. *Der Gerber,* 1910, [36], No. 853, pp.77-80.—This often occurring fault was recently illustrated by samples of lamb-skins (in the white) which showed a marked folding or furrowing of the grain lengthwise instead of the natural breadthwise fold. The furrows were deep, unyielding to strain, and took less dye, so that the dyed leather was streaked. The manufacturer stated that this defect recurred each winter at the cold periods.

In explaining this, the nature of hide itself must first be considered. The grain layer is of fine yielding texture, while the body or core of the skin is of a coarser, less elastic, solider structure. Consequently with an unworked skin, the outer layer will wrinkle up, or as stated in trade parlance, "the grain is longer than the core (Kern)." A hide tanned in its natural condition may then produce more or less of the folded grain referred to. In glove leather manufacture this defect only occurs when dung bating is employed and not with the mechanical working process (Façonniren). This is because the vigorous handling stretches the core and brings it to the same tension as the grain.

The first and most productive cause of the fault as a rule is insufficient soaking. If the interior of the skin be not sufficiently softened, it cannot be remedied in the limes unless these be stale and weak; a fresh lime will not soften. In the dung bate, the softening of the core may be attained, but this is seldom prolonged enough. In the case above cited, the trouble was doubtless due to incomplete soaking, which would be sluggish in winter.

Another factory sent a sample of dyed glove leather showing the defect in question. The manufacturer reported the appearance of the folds while in the white. The soaking was ample, 3 to 4 days. Dung bate was used at 35° for 5 hours. The hides were then fleshed by machine during rinsing with cold water. The writer doubts the wisdom of chilling the hides from the warm bate, as they then acquire a certain rigidity and do not get the full benefit of the mechanical loosening during fleshing. When this is done by hand on the beam, the workman discriminates. In the above case, the bating was probably insufficient. It is a mistake to suppose that the action is hastened at high temperatures. From heating alone, the swelling falls and the bating is thought to be complete, whereas the desired loosening of the hide structure has not been reached. This last depends upon the character of the bate itself and the time employed rather than the temperature. The danger of too prolonged bating is generally overestimated.

Similar defects in grain have also been met with in chrome box-calf. For instance, a tanner had no trouble with salted domestic hides, but with dried hides from distant sources. The explanation is again insufficient soaking. In another case with chrome horse leather, the folded grain showed already after liming, both with salted and dry hides. Warm water treatment and warm bating lessened the fault, which only appeared on chrome tanning, but not when vegetable tannage was employed. This shows that it is necessary to soften also after liming, which gives a hard core. This can easily be shown by experiment. If a hide just dehaired from the lime be only superficially washed and then tawed in alum and salt, the fault distinctly appears.

Another case came from America, of wrinkled grain in chrome-tanned, colored calf. The samples showed the same wavy streaks lengthwise. The manufacturer got about 10% of this class of product. As this was in winter and import ware is largely used in America, the trouble was probably due to insufficient and irregular softening of hard hides. Accordingly a careful sorting of the softened hides is advisable

Production of Cod Liver Oil in Norway. O. A. JACOBSEN. *Ledertechn. Rundschau,* 1910, No. 8, pp. 59-60.—In response to inquiries, the writer supplements his earlier article (abstract, ante p. 144, Feb. number) on this subject. The fish livers not used directly for medicinal oil are stored for the season in barrels, and at the close a so-called crude medicinal or "blank" liver oil is drawn off. The livers are then gently warmed and a "brown-blank" oil obtained; the residue goes to the brown oil boiling pans. This "brown-blank" oil is a fat oil, suitable for fine leather, especially when freed from mucus by further boiling. After steaming the medicinal oils, the residues are let settle and after a time an oil flows off called "sour" liver oil. This is also sold as "blank" oil, a misrepresentation. The residues that do not go to the brown oil boiling pans are warmed and a "press" oil obtained, sometimes sold as "brown-blank" oil, another misrepresentation. The main point is in the boiling. Steam heat is not enough, but direct fire under open cast-iron pans. For this "roasting," 1½ hectoliters of coal are consumed to 1 hectoliter of oil. The mucous matter collects to a cake. The brown oil thus obtained should give no sediment even on long storage. The writer earlier did not think favorably of brown oil and published to that effect, but after 30 years' experience in its boiling and employment, considers it equal to the best moellon for leather. Its dark color is objectionable, but improved manufacture may overcome this. Leather will retain 20 per cent. more oil prepared in this way than of fish oils from any other process. The addition of the dearer blank oil is not of advantage, for a leather treated with such a mixture will on storage develop a resinous coating on the grain. Thorough boiling ("roasting") is essential. The scale of prices for liver oil is remarkable. Pressed oil is sold for 34 pfennigs. To make it suitable for tanners, it must be boiled down with 20 per cent. loss, which makes it cost 41 pf. (based on pressed oil) without reckoning expense of process. The brown oil resulting however, sells for 32 pf. If the press oil is mixed with an equal amount of mineral, giving a mixture worth 25 pf., it is sold to the tanner as brown oil for 32 pf.

Other fish oils contain more stearine than the cod liver oil, but since no liquid fats are removed for medicinal use, they may be used for leather notwithstanding the stearine content.

A future reply to Herr Bogh's criticisms (abstract, ante p. 199, March number) is promised.

PATENTS.

Method of Treating Hides or Skins. U. S. Patent No. 952,703. C. J. GLASEL, Boston, Mass. A tanning drum adapted to support hides by their opposite sides, and subject them to the tanning agent placed in the drum. Means are provided for mechanically working the hides into alternately tense and relaxed conditions.

Machine for Dressing Hides and Skins. U. S. Patent No. 953,936. W. A. WUST, Frankfort-on-the-Main, Germany.

Machine for Treating Hides, Skins or Leather. U. S. Patent No. 953,937. W. A. WUST, Frankfort-on-the-Main, Germany.

Variable-Speed-Rolls Leather-Finishing Machine. U. S. Patent No. 953,-980. W. R. SMITH, Buffalo, N. Y.

Machine for Cylindering and Stretching Hides. French Patent No. 403,027. M. JUSTON AINÉFILS.

Process for Increasing the Resistance of Animal Tissue. French Patent No. 403,334. FRITZ KRIPKE.—Animal fiber, for instance, the gut used in musical instruments, is treated with a reducing agent. Example: 1 part hydroquinone, 1 part alcohol, 100 parts linseed oil.

Process for Mineral or Vegetable Tannage of Heavy Leather. French Patent No. 403,779. J. B. F. E. ROY.—By employing a mixture of salts of alumina containing volatile and non-volatile acids, the volatile acids are expelled and a large amount (35 to 100 per cent.) of insoluble salt precipitated and fixed on the fiber.

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W. H. TEAS . . . . Editor and Manager

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ELECTIONS.

ACTIVE.

Lloyd Balderston, Elk Tanning Co., Ridgway, Penna.

ASSOCIATE.

H. S. Frederick, Northwestern Leather Co., Sault Ste. Marie, Mich.

E. Evritt Van Dine, Troy, Penna.

CHANGES OF ADDRESS.

R. W. Griffith to 54 Fulton St., New York City.

COUNCIL PROCEEDINGS.

At a meeting of the Council at the Grand Union Hotel, New

York City, on Friday, April 29th, 1910, there were present Messrs. Wilson, Reed, Small, Alsop and Griffith.

President Wilson presided.

Mr. H. C. Reed, Secretary.

It was decided:

That the Association hold its next annual meeting in conjunction with the meeting of the National Association of Tanners in Chicago in October.

It was the sense of the meeting that the exact date of the meeting should be announced in the JOURNAL at the earliest possible date.

It was voted that two committees be appointed in connection with the annual meeting,—a local committee and a programme committee, each to consist of three members; that the local committee consist of Mr. Wallin as Chairman; Dr. Levi; and a third man, to be selected by the two; and that the programme committee consist of the President as Chairman; the Secretary; and a third man, to be selected by the two.

The question of a tanners' school was brought up for discussion, and the Secretary reported that he had followed the instructions given him at the last annual meeting, and advised the Tanners' Association that this Association was willing and ready to co-operate with it.

The resignation of Mr. Teas as editor of the JOURNAL was acted upon, it being voted that his resignation be accepted with regret.

Mr. Alsop was elected editor and Business Manager of the JOURNAL, to succeed Mr. Teas, with power to select an Associate Editor.

It was voted that the Secretary be directed to acknowledge the receipt of a bound volume of "*The Collegium*" with the thanks of the Asssociation, and to extend to the members of the I. A. L. T. C. the greetings of the A. L. C. A.

The Secretary was instructed to send a bound volume of the JOURNAL to the International Association with the greetings and good wishes of the American Leather Chemists' Association.

The Secretary was directed to write a letter to the Chairman of each Committee, calling attention to the early date at which of annual meeting is to be held and suggesting the advisability of promptness in getting out the Committee work.

The matter of sending a delegate to the convention of the International Association was discussed at some length, but no action was taken.

The Secretary was directed to put a notice in the JOURNAL announcing to any chemist who might wish to make a change that inquiries have been received from firms requiring chemists, and also to say that the JOURNAL would be glad to publish inquiries from firms who require chemists.

Upon motion, duly seconded, the meeting adjourned.

EDITORIAL.

With this issue of the JOURNAL the present Editor retires because of a business change which precludes the possibility of giving the JOURNAL the time its editing demands. It is with a keen sense of regret that this step is taken, but the regret is tempered by the knowledge that the lines will fall into abler hands.

The editorial management of the JOURNAL has been unchanged during the five years since the publication was launched with more or less apprehension. Thanks to the support of the members this apprehension was quickly dissipated, and a feeling of confidence replaced it, and grew apace with the continued appearance of the publication. The work of the editor has also grown since the inception of the JOURNAL, and at times has been almost a burden. A burden, however, which was made lighter by the thought of the common cause, and because of the peculiar sense of pardonable pride in the welfare of the Association, with the founding of which, the Editor was so closely connected.

At the convention of the A. O. A. C. held in Washington in the fall of 1903, the writer suggested to Mr. H. C. Reed the idea of a national leather chemists organization: the matter was discussed with the result that at the close of the meeting, Mr. Reed and the writer assembled a group of leather chemists and formed the American Leather Chemists Association. To insure stability and influence the organization thus started had to attach to its membership rolls, the names of a majority of the chemists doing commendable work in the tanning industry. Many of these men were conservative almost to a fault, and hesitated to ally themselves with an organization whose future held the possibility of failure. A missionary campaign was undertaken, and resulted in such additions to the membership roll as to leave lack of interest the only possible cause for the failure of the Association. There was no lack of interest, however, and with the succeeding conventions under changed conditions it was soon demonstrated that the Association was a permanent institution.

In view of this intimate association with the beginning and life of the A. L. C. A., and of the continuous responsibility of the JOURNAL since its inception, the feeling of the Editor on retiring from the active work of the Association, may be appreciated. The succeeding Editor is able and qualified, and with the co-operation of the members, the JOURNAL will have a more glorious future. This co-operation is due the Editor and should be accorded without appeal, as this publication is of equal proprietary interest to each of our members.

Thanking the members of the A. L. C. A. for their evidences of confidence, and for their help and courtesy, the Editor herewith makes his retiring bow.

DETERMINATION OF ACIDITY IN TANNING LIQUORS.

By J. H. Yocum, T. A. Faust and G. A. Riker.

Next to the determination of tannin in importance to the tanner, comes the determination of acidity of the liquors which he uses in the tanning operation.

When the tanner takes his stock out of the beam house and places it in the first liquors, it is of the utmost importance that in this preliminary stage, the conditions be such that the hide will absorb the maximum amount of tannin in the subsequent liquors. To effect this, it is necessary that the hide be plumped up at this stage so that the fibers will be extended and made receptive to the action of the tannin. It is a well established fact that the presence of acids in these handler liquors brings about this desired effect.

However, there are only a limited number of acids which do this plumping properly, such as sulphuric, lactic, formic and acetic, while others having a limited capacity in this respect, especially tannins and those acids formed by the hydrolysis of tannin, such as gallic acid, are not to be considered plumping acids. The tanner therefore needs a measure of his plumping acids alone in order to control his liquors.

Since the founding of the American Leather Chemists' Association, various methods have been tried out, with more or less success, but everyone admits that none yet proposed is fully satisfactory. The majority of the methods used are influenced either by the tannin present, gallic acid or some other exterior circumstance, and therefore do not give the tanner the desired information as to the actual amount of plumping action represented by the acid reported by the chemist.

The official method, that is the charcoal method, is about the poorest of any that has been proposed; it is open to several serious objections, it being useless to enumerate them, as we all are acquainted with its defects. Procter's lime water method is affected by carbon dioxide and the gallic acid present, and has been abandoned long ago by the American chemists. Most of the remainder of the methods are either exceedingly laborious or of doubtful accuracy.

The method originated by Koch and introduced into this country with valuable improvements by Reed, known as the alcoholic-gelatine method, is without doubt the most accurate of all, but has the one serious defect, that it includes the gallic acid in the result, and in a tannery where a great deal of chestnut, myrabolams, valonia or other pyrogallol tannins are used, we have found that a great proportion of the total acid reported by the present methods is gallic acid.

Suggestions have been made to measure the plumping capacity of a liquor by immersing a gelatine disk in the liquor, and at the end of a definite time, measure the amount that the disk has swollen. Other empirical methods have been suggested, but it has been found that these were not a true indication of the practical plumping results, consequently these suggestions have been regarded as valueless.

The method which we wish to propose is a modification of the alcoholic-gelatine method, and seems to us to be more in accord with the tanners' requirements than any other.

Gallic acid is precipitated by gelatine in the presence of gum, and we find that on addition of a solution of gum arabic to the gelatine solution, that practically all the gallic acid is precipitated, as well as the tannin, leaving in the filtrate, nothing but the actual plumping acids.

We would state as a result of a series of experiments, that about one-quarter of the gallic acid present in the liquor is absorbed by gelatine alone, although the prevailing opinion is that only a trace of gallic acid is absorbed.

We took varying quantities of gallic acid, added gelatine and a 2 per cent. gum arabic solution, and found in all cases, the gallic acid to be practically entirely removed.

We have added varying quantities of gallic acid to liquors made from catechol tannins, and also to solutions of gallotannic acid. Upon addition of gelatine and gum, we found the same acidity as before the addition of the gallic acid.

We also ran blanks on liquors known to contain only plumping acids, such as acetic and lactic acids, and found that the addition of the gum did not cause any diminution of the acidity, showing that the gum does not absorb plumping acids. We used both the water-gelatine solution and the alcoholic-gelatine solution, and found no difference in results. The gum arabic solution is slightly acid, but can be neutralized with NaOH, using hematin as in indicator. On standing, however, the solution soon becomes acid again, due to fermentation, which may be overcome by the addition of a drop of formaldehyde. A 2 per cent. solution of gum was found most convenient.

For our experimental work we had access to the liquors of several tanneries, where the amount of plumping acid present was known very closely, as chestnut extract was principally used, and the only plumping acids present were those actually added. It is the general belief that acetic acid is present in chestnut extract, but we distilled a number of chestnut extracts and found that the acetic acid did not average over 0.02 per cent. in the extracts. Our results with these chestnut extracts, naturally containing gallic acid, using gelatine-gum were about one quarter lower than with the gelatine alone, and were coincident with the amount calculated as having been actually added, showing that the results obtained by this method will bear out in practice. In another tannery, where practically no pyrogallol tannins were used, we noticed only a very slight difference between the gelatine and gelatine-gum methods, showing that in the absence of gallic acid, the gum has no effect whatever.

We are satisfied with the use of hematin as an indicator. We experimented with no other indicator, as we have titrated thousands of samples from tanneries and have had no trouble with it.

Our method of procedure is as follows with the gelatine-gum method:—

To 15 cc. of the liquor, add 50 cc. of gelatine solution (either water or alcoholic) and 15 cc. of a 2 per cent. solution of gum arabic; make up 200 cc., add about 5 grams kaolin, shake thoroughly, and throw on filter paper. Titrate 40 cc. with N/10 NaOH, which will give the burette reading of 3 cc. of original liquor. Both the gelatine solution and the gum arabic solution must be made neutral to hematin before using.

The alcohol-gelatine method was made provisional at the last meeting of the American Leather Chemists Association, and we would like to suggest this modification with the hope that the gelatine-gum method will succeed the present charcoal method as the official method in another year.

NOTE ON THE ESTIMATION OF CHROMIUM IN ONE BATH CHROME LIQUORS BY MEANS OF THE COLORIMETER.[1]

By J. T. Wood and Douglas J. Law.

The use of the small dipping colorimeter of Schmidt and Haensch for comparing colors of tan liquors was suggested to us by Procter. We have tried the use of it for the estimation of chromium salts. It was thought that by reason of the variation of basicity of used one bath chrome liquors accurate matches could not be obtained. We find that the variation of

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[1] From the *Journal S. C. I.*

basicity of spent liquors from the same process is very small, and does not prevent a good match being made. The average basicity of the unused liquor $\frac{Cr_2O_3}{H_2SO_4}$ was 0.87 (mean of 3 samples), after use it was found to be 0.75 (mean of 8 samples).

The standard for comparison may be a fresh stock liquor diluted to a convenient amount, but a more accurate standard is a spent liquor whose strength has been determined by analysis. In the latter case, however, after about three weeks a new standard must be taken, as the old liquor becomes greener in color, and cannot be accurately matched with liquors which have only just been spent. The liquors are simply filtered to remove organic matter, the standard being placed in the lower trough, and the liquor under examination in the 15 mm. trough.

The following series of comparisons by analysis shows that, although the method is not absolutely accurate, it is quite good enough for purposes of works control. The analyses were made in the usual way by oxidizing and titration with iodine and thiosulphate.

Per cent. Cr_2O_3	
Analysis	Colorimeter
0.505	0.508
0.410	0.437
0.312	0.336
0.840	0.854
0.750	0.735
0.875	0.882
0.312	0.301
0.274	0.266
0.302	0.294
0.249	0.233
0.196	0.187
0.252	0.237

Comparison of results obtained using two different standards.

	Chromic oxide Grams per liter	
	A	B
1	2.96	2.93
2	3.65	3.40
3	3.65	3.40

(A) Diluted stock liquor containing 2.54 grams of chromic oxide per liter as standard·
(B) Used liquor as standard containing 4.10 grams. of chromic oxide per liter.

Attempts were made to use the colorimeter for spent two bath liquors, but it was found that they could not be directly compared owing to varying proportions of reduced chromium salts present in the liquors along with the bichromate. On reducing to chrome chloride, a difficulty is found in making the liquors brilliant enough to match with a standard solution of chromium chloride. A method could, no doubt, be devised, but the process of preparing the liquor would probably take longer than the usual volumetric estimation.

THE VALUE OF THE "NON-TANS" IN TANNING MATERIALS.[1]

By Dr. J. Gordon Parker.

The question of the value of the non-tans in an extract or tanning material has never, to my knowledge, been satisfactorily settled, and has become more acute of late years owing to the introduction of closed autoclaves for the extraction of the wood in the manufacture of extracts, instead of the use of open extraction vats. This has resulted in the manufacture of what are commonly called "pressure extracts," *i. e.,* extracts which are manufactured by extracting the material from which they are made under pressure of one or two atmospheres. It is claimed that the more thorough the extraction which is given the greater is the yield of soluble substances obtained from the wood. The temperature at which the extraction takes place is higher owing to the increased pressure. While this results in a greater yield of soluble substances, it is a well established fact that extraction under pressure and at high temperatures decomposes a certain amount of tannic acid. The object of this investigation was, therefore, to find out, and if possible establish on practical scientific lines, which was the more valuable to the tanner, an extract made by open extraction containing a low percentage of non-tans, or an extract made from the same material by the aid of closed autoclaves or pressure vats containing a lower percentage of tanning, and a much higher percentage of non-tanning substances. The two extracts chosen are two well known French extracts

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[1] From the *Journal S. C. I.*

which are both largely sold in the English market at practically the same price, and the samples with which the experiments were carried out gave the following analyses, which were carried out by both methods of analysis, viz., the present International method and the now obsolete filter-bell method:—

	Extract A		Extract B	
	Present international method per cent.	Old filter-bell method per cent.	Present international method per cent.	Old filter-bell method per cent.
Tannin	30.1	31.3	27.0	29.4
Non-tannins	8.9	7.7	13.6	11.2
Insoluble	0.6	0.6	0.8	0.8
Water	60.4	60.4	58.6	58.6
	100.0	100.0	100.0	100.0

Extract "A" represents a well-known pure French chestnut extract extracted on the open batteries of vats afterwards decolorized by blood and concentrated. Extract "B" represents a similar extract made from the same wood but extracted in closed autoclaves under pressure, and afterwards decolorized by blood.

Before passing to the practical part of the work, the above analyses are well worthy of study. With extract "A" the difference in non-tans is only 1.2, but in extract "B" the difference between the two methods is 2.4. One of the chief reasons why the old filter-bell method of analysis was condemned by the I. A. L. T. C. was the fact that by the filter-bell process part of the non-tans were retained by surface attraction and were reported as tannins (*vide* Comm. Report[1] and Procter and Blockey[2] and, therefore, the purer the extract the less the difference should be between the two methods of analysis.[3] It should be noted that the difference in extract "B" is double the difference in extract "A." In passing, it is undoubtedly the reason why the manufacturers of pressure extracts so strongly protested against the introduction of the new method, and even now will only give a guarantee when it is insisted upon.

The practical tests were divided into four series. The first consisted of taking 12 butts cut from English market hides, the average green weight of which was 74 lb.; these butts were

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[1] *Collegium*, 1907, 253-261.

[2] *J. S. C. I.*, 1903, 22, 482-484.

[3] *Collegium*, 1907, 41-56.

divided into four parts, and two parts from each butt used in each extract. This procedure was adopted throughout the series. In the first series, the butts were tanned in a mixed liquor made from oak bark, myrabolams and gambier for the first 12 days, after which the marked pieces were separated and the further tanning carried out in handlers. These handler pits were made up with the extracts, in the one case "A," and in the second case "B." The goods were handled in these pits daily for five weeks, 2 lb. of extract being added each day; they then passed on to layers, which were made up by taking half the handler liquor and strengthening with these specific extracts; the first layer was made to a strength of 65° Bk., and in order to duplicate as far as possible the conditions of the tanning, for every 24 butts 64 lbs. of cup valonia was dusted in between the butts to keep them apart. At the end of the fortnight, the goods were taken out and given a second layer in the same liquor, after the strength had been raised to 75° Bk., and were left in this for three weeks. At the end of this period a new liquor was made from the leaches consisting of bark, valonia, and myrabolams of 40° Bk. Exactly equal portions of this liquor were put into each pit, and the strength raised from 40° to 85° Bk. by the addition of the specific extract. The butts were put down again, dusted with the same quantity of valonia, and left for four weeks. This makes a total of 16 weeks in the tan yard. The goods were now taken out, allowed to drip for three days, scoured by hand, oiled, rolled, and dried; no vatting, bleaching, or other similar treatment was given, the leather being finished and dried in the natural way. An analysis of the finished leather, gave the following results:—

	"A"	"B"
Hide substance	36.2	37.3
Tanning matters	49.2	48.3
Mineral ash	0.6	0.4
Moisture	14.0	14.0
	100.0	100.0
Tanning figure	136.0	128.5

On the resulting leather being weighed and calculated back on to the pelt weight, these trials gave for "A" extract 72.1

per cent. of leather calculated on the limed pelt weighed, and for "B" extract exactly 70 per cent.

The second series of experiments was carried out in a slightly different manner. The quantity and quality of pelt taken was the same, and the butts were passed through a series of suspender pits containing a mixed liquor for the same period, viz., 12 days, and were afterwards put through handler pits made up exactly as in the first series. The pack was divided into two as before, and instead of the extract being weighed in, it was measured in, in such a way as to keep the liquors in the two sets of pits exactly the same strength of tan as given by analysis. The handlers commenced with an analytical strength of 5 per cent. of tannin; this was gradually increased, until at the end of four weeks the strength of the liquor was 7 per cent. of tan by analysis. The goods were handled in this liquor daily, and each pack treated in the same manner. After a month the goods went through three layers, but these layers were made up by taking a leach liquor containing about 4 per cent. of tan, and making this up with the extract to 8 per cent. tannin for the first layer, 10 per cent. of tannin for the second layer, and 12 per cent. of tannin for the third. The total time of tannage was 17 weeks. The two packs were removed from the pits, allowed to drip, scoured and finished exactly as the first series. The yield in leather calculated on the limed weight was for extract "A" 73.6, and for extract "B" 71.8. This result indicated that the non-tans contained in "B" extract had not played any very important part, as on referring to the original analysis, it will be seen that, made up on the analytical strength, the density of "B" liquors must have been materially higher than "A" liquors. As a matter of fact, the last layer containing 12 per cent. of tan registered for "A" liquor 91° Bk. for "B" liquor 107° Bk.

Having now at my disposal old liquors mellowed from use in the previous series, containing in the one case "A" extract, and in the second "B," it was thought that results could be obtained similar to the results in ordinary tan yard working. Again, as in the first two series, the same number of butts were taken, divided, and tanned in two sets of suspenders of equal strength, but separately, one set containing mellow liquor, containing "A" extract, the other blended with "B." After passing through these suspenders for 12 days (they were strengthened each day), the goods were then put in the handlers, which were made from the layer liquors of the previous test. After four weeks in the handlers, these goods then went into the old layer liquors which had been used for the previous experiment, after which a perfectly new liquor was made with fresh leach liquor raised to 80° Bk. with each of the two extracts. The goods were dusted as before with valonia cup, left in the second layer for three weeks, the layer being afterwards strengthened to 90° Bk. with more extract, and left for five weeks. The subsequent shed work, drying, rolling, etc., was the same. The yields of leather calculated on the limed weight, were for series "A" 73.8, series "B" 71.6. The appearance of the finished leather from these three series of experiments was then compared. Leaving aside the question of color, series "A" were in each case firmer and more solid than "B." The leather was, if anything, thicker and plumper. The leather tanned in the "B" series had a distinctly mellow feel, and would have been too soft for the English market. A comparison of the physical quality of the leather was then made. The following is the mean of six tests from six separate pieces of each:—

SERIES "A."

Loss on washing	19.6
Water penetration test	196 hours
Water absorption test	¾ inch

SERIES "B."

Loss on washing	21.3
Water penetration test	143 hours
Water absorption test	⅞ inch

The above series of experiments appears to prove that as regards actual tanning of leather, better results are obtained both for weight and firmness with an extract containing a low percentage of non-tans, or at least one may certainly claim that in the above work the higher percentage of non-tans have not in any way contributed either to weight or firmness, as in each of the three separate experiments, extract "A" gave better results than "B." It has, however, been claimed that one of the chief advantages of an extract containing a high percentage of non-tans lies it its use as a vatting or retanning agent. In order to test this, 24 butts were now taken, four from each of the three experiments with "A" extract, and four from each of the experiments with "B." These 24 butts were now again divided into two parcels, so that an equal number of "A" butts and "B" butts were in each pack. The whole 24 were now wet back in a weak tan liquor until thoroughly wet through; this lasted three days, after which they were allowed to drip over night. The weights of these butts were carefully noted in the dry state before wetting. Two vats were now prepared, each made up to 100° Bk. with the two extracts. The basis of each liquor was an ordinary clear liquor from the leach of 45° Bk., and sufficient extract was added to raise the strength to 100° Bk. in the one vat with "A" extract, and in the other vat with "B" extract. The temperature of the vats was now brought to 110° F. and the butts handled in, each set being kept separate. They were handled twice the first day, next morning raised, and the strength of the liquor raised to 110° Bk. with their respective extracts, the temperature was again raised to 110° F. and the goods replaced. The third day the strength was raised to a further 10° by the addition of the extract, the temperature raised to 115° F. and the goods replaced. At the end of four days the butts were removed, allowed to drip for four hours, and afterwards rapidly rinsed through a cool sumac liquor; they were now allowed to drip over night, wiped over on the flesh and grain, oiled, and dried slowly in a cool dark room; when in suitable condition, they were hand pinned, oiled, rolled, and finished in the usual manner. The leather was then dried and weighed. All these processes were carefully carried out at the same time and under the same conditions, so as to make the work absolutely comparable. The resulting gain in weight was as follows:—

Pack "A" gained 4.2 per cent. Pack "B" gained 4.4 per cent., or a gain of 2/10 per cent. in favor of the extract with the higher percentage of non-tans. This vatted leather was now tested to ascertain the amount of soluble matter which could be removed on washing and also as resistance to water:—

The following are the results in triplicate:—

SERIES "A."

Loss on washing	21.8 per cent.
Water penetration test	166 hours
Water absorption test	⅞ inch

SERIES "B."

Loss on washing	22.1 per cent.
Water penetration test	130 hours
Water absorption test	⅞ inch

These tests again point to the fact that a high percentage of non-tans in the tanning materials is conducive to water absorption, and does not tend to the production of a leather of a high water-resisting character. This undoubtedly seriously militates against the slight advantage in weight which is obtained in the vatting of the samples with "B" extract.

The above experiments were carried out on a full commercial scale; altogether 48 full size butts were used, each butt being cut into four pieces in order that they could be tanned in the pits which were at our disposal, these being 2 feet 6 inches cube. The resulting tanned leather, therefore, weighed over half a ton, and in each case the general principles and processes of tanning as carried out in this country on a large scale in the tannery were duplicated as far as possible.

It is also interesting to note that the extract "A" in each case penetrated more rapidly than "B," the goods being struck through in the handlers in from seven to nine days sooner than the corresponding pieces in the handlers made with "B" extract. This also means considerable advantage to the tanner.

The above work, had time permitted, would have been extended, and might with advantage have been extended in the direction of further analysis of the liquors at various stages and of the products formed by fermentation, etc., in the pits. This would have necessitated a larger amount of labor than was at the time possible. Several analyses were, however, carried out of the waste liquors, and the development and acidity formed carefully noted, but in no case was there any material difference. On the three tests the acidity of the liquors was measured each day and kept uniform throughout. The hinder liquors from "B" extract always contained correspondingly higher percentages of non-tans, as was only to be expected.

While not claiming that the above work conclusively proves that the non-tans are useless as regards actual formation of leather, it indicates that a high percentage of non-tans in an extract is of no advantage. As it had been noticed that leather always appeared to tan quicker and strike through more rapidly in the extract containing the lower percentage of non-tans than in extract "B;" it was thought desirable to carry out a comparative series of tests on the speed of tanning and to ascertain whether or not the non-tans retard the penetration of the tannin. To this end, a portion of a carefully delimed butt was cut up into a number of small pieces, each 4 inches square. A number of these pieces, chosen as far as possible of equal weight and substance, were then treated in the following manner:

The pieces were thoroughly washed in distilled water in rotating glass churns, the water was then poured off, the pieces of pelt scudded and freed as far as possible from excess of moisture, and then divided into four sets, each of four pieces, marked —1 to 4, and four pieces of each mark were placed into rotating glass churns with a liter of distilled water and churned for 10 minutes, after which to churn 1*a* was added 20 grams per liter of extract A, to churn 1*b*, 20 grams of extract B; churn 2*a*, 20 grams of extract A plus 20 grams of glucose; to churn 2*b*, 20 grams of extract B plus 20 grams of glucose. These churns were then slowly rotated by means of an electric motor, for about 15 minutes in each hour; at the end of six hours a further 20 grams of the specific extract was added to each churn, a further 20 grams after 24 hours, 50 grams after 48 hours, 100 grams 24 hours later, and a further 100 grams at the end of the fourth day. The tannage was then continued for a further two days, making a total of six days. The remaining two sets of pieces were suspended on glass rods in liquors made in the same manner so as to tan slowly, imitating as far as possible the usual commercial process in the tannery; commencing with a liquor of 10 grams per liter, this was strengthened by the addition of 10 grams per day for 14 days, the pelt being handled up, and the liquors well stirred three times a day. From each set of leathers pieces were taken for analysis, and after rinsing through water were subsequently dried, and the percentage of nitrogen estimated by Kjeldahl's method. The results in the following table give the tanning figure, which expresses the number of units of tan combined with 100 parts of dried hide substance.

	After 24 hours	After 48 hours	After 72 hours	After 96 hours	After 6 days
1 A	42	70	94	109	131
1 B	41	69	91	104	126
2 A	43	68	90	102	126
2 B	42	67	88	100	120

STILL TANNAGE.

	After 24 hours	After 48 hours	After 72 hours	After 6 days	After 8 days	After 10 days	After 14 days
A	26	50	71	89	101	109	113
B	27	49	70	86	97	103	108

The above figures confirm in a striking manner the work done by Stiasny (*Collegium,* 1909, 385, p. 395), who showed that the higher the percentage of non-tans present in a tan liquor, the slower the penetration into the pelt.

The above work indicates that the high value placed in some quarters on the "non-tans" of a tanning extract is extremely problematic. It is the intention of the author to carry this work further by means of standard solutions of tanning material containing various percentages of non-tannins of varying constitution.

The author desires to express his thanks to Mr. Van Gijn and others for their assistance in checking many of the "Kjeldahl" and other results.

THE COMPLETE ANALYSIS OF LEATHER.[1]

By Dr. J. Gordon Parker and M. Paul.

Much information valuable to the practical tanner can be obtained from a full and detailed analysis of vegetable tanned leathers, and the method devised by Von Schroeder and published in 1898 (after his death) by Bartel[2] is universally used by chemists. The method is so well known that only a brief summary is necessary. The leather to be analyzed is cut into thin shavings or powdered by means of a rasping machine. From

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[1] From the *Journal S. C. I.*

[2] Bartel, *Ding. Polyt. J.*, 1898, 305; p. 65; *J. C. I.*, 1898, 17, 164-166.

one portion the actual moisture and the mineral ash are determined. Another portion is extracted with petroleum ether for the estimation of the percentage of oil, after which the water-soluble matter, including the uncombined tannins, are washed out by percolation with warm water; finally, the percentage of nitrogen is determined on a third sample by Kjeldahl's method, from which is calculated the percentage of hide substance present in the leather. These various figures can be obtained with great accuracy.

Assuming that a sample of leather gives the following results: —Moisture, 16.5 per cent.; mineral ash, 0.95; fat, 1.00; soluble matter, 18.6; hide substance, 36.6. Von Schroeder calculates in the following manner, admitting as leather substance everything contained in the leather excepting moisture, ash, fat, and soluble matters, *i. e.*, the amount of pure leather is found by subtracting the total of the previous figures from 100. In the above sample the total of moisture, ash, fat, and soluble matter is 37.05 per cent.; the leather substance would, therefore, be 100—37.05 = 62.95. As the hide substance has already been ascertained, the tannin combined can be ascertained by difference, and would be, in this case, 26.35 per cent. The ratio $\frac{\text{tannin combined}}{\text{hide substance}} = \frac{26.35}{36.6} = 71.9$ per cent. is called by Von Schroeder the "Durchgerbungszahl," or "degree of tannage." The knowledge of this ratio is of great value as a means of ascertaining the quality of the leather, but obviously this number alone is of no great value for ascertaining the commercial value of a sample of leather unless the physical properties of the leather, such as penetration of water, tensile strength, flexibility of grain, etc., are also obtained; however, it indicates the "degree of tannage," and to the currier or dresser of leather, whether the leather is likely to be capable of good yield in dressing, the possibility of retannage, and also whether the tanning process has been more or less rational.

The appearance of a section of the leather shows the penetration of the tannin; if, however, a section of leather shows an apparently complete penetration, and at the same time gives a low tanning figure, it can generally be concluded that the tannage has been hastened by some mechanical means, such as drumming or similar accelerating process, and indicates that fibers of the leather have simply been colored, and that the tannin has not completely penetrated and united with the fibers of the hide. The importance of this tanning factor is therefore admitted, and its determination for commercial purposes has become general.

The object of this paper is to draw attention to an error in Von Schroeder's method of calculating this figure. The error is contained both in his first paper, published before his death, and in his posthumous papers, published by his colleague, Bartel.[1] We cannot find that this error has been noted, except by Procter;[2] other publications and books dealing with the analysis of leather, simply quote the method, giving the details of how the analysis should be carried out, without indicating the error to which we refer. This is not on the whole surprising, as since this work was done by Von Schroeder, practically no investigations of this nature have been published, with the one exception of Ronchèse's work,[3] in which he describes his method for the determination of nitrogenous substances by direct titration in the presence of formaldehyde, instead of by distilling off the nitrogen as ammonia.

The error occurs in the calculation in the following manner:—The mineral ash is determined by incinerating a portion of the original leather. This gives the total amount of ashes from mineral matter, insoluble and soluble, including lime, magnesia, alumina, iron, silica, and salts of potassium and sodium. In the extraction of the water-soluble matter, some of this mineral matter, *i. e.*, the soluble portion, including calcium, sodium, potassium, and magnesium salts of inorganic and organic acids, is washed out and calculated as water-soluble matter, existing generally as anhydrous mineral salts and also occasionally as salts containing some water of crystallization. Thus, part of what has been accounted for in the mineral ash is also reckoned in with the soluble matter. Now, in the calculation of the leather substance

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[1] *Ding. Polyt. Journal*, 1897, No. 305, pages 65, etc.

[2] Leather Industries Laboratory Book, page 357.

[3] *Bull. Soc. Chim.*, 1909.

the sum of the four percentages, moisture, fat, mineral ash, and soluble matter, is subtracted from 100. Therefore that portion of ash derived from mineral matter soluble in water has been subtracted twice, and the percentage of leather substance is too low by this amount. By incinerating the dry leather, after extraction of the water soluble matter, the amount of ash derived from the insoluble mineral matter is obtained and by incinerating the water soluble matter the amount of ash derived from soluble mineral matter is obtained.

In the case of the analysis referred to above, the ash consists as follows:—

	Per cent.
Ash from soluble mineral matters	0.82
Ash from insoluble mineral matters	0.13
	0.95

Consequently, Von Schroeder's calculation of the percentage of leather is too low by 0.82 per cent. This alters the "degree of tannage" from 71.9 to 74 per cent., a difference of 2.1 per cent.

In the leather, there only exists after washing, in addition to the leather substance itself, the insoluble mineral matters; therefore, by burning the leather residue after the extraction with water, the amount of ash derived from this insoluble matter is obtained. It is almost correct to calculate the pure leather substance as equal to the dry leather residue, *minus* the insoluble ash. As a matter of fact, the actual amount of insoluble mineral matters in the dry leather residue is slightly higher than the amount of insoluble ash obtained by incineration, because by incineration, the calcium carbonate and other salts are partially decomposed, but this error is very small; for example, the error on the sample, in question containing 0.13 per cent. of insoluble ash is only 0.02 to 0.04 per cent. This error is magnified when the mineral ash is calculated on a sample of the original material, not only because the amount is greater, but also because greater dissociation occurs in the soluble mineral matters, *e. g.*, Epsom salts, or other easily dissociated salts. Moreover, the amount of ashes obtained is very variable with the temperature of incineration depending upon whether an ordinary Bunsen flame or muffle furnace or a blow pipe is used.

It is therefore incorrect to estimate the amount of leather substance as the difference between 100 and the sum of four factors including the mineral ash. For this reason, and also because the ash derived from soluble mineral matter is deducted twice in the above method of calculating the leather substance, we prefer to determine the amount of the leather substance, for the calculation of such an important factor as the "tanning figure," by weighing the dry leather residue, after extraction of the soluble matter, and subtracting from this weight the weight of ash derived from the insoluble mineral matters. This obviates the unsatisfactory method of determining it by the difference between 100 and the sum of four separate factors.

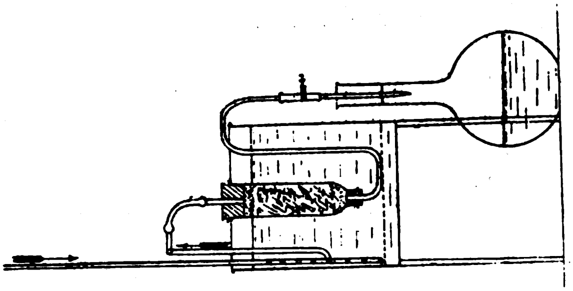
The amount of water included as mineral matter in the water soluble does not affect the result, because the water of crystallization is included as moisture, and the water of constitution is the same in the original leather after drying, as in the dry soluble matter, since the drying is done at the same temperature.

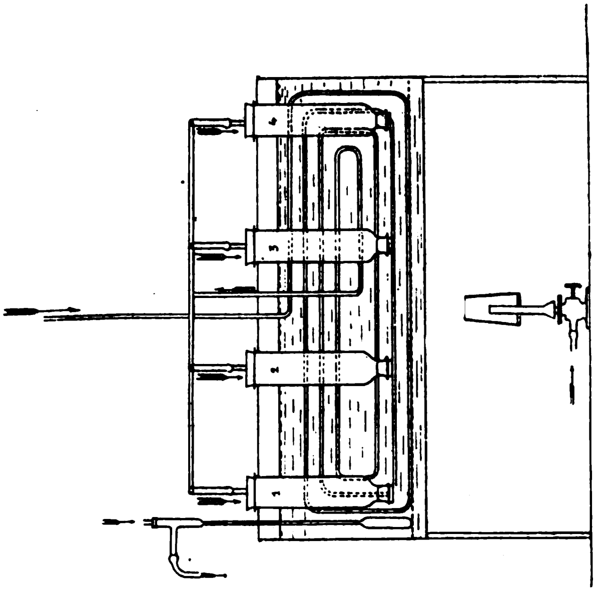
From the above reasoning it is clear that all the figures published by Von Schroeder are too low by the amount of mineral ash derived from the soluble matter. Curiously enough, he has estimated this ash from soluble matter, and given it in a separate column.

We have, therefore, repeated his calculations, making the necessary correction, and find that the "degree of tannage" is higher by 0.5 per cent. to 2.4 per cent. It may be suggested that the error is so small that the correction makes a difference which in practical work could be neglected, as in the leathers analyzed by Von Schroeder the percentage of mineral ash is small, averaging 0.74. This argument would have held good for the tannage of 20 years ago, but under modern conditions the method of tanning leather has undergone a great change, and whereas the average mineral ash of a leather generally did not exceed ½ per cent., nowadays, with the use of extracts, chemically decolorized and bleached by aid of bisulphites and other salts, the mineral ash of which extracts varies from 1.5 to 4 per cent., and in isolated cases, even 6 per cent., the percentage of ash in the leather tanned by these agents may rise considerably above ½ per cent. Evidently it is impossible to say that leather tanned with these extracts, and containing 1.4-1.6, or even 2 per cent. of ash, is adulterated, and the error which in Von Schroeder's tables does not exceed 1 per cent. is multiplied six or seven times if a modern leather be worked out under the same conditions.

To illustrate this, we have analyzed a number of leathers typical of the various tannages produced at the present time; in these tables, we indicate the tanning figure according to Von Schroeder's method of calculation; and in the corresponding column the exact figure obtained by weighing the dry leather residue after the soluble matter has been washed out and deducting from this the quantity of insoluble ash, for estimating the amount of the pure dry leather; in this manner it is possible to check one's results so that they agree within 0.1 per cent. Where the duplicates differ from 100 by more than plus or minus 0.1 it proves an error in one of the other three determinations, either in the moisture, fat, or dry soluble matter, or it may be the use of too high a temperature in the drying of the residue, indicating the presence of catechol-tans which are liable to split up giving off water of combination.

We also venture to point out another matter in connection with this analysis. We consider that it is absolutely necessary in estimating such an important factor as the leather substance that the weight of the resulting dry leather should be ascertained after washing directly; but in order to carry this out, it necessitates a departure from Von Schroeder's method, as his extractor or percolator can no longer be used. The use of Procter's extractor is also unsuitable. The authors have, therefore, devised an apparatus which enables this to be easily carried out. The apparatus consists of a water bath fitted with a thermo-regulator. The weighed quantity of leather is placed in an inverted Procter's filter-bell or small glass vessel. The ends of the filter-bell are plugged with cotton wool, which must be previously tanned and washed, or glass wool may be used. The filter-bell is then connected by a serpentine glass tube, which passes three or four times immersed in the water bath, with a reservoir filled with distilled water. The flow of water can be regulated by a small clamp. As the cold water comes down from the reservoir it must pass four times the length of the water bath before coming in contact with the leather; it thus reaches the temperature of the water bath before it reaches the leather. The first portion of the liquor which comes over contains most of the tannin matters,





sugars, and those mineral matters which diffuse easily, the more difficulty soluble tannins coming afterwards gradually. It is well known that, theoretically, one can continue washing leather for ever, as a certain amount of decomposition is always taking

COMPLETE ANALYSIS OF LEATHERS.

Comparison between Von Schroeder's Calculation and Exact Method.

TABLE I.—Tanned Leathers without Extract.

Class of leather		Moisture	Ashes: Total	Ashes: From insol. mineral matter	Fat	Sol. matter	Pure leather subst.	Total	Leather substance: Hide subst.	Leather substance: Tannin comb.	Degree of tannage $\frac{T.C.}{H.S.}$ %	Difference
1. English sole	S	17.08	0.59	..	0.84	20.0	61.49	100.0	35.37	26.12	73.8	..
	e	17.08	..	0.29	0.84	20.0	61.77	99.98	35.37	26.40	74.6	0.8
2. English sole	S	16.8	0.72	..	0.92	18.4	63.16	100.0	34.9	28.26	80.9	..
	e	16.8	..	0.21	0.92	18.4	63.60	99.93	34.9	28.70	82.2	1.3
3. Pure hemlock, U. S. A.	S	17.06	0.74	..	0.89	17.4	63.91	100.0	38.50	25.41	66.0	..
	e	17.06	..	0.27	0.89	17.4	64.32	99.94	38.50	25.82	67.0	1.0
4. Venezuela sole	S	18.02	0.63	..	0.38	5.45	75.52	100.0	48.05	27.47	57.1	..
	e	18.02	..	0.11	0.38	5.45	76.07	100.03	48.05	28.02	58.3	1.2
5. Californian oak	S	16.72	0.81	..	1.05	16.50	64.92	100.0	33.3	31.62	94.6	..
	e	16.72	..	0.19	1.05	16.50	65.45	99.91	33.3	32.15	96.5	1.9
6. West of England	S	17.22	0.86	..	1.09	20.20	60.63	100.0	35.0	25.63	73.2	..
	e	17.22	..	0.12	1.09	20.20	61.32	99.95	35.0	26.32	75.2	2.0
7. Oak sole	S	17.31	0.46	..	0.73	19.70	61.80	100.0	36.4	25.4	69.7	..
	e	17.31	..	0.05	0.73	19.70	62.20	99.99	36.4	25.8	70.8	1.1
8. Oak sole	S	17.51	0.48	..	0.91	19.05	62.05	100.0	36.9	25.15	68.1	..
	e	17.51	..	0.09	0.91	19.05	62.53	100.09	36.9	25.63	69.4	1.3
9. French pure oak	S	18.08	0.76	..	0.11	7.28	73.77	100.0	42.6	31.17	73.1	..
	e	18.08	..	0.07	0.11	7.28	74.33	99.87	42.6	31.73	74.4	1.3
10. French pure oak	S	18.6	0.58	..	0.42	7.04	73.36	100.0	43.2	30.16	69.8	..
	e	18.6	..	0.04	0.42	7.04	73.82	99.92	43.2	30.62	70.9	1.1
11. Canadian helmlock	S	16.52	0.88	..	2.06	15.1	63.44	100.0	33.6	31.84	94.7	..
	e	16.52	..	0.13	2.06	15.1	66.30	100.11	33.6	32.7	97.3	2.6
Average	S	17.35	0.68	..	0.85	15.10	66.00	100.00	37.98	28.02	73.7	..
	e	17.35	..	0.14	0.85	15.10	66.51	99.97	37.98	28.53	75.1	1.4

TABLE II.—MIXED TANNAGE.

			Ashes						Leather substance		Degree of tannage	
Class of leather		Moisture	Total	From insol. mineral matter	Fat	Sol. matter	Pure leather subst.	Total	Hide subst.	Tannin comb.	T.C. / H.S. %	Difference
12. English sole	S	15.6	1.02	.	0.8	16.6	65.98	100.0	35.6	30.38	85.3	.
	e	15.6	.	0.18	0.8	16.6	66.7	99.88	35.6	31.10	87.3	2.0
13. English sole	S	16.52	0.99	.	1.10	18.2	63 19	100.0	34.7	28.49	82.1	.
	e	16.52	.	0.23	1.10	18.2	63.90	99.95	34.7	29.2	84.1	2.0
14. English sole	S	16.8	0.85	.	0.9	18.85	62.6	100.0	30.1	26.50	73.4	.
	e	16.8	.	0.17	0.9	18 85	62.6	99.92	36.1	27.10	75.0	1.6
15. French sole	S	15.8	1.4	.	1.4	18.1	63.3	100.0	36.0	27.3	75.8	.
	e	15.8	.	0.12	1.4	18.1	64.48	99.90	36.0	28.48	79.1	3.3
16. French sole	S	16 45	1.62	.	1.1	17.8	63.03	100.0	35.6	27.43	77.0	.
	e	16.45	.	0.14	1.1	17.8	64.5	99.99	35.6	28.9	88.1	4.1
17. French sole	S	16.34	1.31	.	0.95	17.5	63.9	100.0	39.2	24.70	63.0	.
	e	16.34	.	0.12	0.95	17.5	65.0	99.91	39.2	25.80	65.8	2.8
18. French upper	S	16.1	1.20	.	2.8	18.7	61.20	100.0	36.8	24.4	66.3	.
	e	16.1	.	0.21	2.8	18.7	62.1	99.91	36.8	25.3	68.7	2.4
19. German split	S	17.02	1.18	.	0	19.0	62.8	100.0	40.9	21.9	53.5	.
	e	17.02	.	0.18	0	19.0	63.8	100.0	40.9	22.9	55.9	2.4
20. German split	S	16.0	1.45	.	0	22.2	60.35	100.0	40.6	19.75	48.6	.
	e	16.0	.	0.25	0	22.2	61.5	99.95	40.6	20.9	51.4	2.8
21. English upper	S	12.65	1.03	.	34.21	3.82	48.29	100.0	30.3	17.99	59.3	.
	e	12.65	.	0.12	34.21	3.82	49.14	99.94	30.3	18.84	62.2	2.9
22 Spanish sole	S	14 9	1.50	.	2.4	13.6	67.6	100.0	40.2	27.4	68.1	.
	e	14.9	.	0.17	2.4	13.6	68.8	99.87	40.2	28.6	71.1	3.0
23. Italian sole	S	16.0	1.7	.	1.35	19.75	61.20	100.0	37.8	23.4	61.9	.
	e	16.0	.	0.2	1.35	19.75	62.60	99.90	37.8	24.8	65.6	3.7
24. English sole retanned	S	16.40	2 4	.	1.3	18.90	61.0	100.0	35.05	25.95	74.0	.
	e	16.40	.	0.14	1.3	18.90	63.2	99.94	35.05	28.15	80.3	6.3
25. American mixed	S	16.87	0.89	.	0.91	13.6	67.73	100.0	37.1	30.63	82.5	.
	e	16.87	.	0.16	0.91	13.6	68.45	99 99	37.1	31.35	84.5	2.0
26. South African sole	S	18.27	1.61	.	1.21	15.2	63.71	100.0	38 2	25.51	66.7	.
	e	18.27	.	0.07	1.21	15.2	65.32	99.97	38.2	27.12	70.9	4.2
27. English drum tanned	S	16.04	1.24	.	1.71	23.95	57.06	100.0	35.84	21.22	59.2	.
	e	16.04	.	0.18	1.71	23.95	58.12	100.00	35.84	22.28	62.1	2.9
28. Spanish sole	S	18.26	1.16	.	0.18	11.75	68.65	100.0	40.55	28.10	69.2	.
	e	18.26	.	0.14	0.18	11.75	69.56	99.89	40.55	29.01	71.5	2.3
29. English sole	S	14.12	0.94	.	0.81	22.92	61.21	100.0	37.3	23.91	64.1	.
	e	14.12	.	0.15	0.81	22.92	61.95	99.95	37.3	24.65	66.0	1.9
Average	S	16.12	1.305	.	2.95	17.24	62.37	100.0	37.10	25.27	68.1	.
	e	16.12	.	0.162	2.95	17.24	63.46	99.94	37.10	26.36	71.0	2,9

TABLE III.—ADULTERATED LEATHERS.

Class of leather		Moisture	Ashes		Fat	Sol. matter	Pure leather subst.	Total	Leather substance		Degree of tannage $\frac{T.C.}{H.S.}$ %	Difference
			Total	From insol. mineral matter					Hide subst.	Tannin comb.		
30. German sole	S	17.6	2.2	..	1.60	22.3	56.30	100.0	34.4	21.9	63.6	..
	e	17.6	..	0.18	1.60	22.3	58.2	99.88	34.4	23.8	69.1	5.5
31. German upper	S	15.50	2.07	..	2.81	28.4	51.22	100.0	30.8	20.42	66.3	..
	e	15.50	..	0.25	2.81	28.4	53.0	99.96	30.8	22.2	72.0	5.7
32. Belgian sole	S	16.78	2.6	..	1.90	20.52	58.20	100.0	34.2	24.0	70.1	..
	e	16.78	..	0.19	1.90	20.52	60.5	99.89	34.2	26.3	61.8	6.7
33. Italian sole	S	17.1	1.91	..	1.8	21.4	57.79	100.0	35.6	22.19	62.3	..
	e	17.1	..	0.17	1.8	21.4	59.5	99.97	35.6	23.9	67.1	4.8
34. American sole	S	17.6	3.2	..	1.6	22.6	55.0	100.0	33.3	21.7	65.1	..
	e	17.6	..	0.28	1.6	22.6	58.0	100.08	33.3	24.7	74.1	9.0
35. English sole	S	17.86	4.82	..	1.37	16.90	59.05	100.0	43.3	15.75	36.3	..
	e	17.86	..	0.15	1.37	16.90	53.75	100.03	43.3	20.45	47.2	10.9
36. Belgian sole	S	17.9	4.95	..	1.2	23.8	52.15	100.0	33.8	18.35	54.2	..
	e	17.9	..	0.21	1.2	23.8	56.83	99.94	33.8	23.03	68.1	13.9
Average	S	17.19	3.10	..	1.75	22.27	55.67	100.0	35.06	20.61	58.7	..
	e	17.19	..	0.20	1.75	22.27	58.64	99.95	35.06	23.48	66.9	8.2

place, but practically, we have found that by extracting 20 grams of leather with a liter of water at a temperature of 55 to 60° C., for 24 hours, the last portion of the water which percolates through gives no precipitate with a solution of gelatine and salt, and only the faintest coloration with iron. With the apparatus here described, it is perfectly safe to leave this going over night; the reservoir, however, must contain slightly less than the requisite quantity of water so that the final percolation may be finished under observation the following morning. We find that a safe temperature for an extraction of leather is from 50 to 55° C.,but if the leather be well tanned, the temperature may be raised to 60° C.; but a temperature of 65° C. must never be exceeded. With under-tanned leather or leather tanned in a drum, by which process the combination of leather and hide fiber is not complete, the temperature must not exceed 55° C. If, after commencing the extraction of a sample of leather at 60°, a precipitate is obtained in the percolate instead of a clear solution, it indicates under-tanned leather, and a fresh sample must then be taken and the temperature reduced. Realizing that owing to dissociation of hide substance and tannin, absolutely exact figures can never be obtained, we therefore suggest that for all practical purposes comparable figures can be obtained by following the above method, viz., 20 grams of leather, one liter of water, extraction 24 hours at a regular temperature of 55° C. It will then be found that in the lost portion of the percolate, less than one part in 10,000 of tannin is present.

In the first of the above tables are cases of pure vegetable tanned leathers, in the tannage of which little or no extract has been used. In the second table, the leathers have been tanned with a mixture of various tanning materials from different countries, together with extracts in varying quantities. In the third table, various samples of commercial adulterated leather, at present on the market, are dealt with. It will be noticed that all of these are adulterated with different common adulterants. As will be seen by glancing at table I., the difference in results by the two methods of calculation, Von Schroeder's and this modified one, is comparatively small, but for the other leathers, the error is enormous, and from this it will be seen that chemists reporting the "degree of tannage" to their clients by Von Schroeder's formula, without the correction, even for non-adulterated leather, show the "degree of tannage" as being considerably lower than is actually the case, and the report, therefore, is liable to be misleading.

The authors do not claim any novelty in this work, but merely wish to establish a more accurate method for ascertaining a figure for the "degree of tannage" of leather, which is of extreme value to the tanner and buyer of leather, as it enables him to judge the quality of the leather and also to check the process of tanning in the tan-yard.

ABSTRACTS.

Analysis of Leather (Cont.). U. J. THUAN. *Le Cuir,* 1910, [3], No. 5, pp. 105-8.—*Determination of Mineral Matter.*—5 gms. of the finely cut leather are ashed in a crucible, best portion-wise with occasional addition of ammonium nitrate. The normal mineral content with vegetable tanned leather may be from 0.2-2%, being less with curried than sole leather. The ash is composed of sulphates of lime, soda and magnesia, with traces of iron and phosphates. In recent times the normal ash of sole leather has greatly increased from the use of extracts, which have been decolorized by mineral substances.

Determination of Fats.—25 gms. of powdered or finely cut leather of known water content are extracted in a Soxhlet apparatus 3 to 4 hours with about 100 cc. of CS_2, petroleum ether, $CHCl_3$ or ordinary ether; the first solvent is best. This is finally distilled off and the extract dried at 100-150° to constant weight. A special tube of filter paper to contain the leather during extraction is preferable. Sometimes with curried leather, especially if not finely divided, it is well to make a second extraction. Some suppose sole leather to be free from fat; this is not strictly correct, for the fat may amount to 0.2 to 2.5%, including a small amount of natural fat and oils added to prevent the grain from cracking when dry and to retard oxidation of the uncombined tannin.

Determination of Water Soluble Substances.—The residual leather (originally 25 gms.) from the Soxhlet extraction is freed from solvent by heating on the water-bath and then transferred to the bottle of a Koch percolator and soaked for 12 hours, and then let percolate for 2 hours at ordinary temperature, giving a liter of extract.

(To be Continued.)

Tannage with Monazite Residues from Thorium Extraction. M. PARENZO. *Collegium,* 1910, No. 403, pp. 121-4.—Garelli first made public in 1907 that the salts of the rare earths, cerium, lanthanum, didymium, neodidymium, thorium, zirconium, etc., have tanning power. The action is especially marked with the trioxides and is probably analogous to that of alum. The writer has made further experiments under M. Garelli's direction with chlorides and nitrates prepared from the monazite residues. After the extraction of thorium, these residues consist of crude carbonates, containing 50% of cerium carbonate, together with other earths. The product from the tannage was a glove leather superior to ordinary alum leather in water resistance. Although this work had a theoretical object, the process has industrial possibilities, for the Auerbach mantle industry produces a large surplus of cerium resides, which can be sold at a low price.

To determine the most favorable conditions, tanning experiments were made upon unchromed hide-powder under varying conditions. With the nitrates it was found that with a solution containing 0.43 gram sesquioxide (determined by evaporation and ignition), 11.62% of this was fixed by the hide. Increasing the dilution increased the absorption; with 0.108 gm. 22.22% was fixed. The addition of sodium chloride increased the last to 31.48%. Similar results were obtained with the neutral chlorides, as might be expected, the amount fixed in this case was not augmented by addition of sodium chloride.

The Analysis of Dark Fats and Oils. C. STIEPEL. *Seifen-fabrikant* [29], 509, 534.—*Saponification Number.*—If a fat (5 gms.) by the usual method gives too dark colored a soap solution for recognition of the color change, an amount of $BaCl_2$ sol. is added, equivalent to the alcoholic KOH used for saponification. After vigorous shaking, 300 to 400 cc. H_2O are added and heated 30 minutes longer with reflux condenser. The Ba soap separates and carries with it the coloring matter. The excess of alkali, now in the form of $Ba(OH)_2$, is titrated in the clear solution with HCl, phenolphthalein. If the precipitated soap interferes, it may be filtered off and an aliquot part of the filtrate titrated.

Free Fatty Acid and Neutral Fat.—Another 5 gms. of fat are boiled with 50 cc. of 50% alcohol and 1.5 gms. dry Na_2CO_3 beneath the reflux condenser until the free fatty acid has gone into solution as soap. Then 50 cc. 0.5 N. alcoholic KOH are added and boiled till saponification is complete. The total soaps and excess of Na_2CO_3 are precipitated by 150 cc. of $BaCl_2$ sol. (about 5%), then the whole diluted to about 400 cc., warmed some time and titrated on cooling with oxalic acid instead of HCl. The second saponification number thus found represents the neutral fat which, subtracted from the first number representing total fat, gives the free fatty acid.

Saponification Number of Dark Colored Fats. F. MARX. *Chem. Ztg.*, 1910, 124.—To make the determination, the author employs a much simpler process than that of Stiepel (above) 2.5 gms. fat are stirred with 50 cc. alcohol in a porcelain dish and the acid number determined by titration with 0.5 N. alkali (phenolphthalein). The liquid is then transferred to a 250 cc. flask, rinsing with benzol and boiled with 25 cc.

0.5 N. alcoholic alkali as usual. The product is then returned to the dish, rinsing with alcohol and titrated. The white background permits the color change to be distinctly seen.

Saponification Number of Dark Colored Fats. F. MAYER. *Chem. Ztg.*, 1910, 238.—In the analysis of dark colored mineral cylinder oils thickened with tallow, the author dissolves 10 gms. oil in benzol, boils with 25 cc. 0.5 N. alcoholic alkali for 1 hour, shakes the product in a separatory funnel with 30 cc. water, separates and extracts twice more with 25 cc. water, and titrates the united water extracts for excess of alkali.

Review of the Chemistry and Analysis of Fats for 1909. W. FAHRION. *Zeit. angew. Chem.*, 1910, [23], 446.—In the purely scientific direction the work of Ad. Grün (*Habilitations-schrift*, Zürich) on the constitution of ricinoleic acid and synthesis of the glycerides is important. For fat extraction, carbon tetrachloride does not appear to replace benzine as it is poisonous, too dear, too heavy and prone to attack iron and copper. According to O. Rammstedt (*Chem. Ztg.*, 1909, 93), it gives too high values with oil seeds and cake, and the last traces are difficult to remove. C. Stiepel (*Seifensieder Ztg.*, [36], 1299,) has found in soap stock, a residue from the refining of American cotton-seed oil with alkali, considerable amounts of petroleum ether soluble albumens which add to the saponification number. He, therefore, saturates an alcoholic solution of the fat with dry HCl gas, the free fatty acids then forming ethyl esters. The diluted solution is then extracted with petroleum ether and the extract shaken with KOH lye of 15°, which dissolves the impurities without attacking the ester. The petroleum ether extract is next evaporated and saponified as usual.

In the determination of iodine numbers of unsaturated acids, the Wijs method seems to be the favorite. The glacial acetic acid must be 100°; H. Dubovitz (*Seifenseider Ztg.*, [36], 158,) corrects it with acetic anhydride. The old Hübl and Hübl-Waller methods still have many supporters. The hexabromide test according to Lewkowitsch (Report of International Analysis Commission, VII Congress), is suited to detect fish oils in other oils. The unsaturated fatty acids are isolated by the Pb salts and brominated in ethereal solution. On treatment of the separated bromides with benzol, linoleic hexabromide goes into solution, while the octobromide of the fish oils remains undissolved; melting-point above 180°. Halphen (*ibid*) recommends addition of bromine drop by drop to permanent yellow in a cooled solution of 1 gm. fat in 5 cc. ether; 5% of whale oil in tallow gives a precipitate. Arnaud and Posternack (*Chem. Zentralbl.*, 1909, II, 1317,) find that higher fatty acids with triple union (stearolic and behenolic acids) absorb in acetic acid solution at 50-60° 2 atoms iodine almost instantly. Oleic acid under these conditions takes up no iodine. H. Kuensell (*Berichte*, [42], 2440,) finds that the glycerides of the above acids absorb from the Hübl solution 1 mol. ICl; 1 mol. Cl and Br are easily absorbed, a second molecule only on continued exposure to light.

The Influence of Vegetable Tanning Materials Upon the Rendement. JOH. PAESSLER. *Ledertechn. Rundschau,* 1910, No. 14, pp. 105-8.—In the choice and employment of material, four points are to be considered: (1) original cost, (2) efficiency of leaching, (3) stability of the tanstuffs, (4) degree of absorption of the tannin or weight-making power.

(1). In rating the cost of original material, this should be based on the tannin content. The following table shows the average relative values of materials ready for use:

	Cost of 100 kg., marks	Per cent. tans	Cost of 1 kg. tans, marks
Oak bark	10.50	9	1.17
Oak wood ext.	25	25	1.00
Valonia	25	27	0.93
Chestnut wood ext.	24	28	0.86
Pine bark	6.50	10	0.65
Quebracho wood	12	19	0.63
Dividivi	24	28	0.63
Mimosa bark	20	33	0.61
Trillo	24	40	0.60
Myrobalans	15	30	0.50
Mangrove bark	15	38	0.39

Strictly speaking, the prices of crude materials and extracts are not directly comparable, since the last are better utilized. Also the richer materials utilize better than those poor in tannin. A more rational computation would therefore be based on the amount of *utilizable* tans which would lead too far in the present discussion. It may, however, be stated that such a comparison would give even far more divergent prices than the above.

(2). As to the extractability of the tannin, this cannot be pushed to the limit; in general the best utilization is not the most complete possible. The less soluble tans are of inferior value in leather-making and the most expensive to use.

(3). In practice not much account is made of the change undergone by various tan-stuffs during employment. Fermentation decomposition with acid formation is not meant here, but the gradual transformation of the soluble into insoluble tans which precipitate and are generally unutilized. The author published some years ago (*Gerber Zeitung,* 1904, Nos. 60-64,) the results of experiments made at the Freiberg Versuchsanstalt touching this point. Quoting from these the percentage of total tannin lost after 60 days' standing of 2° Bé. liquor was: Mangrove, 0; mimosa bark, 2; quebracho wood and extract, 3 to 4; cold soluble quebracho extract, 3 to 4; gambier, 0; oak bark, 7.5; pine bark, 10; chestnut wood extract, 11.5; oak wood extract, 12.5; knoppern, 16;

trillo, 23; myrobalans, 26; valonia, 29; dividivi, 29. These figures show that the loss by decomposition may be a considerable factor in the rendement in some cases. The stability of mangrove and mimosa is remarkable and these materials deserve more attention.

(4). The weight-giving powers of various tanning materials are well appreciated in practice, although they can thus be only roughly estimated, since they are not used singly, but in mixture. Experiments have lately been made in the Versuchsanstalt upon various materials to determine this element. Liquors were used of 6 to 8° B. and applied to uniform pieces of cow-hide. The tannage was begun with weak liquors, which were gradually raised to 5%. The acid contents began with 0.1, increasing to 0.6%; experiments were also made without acid. The completest tanning through and highest rendement were with quebracho wood, quebracho extract not cold soluble, mimosa bark, oak wood, chestnut wood, oak bark, pine bark, mangrove and valonia in the order named. Next came knoppern, dividivi, myrabolams, sumach, tannin and last cold soluble quebracho extract, this being especially low. Cold soluble quebracho is therefore best suited for leather sold by surface measure. Mimosa and mangrove give good yields, and now that the objectionable color of the last is overcome by Arnoldi's process, are promising materials.

Fundamental Rules of Practice; Extraction (Cont.). L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, No. 12, pp. 89-90.—Procter and Parker (*Jour. Soc. Chem. Ind.,* 1895, 635,) and Eitner (*Gerber,* 1895, 145,) have studied the influence of temperature upon extraction. These important investigations have not received enough attention among practical men; the writer quotes in tables their results, which are reprinted here.

Percentage of total tans extracted in saturated solution (Parker and Procter):

	Oak bark	Myrobalans	Valonia trillo	Valonia whole	Natal mimosa	Sumac	Quebracho wood	Mangrove bark
15°	61.5	79.2	70.5	64.4	66.3	70.0	35.2	61.6
15-30	70.8	83.6	74.4	72.4	90.6	86.7	46.5	76.3
30-40	83.3	89.7	85.9	84.4	94.1	91.1	54.4	82.5
40-50	85.4	93.1	90.8	94.0	94.4	99.0	69.6	87.7
50-60	88.5	96.4	100.0	99.2	95.0	100.0	76.0	96.2
60-70	94.8	96.7	98.7	100.0	98.4	93.6	80.2	94.7
70-80	95.8	96.9	99.2	98.4	100.0	88.7	88.0	96.7
80-90	100.0	97.5	94.4	96.0	96.3	83.3	100.0	100.0
90-100	100.0	100.0	93.6	94.4	94.1	81.8	89.9	65.7
½ hour's boiling	94.8	98.3	91.5	90.4	91.9	74.9	....	....

Percentages extracted, original material = 100 (Eitner):

A. EXTRACT.

	Atmospheres additional pressure			
	0	2	4	6
Pine bark	29.06	32.76	31.54	30.72
Oak bark	22.14	23.79	23.88	24.04
Cajota bark	40.54	41.41	33.14	26.38
Mimosa bark	42.10	45.00	43.52	41.33
Hemlock bark	13.70	14.07	13.73	12.70
Willow bark	9.16	14.95	17.49	19.39
Myrobalans	41.73	44.19	45.98	44.12
Algarobilla	68.62	63.06	49.25	48.85
Dividivi	69.40	64.72	55.90	46.56
Valonia	49.23	50.70	47.79	41.45
Knoppern	45.23	43.87	41.43	35.90
Sumach	43.38	52.33	51.10	47.48
Oak wood	9.76	10.96	23.60	24.81
Quebracho wood	23.91	24.38	25.39	26.23
Tannin	100.12	100.59	100.16	92.79

B. TANNING SUBSTANCE.

	Atmospheres additional pressure			
	0	2	4	6
Pine bark	16.24	12.92	8.58	6.49
Oak bark	11.07	7.99	5.62	3.22
Cajota bark	21.75	21.45	11.41	2.27
Mimosa bark	31.61	30.75	29.98	26.60
Hemlock bark	9.30	8.34	4.50	2.13
Willow bark	4.80	3.16	1.59	1.59
Myrobalans	25.02	23.02	14.52	12.49
Algarobilla	36.44	24.04	8.37	8.47
Dividivi	45.12	33.14	18.08	14.93
Valonia	29.97	27.28	24.78	18.92
Knoppern	29.32	27.08	23.78	17.73
Sumach	22.85	22.70	11.27	8.87
Oak wood	6.44	6.50	5.52	2.57
Quebracho wood	21.05	21.50	18.42	13.60
Tannin	94.76	85.55	63.49	39.14

C. NON-TANS.

	Atmospheres additional pressure			
	0	2	4	6
Pine bark	12.82	19.82	22.96	24.23
Oak bark	13.07	15.80	18.26	20.82
Cajota bark	18.79	20.00	21.73	24.11
Mimosa bark	10.49	13.54	14.25	14.73
Hemlock bark	4.40	5.73	8.20	11.60
Willow bark	6.00	10.15	15.90	17.80
Myrobalans	16.72	21.17	31.46	31.63
Algarobilla	32.18	39.04	40.88	40.38
Dividivi	24.28	31.58	37.26	31.63
Valonia	19.26	23.42	23.41	22.53
Knoppern	15.92	16.78	17.65	18.25
Sumach	20.53	29.63	39.83	39.61
Oak wood	3.32	4.46	18.08	22.34
Quebracho wood	2.86	2.88	6.96	12.63
Tannin	5.46	15.04	36.67	53.65

It is seen from the first table, that while in general the amount extracted increases with the temperature until the maximum 100 is reached, any further heating lowers the yield. This is especially evident in the second table, where temperatures far above boiling were employed. For example, with oak bark, which at atmospheric pressure or boiling gave 11.07% tans, these were decomposed and reduced to 3.22% at 6 atmospheres pressure, while the non-tans increased. The practical conclusion for the tanner is that in extraction of vegetable materials, not only is it useless but even harmful to exceed 100°. The tables also show that for the best extraction, temperatures vary for different materials, being at 50-60° for trillo and sumach, 90-100° for myrabolams. It might be concluded that it would be best to extract each material separately at its own suitable temperature; this is, however, not essential, since in practice a mixture is extracted at gradually increasing temperatures, so that each material is finally treated at the most favorable temperature.

(To be Continued.)

School of the Tanner; Extraction. A. SCHMIDT. *LeCuir*, 1910, [3], Nos. 6, 8; pp. 125-7, 182-4.—Parker and Procter's researches (see Manstetten, above) are quoted and discussed. For each material there is a critical temperature at which the extraction is complete; to exceed this would be even detrimental, for the difficultly soluble non-tans would go into solution to be afterwards deposited, interfering with the tannage. Another ill effect of over-heating is to decompose with loss some of the tannin previously dissolved, as well as to discolor the extract and render it turbid. This inconvenience would result with oak, for instance, if 80° were exceeded, with myrobalans at 90°, mimosa at 70°, sumac at 50°, etc. There are many who extract sumach with boiling water, but Parker and Procter's tables show that 10-15% more materials are required to yield the same product as an extraction at 50-60°.

In extraction, it is best to leach in fractions with gradually increasing temperature until the maximum referred to is reached. For those tanners who cannot adopt the complete rational method, simpler combination processes may be used. For instance, after making the extraction in a single open vat in the cold, the mixture is heated up by indirect to a moderate degree, say 40 to 50°, and more tannin dissolved. This method has the advantage of giving a concentrated liquor. Another method is to withdraw the extract made at a low temperature, replace by fresh water or old liquor and extract at increased temperatures. The author next describes systematic extraction in open vat series by the circulation process, following Manstetten (abstract, this JOURNAL, 1908, [3], 285,). He illustrates this by an additional drawing showing the vat series in cross section, each vat being at a lower level than the preceding one.

(*To be Continued.*)

Deliming and Bateing. ANON. *Ledertechn. Rundschau,* 1910, No. 15, pp. 115-116.—The writer does not share the opinion of some that mineral acids cannot be used for deliming without injury to the grain. Twenty years ago, when extract tanning was in a primitive stage, he observed that the slightest, variation in bateing affected the color of the leather and arrived at the following principles: (1) a good color can only be obtained with pelt absolutely free from lime, (2) lime can be completely removed without injury to the hide only by neutralization and not by hand work or bateing alone, (3) the vigor of the acid is immaterial, merely the amount determines the result, and especially the solubility of the lime salt produced. Hydrochloric acid used judiciously is the cheapest and gives the best results. Upper leather is best delimed warm up to 30° in the drum, or reeled, sole leather is delimed without warming, best suspended and rocked. Very weak acid is used at first; the dilute acid is added to the deliming bath until this just reddens blue litmus paper and this is repeated as the lime of the hide becomes neutralized. As the deliming proceeds, the final tests are made with litmus or phenolphthalein upon sections cut from the hide; when complete, the interior should no longer give an alkaline reaction. If the acid be added so as to keep the bath only slightly acid, there is no danger of injury to the hide. If sulphuric acid be used, the resulting gypsum is washed out with difficulty and remains in part in the leather. In using this acid, it is of advantage to remove by washing and mechanical means as much of the lime as possible before applying the acid. With the above precautions there is no need of the more expensive lactic and formic acids on the score of safety. Also even in the special cases where a dung bate is of advantage this last is favored by first deliming separately.

White Calf-Skin Leather for Saddlery. *Magyar* BORIPAR, through *Ledertechn. Rundschau,* 1910, No. 14, pp. 108-9.—In Hungary the following process is employed for fine white leather, giving besides a fine appearance.

greater water resistance than the ordinary alum leather. After good softening and stretching, the liming is begun with 2% quicklime, the next day 2% more is added, the hides let lie 2 days, and 2% lime, 1% sod. sulphide added. This is repeated on the 6th day, and 2 days after 2% more lime added. The dehairing is made the 10th day. After rinsing, the hides are then drummed for 1 hour with a pickle of 1% H_2SO_4, 7½ kg. salt in 55 l. water to 50 kg. white hide. After draining 24 hours the hides are milled 25 minutes in a solution of 1½ kg. salt, 1½ kg. Glauber salt in 37 l. water, then 25 minutes more at 25° in a solution of 2 kg. salt in same amount of water. A previously prepared alum solution is added and milling continued 3 hours. This solution is made by dissolving 6 kg. alum. sulphate in 37 l. water, leaving slowly cool and cautiously adding with stirring 6½ kg. sod. carbonate in 37 l. water. The preparation of the fat liquor is made with great care. 22 l. castor oil are placed in a stone jar, which is cooled by surrounding water in a tub. After cooling to 15°, 130 g. H_2SO_4 are added and stirred 15 minutes. This is best begun at 8 a. m. and the same operation repeated at 11, 3 and 6 o'clock, with good stirring after each addition of acid. The same is done the next day every 3 hours until nearly 1½ kg. acid have been used. The third day the oil is transferred to a clean vat provided with a cock at the bottom. This is filled two-thirds full with water at 30° and 15 kg. salt stirred in. For 5 hours the stirring is repeated every half hour and the oil then let collect at the surface. The same operation is repeated the 3 following days, using 12, 9 and 7 kg. salt respectively. Of this oil, 3½ kg. are mixed with 30 l. water of 35° C. and milled 35-40 minutes with 50 kg. wet leather. The currying begins by applying to the grain a paste of talc with 2 parts glycerine and 4 parts water, which is let dry. The leather is then dipped in warm water, rolled up and let lie over night, then stretched. It is of advantage to let the leather rest 8-10 days before adding the fat liquor. This last may also be replaced by others more easily made, suited for white leather, or the so-called "nourishment" used for glove leather may be used.

PATENTS.

Machine for Splitting Leather. U. S. Patent No. 955,266. PETER HELDMAN, Frankfort, Germany.

Vacuum Pan. U. S. Patent No. 955,483. FRITZ TIEMANN, Tucuman, Argentina.

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INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS.

The next Conference of the I. A. L. T. C. will be held in the Amphitheater of the Chemical Section of the University of Paris, September 18th to 22d, 1910.

A cordial invitation has been extended to members of our Association to attend the Conference.

LOSS OF ACID IN TAN LIQUORS.

By Lloyd Balderston.

It has long been accepted as true that the natural plumping acids in tan liquors are produced by the action of bacteria. It has not been fully shown what are the necessary conditions for the production of lactic and acetic acids in the liquors, but it is well known that if liquors containing acid are allowed to stand exposed to the air and not in contact with hide, the acid disappears. The loss of acid is more rapid in warm weather, and is accompanied by the growth of a film on the surface of the liquor.

Under the microscope this film is found in most cases to consist entirely of yeast cells. Several kinds have been found, but they have not yet been identified with any of the named species. They consists of long slender cells, budding at the side near one end. In order to determine whether the loss of acid is directly due to these yeasts, a series of experiments was tried in August 1909. A brief statement of the results of these experiments was given by Mr. Alsop at the Washington meeting of the A. L. C. A. in December, 1909, and appears in the JOURNAL for February last.

Ten 150 cc. samples of sapped liquor from an oak tannery were sterilized in bottles and nine of them inoculated with nine separate organisms which had been isolated from tan liquors. Four of these were yeasts which grow throughout the liquor, and three of the four ferment glucose. The other five grow at the surface, forming a film, and do not ferment any kind of sugar.

The acidity of the liquor at the beginning was 0.80 per cent. in terms of acetic acid. At the end of two weeks the blank showed 0.78 per cent. and at the end of three weeks, 0.82 per cent. The variations here shown are probably due to inaccuracies of titration. At the end of two weeks all of the inoculated samples were examined to see if they contained the organism which had been introduced and no other. All were found to be pure cultures but one, the none-fermenting bottom yeast, which seemed to have failed to grow. The five samples which had been inoculated with surface yeasts showed 0.34 per cent., 0.36 per cent., 0.30 per cent., 0.28 per cent., and 0.36 per cent. total acid, in terms of acetic. At the end of three weeks, the same five gave 0.28

per cent., 0.28 per cent., 0.26 per cent., 0.22 per cent., and 0.30 per cent. The samples in which the three fermenting yeasts had grown gave at two weeks 0.80 per cent., 0.82 per cent., and 0.78 per cent., and at the end of three weeks, 0.82 per cent., 0.86 per cent., and 0.78 per cent. Broadly speaking, it seemed that the surface yeasts had in three weeks destroyed 60 per cent. of the acid, and the others had destroyed none. A similar experiment tried in April, 1910, showed less decrease of acid because of the low temperature prevailing at the time.

It is not certain that yeasts are the only agents which destroy the acid in standing liquors, but the fact that in closed bottles no such yeasts grow and no loss of acid takes place seems to point to such a conclusion. Whether the growth of these yeasts in the tan vats does any considerable damage is difficult to determine, but they do to a great extent impair samples collected over a period of time. They do not seem to affect any constituent of the liquors which concerns their tanning value except the plumping acids, but they act on these to such an extent that samples taken day by day and kept for a time may give a very misleading idea of the quantity of acid present in the vats. In cold weather the samples keep fairly well, but in summer an acid determination taken from a sample collected during some weeks will often show less than half the actual acid of the liquors sampled.

An experiment illustrating this was tried in April, 1910. Daily samples of two liquors were taken and put into covered vessels. Each day the acid of that day's sample was determined, and at the end of two weeks the acid percentage of the liquor in each of the covered vessels was found. For liquor No. 1 the daily tests varied from 0.46 per cent. to 0.58 per cent. in terms of acetic acid, the average being 0.535 per cent. The test of the liquor in the vessel which had been accumulating for two weeks showed 0.44 per cent. For liquor No. 2 the daily tests ranged from 0.47 per cent. to 0.585 per cent., averaging 0.539 per cent. In this case the sample which had stood gave 0.40 per cent. The weather during these two weeks, excepting two days, was very cool, or the fall in acidity would undoubtedly have been greater.

Other samples of the same liquors were collected during the same time, in the same manner, and an antiseptic put into each vessel at the beginning. Tests from these at the end of the time showed for liquor No. 1, 0.54 per cent. and for No. 2, 0.53 per cent. Analysis showed that the per cent. of tannin and other constituents of the liquors had not been altered by the antiseptic.

It seemed desirable to find out whether the volatile or non-volatile acid fell off more rapidly. Six samples were accordingly tested and set aside in open bottles and samples from them examined every few days afterward to determine the proportion of volatile and non-volatile acids. A summary of the results is given in the table.

If only sample No. 1 were considered, we might conclude that the volatile acid fell off much more rapidly than the non-volatile. An average of all the results shows, however, that the loss is about the same proportionally for the two sorts of acid. The first four samples are all from the same oak tannery, 1 and 2 being composites from the regular samples of new and sap liquors respectively. Nos. 3 and 4 are similar composites of special samples taken from the vats on the day of shipment. No. 5 is a composite of sapped liquors from another oak tannery and No. 6 a similar composite from a hemlock tannery.

It will be observed that No. 3 has behaved very differently from the others. It was a sample of new oak liquor which had not stood in a sample vessel. In 11 days its proportion of lactic acid seems to have increased so as to be greater than that of the regular sample, and after that to have fallen off. (The results for this sample on June 6th are probably in error.) Further experiments are in progress to discover whether lactic acid in a bottled sample may under such conditions actually increase.

Lactic acid seems to decrease more rapidly in sapped liquors than in new, and the growth of the yeast film is more rapid on the sapped liquors. The reason for this difference is still a matter of conjecture.

It is evident that if samples are collected over a period of time, some sterilizing material must be used, if these samples are to give a correct measure of the acid in the liquors. Even if the samples are taken directly out of the vats, the acid content may not be correctly determined unless they are examined at once.

Sample	Date	Volatile acid Per cent.	Non-volatile Per cent.	Total acid Per cent.
No. 1	May 19	.44	.39	.83
	May 21	.43	.40	.83
	May 24	.38	.39	.77
	June 6	.28	.30	.58
	June 13	.16	.29	.45
No. 2	May 19	.48	.43	.91
	May 21	.44	.44	.88
	May 24	.39	.37	.76
	May 30	.33	.35	.68
	June 6	.24	.27	.51
	June 13	.20	.16	.36
No. 3	May 19	.40	.31	.71
	May 21	.41	.32	.73
	May 24	.45	.33	.78
	May 30	.43	.42	.85
	June 6	.30	.29	.59
	June 13	.35	.33	.68
No. 4	May 19	.63	.50	1.13
	May 21	.55	.48	1.03
	May 24	.53	.45	.98
	May 30	.45	.41	.86
	June 6	.38	.28	.66
	June 13	.32	.28	.60
No. 5	May 19	.48	.34	.82
	May 21	.44	.30	.74
	May 24	.40	.34	.74
	May 30	.38	.27	.65
	June 6	.32	.23	.55
	June 13	.24	.23	.47
No. 6	May 19	.43	.34	.77
	May 21	.44	.32	.76
	May 24	.43	.30	.73
	May 30	.37	.26	.63
	June 6	.31	.23	.54
	June 13	.25	.19	.44

VEGETABLE TANNING MATERIALS.[1]

By John H. Yocum.

When our tanners had the virgin forest to depend upon, hemlock and oak bark were the only vegetable tanning materials in use in this country, and they yet remain the source of greatest supply of tannin.

The yearly cut of hemlock bark is between 800,000 and 900,000 tons and oak bark from 300,000-400,000 tons. The peel of hemlock has decreased about one-third in the last ten years, while the peel of oak bark has remained nearly stationary.

Because of increased production of leather during this period and because of the decrease in the peel of hemlock bark, it has become necessary to reach other sources of tannin supply.

The first development to meet these conditions was the making of chestnut wood extract, which has now reached a very important stage, from 450,000-500,000 bbls. being produced yearly. In addition chestnut wood is being used at many southern tanneries directly in the leaches. Tanners have found that the liquors obtained by this method are insufficient in strength for their purposes, so some of them have added evaporating plants to their leach houses to concentrate their liquors to a sufficient strength for their use.

A barrel of chestnut extract is practically equal to a ton or cord of either oak or hemlock bark, and while the yield from various extract factories differ, generally a cord of wood (128 cubic feet) yields a barrel of the 25 per cent. tannin chestnut extract.

Quebracho extract is made from quebracho wood, a product of the River Platte Valley in South America. This wood contains from 18-24 per cent. tannin.

The solid quebracho extract contains about 65 per cent. tannin and is sold in this basis. The yield of extract is generally one ton of solid extract from about three and one-half tons of the wood. One ton of the solid extract is considered equivalent to nine tons of oak or hemlock bark.

There are now being imported about 60,000 tons of this solid extract or its equivalent in wood; as there are two factories

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[1] From the *Journal of Industrial and Engineering Chemistry.*

manufacturing liquid quebracho in this country, the equivalency of this quantity of quebracho is 540,000 tons of oak or hemlock bark.

The tariff on this product was formerly one-half cent per pound but it has been raised three-fourth cent per pound in the new tariff bill.

Mangrove bark and mangrove extract are also imported in quantity. Mangrove bark grows on the low shores of salt waters everywhere in the tropics. Along the Gulf of Mexico, mangrove averages, when properly cured, about 30 per cent. tannin that from the East coast of Africa about 40 per cent. tannin. East Indian and Borneo, between the two; this product enters free of duty, so that no accurate data is obtainable as to the quantity imported, but this no doubt is more than 20,000 tons annually, equivalent to more than 60,000 tons of oak or hemlock bark.

In the East Indies are two factories making solid extract from this bark, which comes upon our market as mangrove cutch; the quantity being brought in is not large now on account of the duty of seven-eighth cents per pound, which the new tariff has placed on this product. It formerly came in free.

Myrobalans are the fruit of an Indian tree, the harvest ranging from 30,000-45,000 tons per year. The United States is taking from one-third to one-half the production. Myrobalans contain about 30 per cent. tannin. What is now being used in the tanning trade in this country will represent at least 45,000 tons of oak or hemlock bark. It comes in free of duty.

Valonia, the cup of an acorn obtained in Asia Minor and Greece, is being imported in quantity; it contains about 40 per cent. tannin. The harvest is from 50,000-60,000 tons per year. What is being brought into this country is equivalent to about 40,000 tons of bark per year. It comes in free of duty.

Divi-divi, wattle bark, etc., do not come into this country in any quantity.

Palmetto extract and canaigre are not produced in sufficient quantities to be commercially considered. Sumac and gambier are imported in large quantities, but do not go into the same trade that uses our native barks and cannot be compared with them.

From the estimates given of what the various tanning materials in use here are equivalent to in bark, it is seen that in total 2,300,000 tons are represented, about one-third being imported materials. At a fair valuation, these materials cost the tanner about $23,000,000, the importations being about $7,000,000 per year.

From a chemical view-point, tannins are divided into pyrogallol tannins, such as those from chestnut wood, myrobalans and valonia; and catechol tannins, such as from quebracho, hemlock, mangrove and oak bark. But from the tanners' view-point, the color and characteristics of the leather made from these various materials is of more importance.

Arranging these materials as to their color, that is from a light yellow to a dark red we have sumac myrobalans, valonia, bleached quebracho, oak bark, natural quebracho, chestnut, West Indian mangrove, hemlock, and East African mangrove.

It is important to a tanner of oak so far as color is concerned that if he uses chestnut, to also use quebracho, so that a duplication of the oak color be obtained. There are many combinations that can be arranged from these materials to duplicate the oak, hemlock or union colors so long established as standards in the sole leather trade.

The color of the leather produced is not the only characteristic which the tanner has to consider in the use of tanning materials; some wish hard leathers, some soft. It is well established that sumac is not suitable for hard leather; it is used on sheep and other soft leather exclusively. Myrobalans are considered a soft tannage. Valonia and chestnut are considered hard tannages. Oak, hemlock, mangrove and quebracho are used on both hard and soft tannages. There seems good reason to believe that by proper manipulation soft leathers can be obtained from any of these materials.

Palmetto extract which often contains as much as 12 per cent. of ash from salts soluble in the extract, the extract containing about 20 per cent. tannin invariably makes soft leathers when used alone. Sulphited quebracho extracts which contain a large per cent. of ash also make soft leathers, and it is a well-known fact that hemlock liquors treated with common salt will tan sheep skins as soft as does sumac.

From this it is a fair conclusion that salts in tanning solutions have a tendency to soften the resulting leather.

In tanning pickled sheep skins, that is, skins cured in NaCl and H_2SO_4, unless the tanning solution is salted; that is, treated with NaCl, the skins plump and lose their value, becoming hard and tinny when tanned; that is, NaCl counteracts the action of the H_2SO_4 on skins.

The tanners of the hardest sole leather use H_2SO_4 as a plumping agent, using hemlock, oak, mangrove, valonia, chestnut, myrobalans and quebracho in various mixtures and proportions. It follows that the character of leather as to softness or hardness is more dependent on the relation of plumping acids to soluble non-tannins than it is on the character of the tanning material used.

In using the term soluble non-tannins, I wish to include the effect not only of soluble inorganic salts, but also the similar effect of organic non-tannins natural to the tanning material.

The character of the organic non-tannins varies both as to their ability to furnish plumping acids and non-plumping acids, and likewise as to their depression of plumping acid action on the skin.

It is quite true as a rule that the pyrogallol tannins do not give the hard leathers that the catechol tannins produce, yet this may not of itself be due to the character of the tannin, but may result from the fact that gallic acid and non-plumping acid is usually present in the tanning solutions made from these materials.

The subject is a broad one and needs much investigation, but sumacs and nutgalls of the pyrogallols series show the largest changes into gallic acid and give the softest leather, while valonia of the same series shows small changes into gallic acid and gives a firm leather. On the other hand, chestnut extract contains in its extracted form gallic acid, and not subject to much further changes into this acid, gives a firm leather.

Palmetto is of the catechol series, but gives a soft leather, which as I have noted before may be due to the presence of excessive quantities of inorganic salts, yet all the rest of this series are used for heavy leather tannages.

The nature of the combination of hide with tannin is not fully understood at present, but the tanner has had the experienced knowledge of generations in the use of raw vegetable tanning materials. This knowledge seems to have brought the practical tanner to conclusions, and he has determined in his own mind what raw material he wants to use to produce a certain result.

It lies with the chemist to determine the reactions between the different tannins, non-tannins and their relations to salts and acids before the final decision can be reached as to the weakness or strength of the rule of thumb methods now followed by the tanner in determining the kind of tanning material to be used by him.

DYEING LEATHER.[1]

By F. E. Atteaux.

The art of dyeing leather was known to the early Egyptians over three thousand years ago. They produced finely colored leather, samples of which have been found and preserved.

The Chinese and various Oriental tribes also understood the art, and produced highly colored and embossed leather, similar to morocco. They were the first to introduce colored leather in Europe.

After a time the races of Europe began to learn the process of manufacture and coloring leather for their own consumption. As time went on the art of dyeing leather increased. Processes were improved and at the present time the methods employed are radically different from those used only a few years ago.

Formerly vegetable coloring matters were in great demand for dyeing leather, but now these products have been replaced one by one with the artificial dyestuffs, and to-day only a few vegetable colors are used, the most important of which are logwood and fustic.

Of the artificial or so-called aniline dyes, those especially adapted for leather dyeing are the acid, basic, direct and alizarine dyestuffs.

These act differently on different tannages.

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[1] From the *Journal of Industrial and Engineering Chemistry.*

Chrome Tannage.—The process of dyeing the different kinds of chrome-tanned leather such as calf, sheep, goat and heavy leather, also pig and horse hides are similar and the formula used on one may be applied to all, with good results, the only difference being a slight variation in body or shade due to the nature of the skin and the method of chrome tannage.

Before dyeing, the skins should be thoroughly washed and if necessary cleared with dermiforma or lactic acid; then if desired a bottom of some vegetable coloring or tanning matter may be applied, such as gambier, sumac, quebracho or fustic, but this is not necessary only where basic colors are used, when a tannin mordant or bottom is required.

To obtain best results for sumac or gambier bottom, drum for 20 minutes at 100° F., neutral, with 3-6 per cent. of extract. the amount used depending upon the strength of bottom.

The liquor is then run off and ½-1 per cent. tartar emetic is added, dissolved in a sufficient quantity of water, and drummed 15 minutes longer at normal temperature; rinse well before dyeing.

Fustic is applied in the same manner as the sumac with the exception of the tartar emetic bath which may be omitted.

From 1-3 per cent. of the extract may be used. This makes a good bottom for acid, direct or alizarine dyes, but should not be used for basic dyes, as it has but little affinity for them.

On dyeing heavy chrome leather with fustic this process and the fat-liquoring may be combined by first dissolving the fustic and then adding it to the drum together with the fat-liquor and drumming 20-30 minutes.

Alizarine colors can be dyed directly upon chrome leather either with or without a vegetable bottom. They are dyed with the percentage of color required to obtain shade for 20 minutes at 120° F. in neutral or slightly acid bath. If acid is used the best results are obtained by using 1-2 per cent. acetic acid.

These colors are used mostly on calf and heavy leather.

Alizarine orange R and alizarine yellow G are the most extensively used of these colors. By shading with logwood or alizarine blue a variety of tans and browns can be obtained.

Direct colors dye leather in a neutral or slightly alkaline bath.

They are drummed for 20 minutes at 120-130° F. From 1-3 per cent. of color should be used, the quantity depending upon the shade desired. If necessary ¼-½ per cent. of sal soda may be added to drum and this will insure the leather against acidity.

Wash leather well after dyeing.

By using 4 per cent. soluble oil, or some other light fat-liquor in the dye solution it is possible to fat-liquor and dye in the same bath.

Any of the direct colors can be used and by the combination of colors a great variety of shades can be produced.

Direct blacks are now used extensively in combination with logwood for producing black on calf and cow hides.

Basic colors are dyes similar to the *direct* colors only in a neutral bath at 110° F.; by adding ¼ per cent. bichromate of potash to drum after dyeing and running 15 minutes longer it will produce darker shades. These colors are used on all classes of chrome-tanned leather.

Phosphine produces various shades of tan ranging from a light yellow to the brown.

Bismarck and chocolate-browns, malachite-green, fuchsine auramine, methyl violet and methylene blue are colors of this class. They are fast to nearly all fat-liquors excepting a strongly alkaline fat-liquor which is liable to strip the color.

Acid colors are dyed by using ¼-½ per cent. sulphuric acid with the dyestuff. This is not necessary with all acid colors, some of which will dye neutral but many of them will not color the leather unless acid is used.

Acetic or formic acid may be used in place of sulphuric.

Leather can be drummed in a weak acid solution and color added in small quantities until the desired shade is obtained.

With these colors it is best to use a neutral or light fat-liquor, or fat-liquor before dyeing. Golden and coffee-browns are combinations of dye belonging to this class.

Colors very fast to light and fat-liquor can be obtained by dyeing the leather with 2 per cent. of dye in a drum for 20 minutes at 120° F. in a neutral bath.

The leather is then washed and run through a cold bath, composed of 2½ per cent. nitrite of soda and 5 per cent. hydrochloric acid for 15 minutes. It is then washed and put through developing bath of 1 per cent. of phenylamine, diamine, meta-toluine diamine or some other developer for 15 minutes. The bath should be kept cold because resulting colors are apt to be dull or rusty if temperature of bath is too high.

The leather is then fat-liquored, dyed and finished.

Primuline, boma black BH and developed brown R can be dyed by the above formula, good bright colors resulting.

Sulphur colors can also be dyed on leather by first dissolving the dyestuff in as little sodium sulphide as possible and adding it to the drum with 5 per cent. salt and drumming for 20 minutes at 110° F.

India Tan.—Before dyeing India goat or sheep skins it is best to clear them with ½-1 per cent. tartar emetic or 1-2 per cent. lactic acid, or if necessary re-tan with sumac and then wash thoroughly.

Basic and acid colors are the only class of dyestuffs used upon India skins with satisfactory results.

Direct and *alizarine* colors will not dye to advantage and it is considered a waste of material and time to use them.

Basic colors dye India-tanned leather very easily as the tannage acts as a mordant, and readily takes up the dye. They produce very bright colors, and are dyed by drumming at 120° F. in a neutral bath for 20 minutes. Two per cent. of the dyestuff produces a full shade.

If an excess of color is used bronzing results, but this may be overcome to a certain extent by using a small percentage of acetic acid with the color.

To dye with acid colors, the skins after being cleared are dyed as follows:

For 1 per cent. color use 0.25 per cent. sulphuric acid, the ratio varying with the amount of color used; they are dyed similar to the basic colors with the exception of the addition of acid; the skins which have been previously treated with sumac and sulphuric acid do not require the addition of acid with the color, as the acid retained in the skins is sufficient to drive on the color.

Acid colors are much faster to light than basic colors and produce bright shades.

Leather red 3B, tartrazine, orange A conc., induline and acid green are all extensively used.

Vegetable Tan.—Acid and basic colors can both be used upon sumac, gambier, quebracho and other tannages of this class. They are dyed in the same manner as India-tanned skins.

The various combination tannages are also colored in a like manner. If a basic dye will not color with good results the leather should be drummed with sumac and afterwards treated with tartar emetic. The color will then go on properly.

Bark-tanned sheep leather, hemlock splits, etc., are dyed very easily with acid colors and sulphuric acid. If basic colors are desired the leather should be treated with sumac before dyeing. For clearing bark-tanned skins ½-1per cent. borax, and the same quantity of Wyandotte tanners' soda gives good results, but if light shades are desired after clearing the skin with borax or Wyandotte tanners' soda then give them sumac and run for a few minutes in a solution of sulphuric acid of 1 per cent. of the weight of stock. Leather will be much lighter in color.

1½-2 per cent. tin crystals can be used with sumac to good advantage.

Heavy oak or hemlock sole and belting leather are colored by brushing on solution of dyestuff, made up as follows:

½-2 oz. of color are dissolved in a gallon of water; acetic acid or methyl alcohol renders the color soluble.

Gum tragacanth and casein can be used as thickeners. Both acid and basic colors can be used with the gum tragacanth but only acid colors with casein, as the alkali used to cut the casein, will precipitate a basic color. For this reason basic colors cannot be used in any finish or seasoning containing alkali.

Potassium titanium oxalate will produce a yellow shade similar to fustic upon any vegetable-tanned leather; it not only acts as a mordant but gives a good yellow bottom for the color. It does not work on chrome leather unless the leather has been previously treated with vegetable tanning material. It is dyed by drumming ½-2 per cent. of the compound in a neutral bath at 100° F. for 20 minutes; by using from ⅛-1 per cent. chrome with potassium titanium oxalate various shades of tan and light browns can be obtained depending upon the amount of chrome used.

Basic colors can also be used in combination with potassium titanium oxalate.

Alum leather is dyed both in a drum and by brushing on color.

Methylene blue and roseine produce delicate tints of blue and pink which are used for fancy leathers. All the basic colors give fine tints and acid colors can also be used on this class of leather.

Chrome, alum and vegetable ooze leathers are dyed with same class of colors previously given under the head of tannages to which they belong and are dyed in the same manner.

For a *black* ooze, the leather is first drummed with a yellow shade Bismarck or potassium titanium oxalate. A direct yellow-brown can be used on chrome ooze; then the leather is drummed with 2-4 per cent. logwood crystals for 30 minutes, ½ per cent. alkali being added to force on the color.

A striker of acetate of iron or burnt copperas and copper sulphate is then used. It is next fat-liquored and then dyed with ½-1 per cent. of neutral or leather black; drummed for ½ hour at 120° F. and fat-liquored again and then finished.

The amount of aniline color and logwood crystals used depends largely upon the tannage and shade of black desired.

Nigrosines are generally classed as basic colors, but they belong to a series of colors known as ingrain colors. They are extensively used in seasonings and finishes for blacks. They can be dyed on chrome leather, either in a neutral or acid bath, but do not give good results when dyed on vegetable tannages.

A fine blue black shade is obtained on the flesh side of the leather by using a little nigrosine in with the logwood when dyeing.

A small percentage of nigrosine brushed on alum ooze leather gives light shades of gray and slate.

SOUTH AFRICAN WATTLE BARK.[1]

According to the report of the Durban Chamber of Commerce for 1909 the past year showed a marked increase in the production and export of black wattle bark. The results of the year's trade were extremely gratifying, as not only was the production nearly half as large again as in the previous year, but

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[1] From the *Leather Trades' Review*.

the prices realized were better. The price c.i.f. London, Hamburg and Antwerp fluctuated between £8 5 s. and £8 17s. 6d., against £7 5s. and £8 15s. in the previous year. The grower did not get the full benefit of the higher selling price, owing to the increased cost of transport from farm to rail, caused by the suspension of ox transport due to tick fever.

Contrary to expectations, the exports of wattle bark to Australia have practically ceased. This fact is explained by the higher rates of wages and the labor troubles in Australia.

The sowing of new plantations has proceeded on a large scale. A feature of these operations has been that considerable areas have been sown in the coast districts. A few years back the midland districts were considered the only suitable portion of Natal for the growth of wattles, but this has now been recognized as incorrect.

The figures compiled by the South African Statistical Bureau show that 36,050 tons of wattle bark, valued at £197,489, were exported in 1909, as against 25,287 tons, valued at £137,876, during 1908, an increase of 42½ per cent. in weight and of 43½ per cent. in value.

PRACTICAL SCIENCE NOTES FOR THE TANNERY.[1]

For 20 years leather chemistry throughout the world has been making rapid strides, and now, with two large and successful schools in this country, the desire for research has come well to the fore. As to the utility of research along proper lines, no better argument could be advanced in its favor than the great advantages which have been obtained for the leather trade by the growth of the chrome leather industry, which industry is purely an application of science to practice.

Our immediate needs in the direction of contributions to our knowledge of the liming process include:—

1. A more rapid and accurate method for determining the dissolved hide substance.

2. A clearer idea of the nature of the dissolved hide substance, *i.e.*, the nature of the decomposition products, the gelatoses, gelatones, peptones, amino acids, etc.

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[1] Abridged from the *Leather Trades Review*, June 8, 1910.

3. Methods for distinguishing and separating the various decomposition products so that we may determine the extent to which the hide substance has been hydrolyzed, and consequently the solvent power of the lime liquor.

4. A clearer conception of the difference between the action of the bacteria and the action of the lime liquor as a solution of calcium hydroxide.

We know so little about the foregoing points that we may be said to be entirely ignorant as to the inner reactions of liming. The proximate analysis of the nitrogenous matter, which passes under the name of "dissolved hide substance" is given in Professor Procter's Laboratory Book, but, as will be seen, there is room for much improvement in the methods used. Eitner divides the dissolved hide substance into three classes, viz., dissolved hide substance in combination with lime, organic substance uncombined with lime, and peptones. The methods used to determine these three classes are purely empirical and of doubtful accuracy. Probably the best method yet known for the proximate analysis of hydrolyzed gelatine products is that used by Wood and Trotman, also by Trotman and Hackford (J. S. C. I., 1904, pp. 1071, 1072). In this case the peptones are separated by the addition of bromine to the solution of the peptone containing zinc sulphate. Dr. Stiasny has contributed to our knowledge on this point, and has devised methods for the determination of hide substance dissolved in lime and soak liquors by the use of formaldehyde, which is really an application of Ronchèse's method of ammonia estimation. The two methods have not proved wholly satisfactory. The analysis of the decomposition products is not of direct interest to the tanner; but it is of great interest to the technical chemist, and the solution of even one of the foregoing problems would materially increase our knowledge of the structure of the skin, leading ultimately, we believe, to the production of better leather.

The International Association of Leather Trades' Chemists appointed a Tannin Analysis Commission, which did excellent work of inestimable value to the trade. They have recently appointed a commission for the preservation, cure and disinfection of hides and skins which so far as can be seen bids fair to eclipse its predecessor in the magnitude of the issues and amounts involved. Thus, having appointed these two commissions, which are doing such excellent work, why not extend the principle and appoint commissions to elucidate other points? One of the admirable features of the American Leather Chemists' Association is the method they have of appointing small sub-committees or commissions to examine and report into the various methods of analysis which fall within the scope of the leather chemist. For instance, they have had a commission inquiring into the question of the acidity of tan liquors, for some years back. Another sub-committee is inquiring into methods of leather analysis, and another into methods of filtration, and several others. These bodies report from time to time, and so definite progress is made. Professor Procter said, when a similar scheme was mooted at the meeting of the British Section in London last November, that in the system of commissions the chairman did all the work. This is probably true, but better that than nothing, and I recommend to the Executive of the I. A. L. T. C. the following subjects as suitable for commissions, should they approve the principle:—

(*a*) The foregoing question of lime liquor analysis.
(*b*) The qualitative analysis of tanning materials.
(*c*) Leather analysis.
(*d*) The acidity of tan-yard liquors estimation.
(*e*) The bacteriology of leather manufacture.

ABSTRACTS.

Report of the German Section's Commission on Tannin Analysis. J. PAESSLER. *Collegium,* 1910, Nos. 407-8, pp. 157-171.—The Chairman reports the results of continued comparative analyses made in trial of the Zeuthen method (abstr. this JOURNAL, III, 395; IV, 298). For this method Freiberg ready chromed hide powder was used and for the official method Freiberg chromed American and Vienna white hide powders. The determination of the water in the extracts was made both direct (*a*) and indirect (*b*) by evaporation of 50 cc. unfiltered solution. For the determination of total solubles, it is imperative that the solutions be clear according to the definition of the I. V. L. I. C. The Berkefeld filter was used without kaolin. We give below with some condensation, the author's tables. The analysts taking part were: (A) Dr. Allen of Hamburg, (W) Herr Weisspflock of the Freiberg Tanning

School, (M) Dr. Moll of Brieg, (P) Dr. Philip of Stuttgart, (S) Dr. Sichling of Worns, (F_1) and (F_2) Drs. Sluyter and v. Schroeder of the Freiberg Versuchsanstalt.

	A.	W.	M.	P.	S.	F_1	F_2	Maxim. differ.	Mean
I. Chestnut Extract, liq.									
Water, direct (a)	..	58.75	58.2	58.4	58.15	58.6	58.2	0.6	58.4
Water, indirect (b)	..	58.75	58.3	58.6	58.35	58.45	58.3	0.45	58.45
Total solubles	..	40.6	41.25	41.1	40.25	40.5	41.1	1.0	40.8
Non-tans:									
Zeuthen	12.4	12.9	12.35	12.3	12.65	12.3	12.7	0.6	12.5
Official, Freib. hide	12.45	12.9	12.4	..	13.1	12.2	12.8	0.9	12.65
Official, Amer. hide	12.0	13.0	11.35	11.1	11.9	13.45	12.65	2.35	12.2
Official, Vienna hide	12.15	12.65	11.4	10.9	11.3	11.6	12.1	1.75	11.7
II. Oak Wood Ext., liq.									
Water, direct (a)	..	57.5	56.8	57.1	56.65	57.15	56.4	1.1	56.9
Water, indirect (b)	..	57.1	56.9	57.4	56.65	57.4	56.75	0.75	56.9
Total solubles	..	42.15	42.5	42.2	43.3	42.2	42.2	1.15	42.4
Non-tans:									
Zeuthen	15.65	15.0	15.65	15.0	15.55	14.9	15.2	0.75	15.3
Official, Freib. hide	15.3	14.85	15.65	..	16.3	15.55	15.1	1.45	15.45
Official, Amer. hide	14.75	17.4	14.55	14.5	15.6	16.1	15.8	2.9	15.5
Official, Vienna hide	14.45	15.9	14.8	14.2	15.2	15.55	15.55	1.7	15.1
III. Pine Bark Ext., liq.									
Water, direct (a)	..	68.4	68.05	67.5	68.4	68.25	68.35	0.9	68.15
Water, indirect (b)	..	68.1	68.3	67.3	68.4	68.55	68.3	1.25	68.15
Total solubles	..	27.9	28.0	29.9	26.6	28.45	29.4	3.3	28.4
Non-tans:									
Zeuthen	..	9.75	9.55	9.6	9.55	10.3	9.4	0.9	9.7
Official, Freib. hide	..	9.65	9.6	..	9.75	10.3	9.65	0.7	9.8
Official, Amer. hide	..	10.15	9.3	9.5	9.65	10.45	9.85	1.15	9.8
Official, Vienna hide	..	10.05	9.4	9.3	9.4	9.65	9.65	0.75	9.6
IV. Quebracho Ex., liq., cold sol.									
Water, direct (a)	..	53.65	53.75	53.1	53.8	53.55	52.75	1.05	53.4
Water, indirect (b)	..	52.9	53.05	53.8	53.0	52.9	52.9	0.9	53.1
Total solubles	..	46.8	46.25	45.5	46.35	46.4	46.55	1.3	46.3
Non-tans:									
Zeuthen	7.3	7.2	7.0	6.9	7.1	7.1	7.2	0.4	7.1
Official, Freib. hide	7.8	7.2	7.05	..	7.25	8.2	7.25	1.15	7.45
Official, Amer. hide	7.15	8.15	7.05	6.5	7.65	8.2	7.85	1.7	7.5
Official, Vienna hide	7.05	8.45	6.95	6.2	7.2	7.85	7.85	2.25	7.35

V. Quebracho
Ext., liq., reg.

	A.	W.	M.	P.	S.	F_1	F_2	Maxim. differ.	Mean
Water, direct (a)	..	59.4	..	..	58.85	58.75	58.5	0.9	58.9
Water, indirect (b)	..	58.3	..	59.8	58.65	58.5	58.45	1.5	58.7
Total solubles	..	38.5	..	38.6	38.0	38.65	39.2	1.2	38.6
Non-tans:									
Zeuthen	3.4	3.05	..	3.5	3.0	3.1	3.35	0.4	3.2
Official, Freib. hide	3.75	2.85	..	..	3.3	4.3	3.55	1.45	3.55
Official, Amer. hide	3.65	3.9	..	3.2	3.35	3.9	3.4	0.7	3.6
Official, Vienna hide	3.5	4.1	..	3.3	3.05	3.45	3.25	1.05	3.45
VI. Quebracho									
Ext., solid, reg.									
Water, direct (a)	..	13.4	13.45	13.8	13.05	12.25	12.25	1.55	13.0
Water, indirect (b)	..	12.35	11.5	13.2	12.7	11.1	11.3	2.1	12.0
Total solubles	..	78.1	79.0	76.7	78.25	77.75	78.25	2.3	78.0
Non-tans:									
Zeuthen	6.4	5.7	6.5	5.6	5.4	6.2	6.2	1.1	6.0
Official, Freib. hide	6.45	5.7	6.3	..	6.0	6.5	6.05	0.8	6.2
Official, Amer. hide	6.15	8.35	5.95	5.2	6.1	6.4	6.2	3.15	6.3
Official, Vienna hide	6.0	6.95	5.7	5.4	5.8	5.5	6.1	1.55	5.9

Discussing these results, the author finds that in the water estimation there is little choice between the direct and indirect methods, the maximum differences and general averages being about the same. The discrepancies are greater in total solubles, owing to the personal equation in judgment of optical clarity. This is especially marked in the pine wood extracts and it is desirable that this material be experimented upon for uniformity; the author proposes an extraction with a few cc. chloroform. In the non-tan determination the best concordance (minimum differences) was reached by Zeuthen's method; next came the official method with Freiberg chromed powder, and much less favorably with American and Vienna hide. The total averages are much the same for all four variations. It is desirable that at the Paris conference this fall the German Section recommend the adoption of the Zeuthen method.

VII. Blank Tests for Solubles in Hide Powder.

Milligrams solubles in 50 cc.:

	A.	W.	M.	P.	S.	F_1	F_2
Zeuthen's method	11.7	6.5	4.5	3.5	4.35	5.7	5.0
Official method:							
Freiberg hide	4.8	5.5	6.0	...	3.9	7.5	11.4
American hide	3.9	7.0	2.7	3.0	4.0	7.8	7.4
Vienna hide	2.0	6.5	2.5	0.5	4.25	4.2	7.4

These differences are not considered of practical significance, since the presence of tannin makes the conditions different in actual analysis. For instance in some cases a chromed hide powder was found to contain much solubles yet gave no higher results in comparative analyses.

The higher solubles in this case appeared due to the great swelling powder of the hide, preventing washing; with another lot which swelled less, the author found only 1 to 3 mgs. soluble. Either powder, however, gave the same non-tans.

An attempt was made to include with the above series analyses with the various brands of white hide powder which had been chromed, washed, dried and re-ground. It was found, however, that the meal was too fine for use and did not completely de-tan. It, therefore, appears that in the shake method, the hide powder should be used moist directly after chroming, or else chromed in its original preparation.

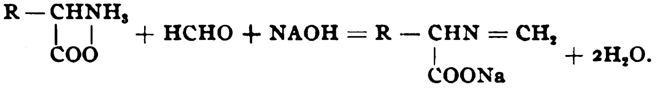
Old Limes. E. STIASNY. *Collegium,* 1910, No. 410, pp. 181-7.—There is no simple method for differentiating the various forms of decomposed hide substance present in old soaks and limes. The total N contents (Kjeldahl) does not do this nor does the direct titration of the ammonia (after deducting lime). The same may be said of Bennett's method (This JOURNAL, May, 1909,) for ammonia. This fails when sulphides are present, also the author could not verify the constancy of Bennett's factor, mg. N ÷ cc. 0.1 N HCl.

Reference is made to the author's own method, (abstr. this JOURNAL, (3) 398) where formaldehyde is used liberating from the neutral amino-acid an equivalent of free acid which can be titrated in presence of phenolphthalein. In the case of old limes, the zinc sulphate added to remove the sulphides also partially precipitates dissolved hide. To avoid this error the following modification is used, 50 cc. of the filtered lime are neutralized with 10% acetic acid (phenolphthalein) and a slight excess of 1/10 N. iodine solution added. Next 1/5 N. NaOH is added to alkaline reaction and after addition of 10 cc. neutral 40% formaldehyde, the titration is finished with alkali. A test of this method by Mr. Wilkinson gave titration differences in cc. 1/5 N. NaOH showing that $ZnSO_4$ gives too low results and that the iodine method is correct.

Without sulphides		With addition 10 cc. 10% sod. sulphide	
Without $ZnSO_4$	Using $ZnSO_4$	Using iodine	Using $ZnSO_4$
7.4	4.8	7.4	4.6

Salting out with sodium chloride is sometimes used to determine dissolved hide. 50 cc. of liquor by the formaldehyde method gave an alkali difference of 7.6 cc. 1/5 N. and a parallel test with a salted and filtered solution gave 5.4 cc. showing that the salting out is only partial.

The formaldehyde method can be employed to gain information relative to certain nitrogenous substances present which do not react with formaldehyde. The principle is to determine the partially hydrolyzed proteids by the above method and to then subject an equal sample to complete hydrolysis by boiling 6 hours with 20% HCl, reflux condensers. The product is likewise analyzed and the ratio of the two formaldehyde (or alkali) figures give the extent of hydrolysis in the original lime. Another method of expression is based on the total nitrogen. For instance a gelatine solution containing 49.5 mgs. N after complete hydrolysis required 7.6 cc. 1/5 N NaOH or 1 cc. alkali correspond to 5.8 mg. N. This ratio will differ for the various decomposition products of different proteids. For example, if monamino acid be hydrolyzed, each cc. 1/5 N NaOH will correspond to 2.8 mg. N found by Kjeldahl:



$$\begin{array}{l}\mathrm{R-CHNH_3}\\ \quad |\ \ |\\ \quad \mathrm{COO}\end{array} + \mathrm{HCHO} + \mathrm{NAOH} = \mathrm{R} - \underset{\mathrm{COONa}}{\underset{|}{\mathrm{CHN}}} = \mathrm{CH_2} + 2\mathrm{H_2O}.$$

By experiment 10 cc. of 1% glycocoll solution containing 18.7 mg. N required 6.75 cc. 1/5 N NaOH or 1 cc. NaOH = 2.77 mg. N (theory 2.8). This ratio will also apply to ammonium salts.

With the three protein decomposition products, lysin, arginin and histidin containing 2, 4 and 3 atoms N to the molecule, each liberates one equivalent acid on condensation with formaldehyde. Hence 1 cc. 1/5 N NaOH = 5.6, 11.2 and 8.4 mg. N in these three cases respectively. These variations may be utilized in estimating the relative amounts in mixtures.

PATENTS.

Leather Skiving Machine. U. S. Patent No. 958,124. Carl A. Hirth, Canstatt, Germany.

Automatic Tanning Machine, Re-issue. Original number 782,193. Charles J. Glasel, Boston, Mass.

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ELECTIONS.

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ASSOCIATE.

Charles A. Boler, 135 South Second St., Philadelphia, Pa.

CHANGES OF ADDRESS.

Joseph H. Russell to c/o Armour Leather Co., 167 Lake St., Chicago, Ill.

ANNUAL MEETING.

The Seventh Annual Meeting of the American Leather Chemists Association will be held this year in conjunction with the meeting of the National Association of Tanners, in Chicago, Thursday, Friday and Saturday, October 6th, 7th, 8th, 1910.

Further particulars in regard to the meeting will appear in the September JOURNAL.

H. C. REED, Secretary.

AN IMPROVED FORM OF SOXHLET FOR TANNIN EXTRACTION.

By C. R. Delaney.

That the principle of the soxhlet siphon extractor is extremely good, but that modifications of the detail of the apparatus are required to suit the exigencies of the materials extracted is evidenced by the number of continuous siphon extractors now on sale in the stores devoted to physical and chemical apparatus. The one illustrated herewith is modified or improved to suit the needs of the tannin and is particularly adapted to all those materials (dye woods, barks, etc.), part of whose extractives are damaged or converted by continued boiling. It is a well-established fact that if any solution of tannin be continuously boiled, the tannic acid is partly converted into gallic acid and partly into those peculiar anhydrides of tannic acid, insoluble in cold water, which are known as "reds."

It is obvious then, that to insure a correct approximation of the tannin content of any given sample it must be either extracted with cold or warm water, or that if extracted with boiling water, the resulting solution must not be boiled. The first, is not desirable for the reasons that all the extractive or that part soluble in water will not be dissolved unless an excessive quantity of water is used which must afterward be concentrated, with its attendant danger, to sp. gr. 1,005.

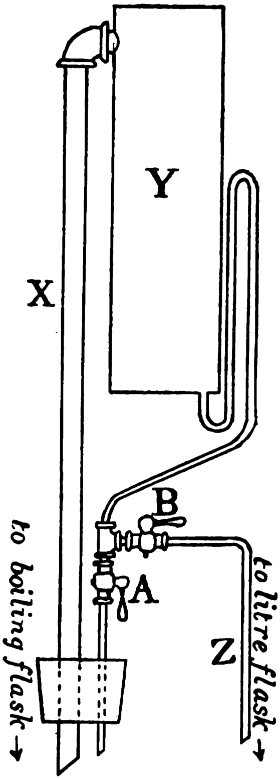
The second is especially desirable, however, for a quantity of boiling water not exceeding 1,000 cc. will extract the last vestige of tannin in 10 grams of crude bark or leaf. The regular form of soxhlet will completely ruin any test on tannin if the solution in the flask be continually boiled while the sample is being extracted as the following figures on a standard sample of pure sumac leaf will show:

DRY BASIS.

	Total solids Per cent.	Tannin Per cent.	
Percolation at 170° F.	48.75	31.42	Mean of 2 analyses
Ordinary siphon soxhlet ..	60.21	30.97	1 analysis
Improved soxhlet.........	59.45	36.17	Mean of 4 analyses

The first two analyses were made by one of the most eminent firms of tannin chemists, the third by the writer and numerous analyses made by the highest authorities upon this same sample indicate the accuracy of the latter figures. These analyses are calculated on an absolutely dry basis.

Objection has been made that by the soxhlet, with its higher



Improved siphon soxhlet, as used by C. R. Delaney

extraction temperature than the ordinary 170° F. percolator, some part of the tannin is destroyed. This objection is futile for with this modified soxhlet an average of 3 per cent. higher tannin is steadily maintained, not only by this laboratory but by others adopting the modification, in place of the percolator.

The apparatus explains itself. It is all of copper, and taps and bends of one-eight inch (iron pipe size) brass. X is ¼ inch pipe. When the apparatus is connected up, with a large necked Erlenmeyer flask and a condenser as usual, the steam runs through the tube X and into the body Y, thence to the condenser—not illustrated.

Then the tap A is shut and B opened and when the siphoning action starts, the liquid extract, rich in tannin, goes into a liter flask at the point Z. After about 600 cc. have run into the flask, the taps are reversed, *i.e,* A opened and B shut and the usual automatic siphoning set up. The liquid may be boiled practically with impunity after 5 siphonings have been run through Z, for the per cent. of tannin left is very small and not so liable to decomposition as the first few extractions.

The small cocks and pipe may be secured from the Frasse Co., Cortland St., New York City.

TANNING SCHOOL.

The National Association of Tanners, meeting in Chicago on July 1st, heard and adopted the report of their committee on the establishment of a Tanning School. The committee recommended that the school be organized as a department of the Pratt Institute, Brooklyn, N. Y.; all matters of administration to be in the hands of the officers of the Institute. It is expected that the school will be open for a limited number of students in the fall of 1910, and that it will be fully equipped by September, 1911.

It is proposed to establish 8 or 10 scholarships of $250 each, to be awarded through the officers of Pratt Institute and to engage an expert research chemist to conduct experiments along lines outlined by the Association; the money for both these purposes to be raised by the Association. The requirements for admission to the Institute are very flexible, the main emphasis being laid on the student's character and habits.

The courses will be arranged to meet the needs of students with a high school education, of college graduates, and of men who have had experience in tanning. The work will be grouped in two courses, A and B, as follows:—

COURSE "A."

A ONE-YEAR TRADE AND TECHNICAL COURSE.

(*a*) The practice and principles of tanning. A practical lecture course on the latest and best methods of the art in all its various branches

(*b*) Practical tanning and finishing—in school tannery. About three full days per week should be devoted to this kind of work and it should be conducted as closely as possible as similar work would be conducted in a factory.

(*c*) Elementary principles of practical chemistry related to the tanning industry—lectures and recitations.

(*d*) Chemical laboratory practice (related as closely as possible to work in tanning).

(*e*) Industrial chemistry—general descriptive lectures regarding chemical industries closely related to tanning.

(*f*) Industrial chemical laboratory practice (in industries closely related to tanning, such as dyeing, testing of dyes, soap making, manufacture of chemicals entering into tanning operations, etc.). This work is, of course, elementary.

(*g*) Mechanical draughting, and design and construction of tanneries. (A brief elementary course.)

(*h*) Power plant operation and mechanical transmission of power. (A brief course containing only the most important practical ideas.)

(*i*) Electrical practice and electrical transmission of power. (A brief course containing only the most important practical ideas.)

COURSE "B."

A TECHNICAL COURSE FOR LEATHER SPECIALISTS.

(For college graduates of four-year courses in Chemistry—therefore the equivalent of a five-year course.)

(a) The practice and principles of tanning. A lecture course on the latest and best methods of the art in all its branches in which these students would be able to take up many matters far beyond the grasp of men in Course "A."

(*b*) Practical tanning and finishing—in school tannery. This course would include much of the same kind of training as is included in the parallel course with the other men, but also would include investigations into new processes and methods, etc.

(*c*) Chemical research—laboratory investigation and problems related to the tanning industry.

(*d*) A series of lectures by experts and specialists in various departments of the tanning industry and closely related industries, on advanced problems in the art of tanning, dyeing, finishing, etc., and in economical questions relating to the industry.

(*e*) Industrial Chemistry. General descriptive lectures regarding chemical industries related to tanning with trips of factory inspection.

(*f*) Industrial chemical laboratory practice (in industries closely related to tanning, such as dyeing, testing of dyes, manufacture of dyes, soap-making, manufacture of chemicals entering into tanning operations, etc., etc.). Students in this course could undertake work far more comprehensive than that done under the corresponding heading in Course "A."

(*g*) Advanced chemical analysis of barks, extracts, oils, fats, waxes, etc., and of similar materials.

(*h*) Problems in design and construction of tanneries, arrangement of power plants, design of factory equipment, etc.

(*i*) Study of design, operation, and maintenance of electrical and mechanical power plants and power transmission.

(*j*) Thesis—original investigation, or some piece of important independent work valuable for publication.

A NEW STANDARD METHOD OF COLOR MEASUREMENT.[1]

By Prof. H. R. Procter.

Although it may be admitted that the official method of measurement and registration of the color of tanning extracts has served a useful purpose as enabling sellers and buyers to fix

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[1] *Journal of the Society of Chemical Industry*, June 15, 1910.

a definite numerical standard in contracts, it is obvious that it fails in other respects to give much useful information as to the actual color of the material. It is certain that no merely optical test can give complete information as to the color which will be given to the leather, since this depends not only on the coloring matters present, but on their relative affinity for the hide and even upon the previous preparation of the latter, and it is only necessary to quote the extreme case of logwood extract, which itself is yellow, but dyes an alumed leather violet. The difficulty, however, of producing the same shade on different samples of pelt, and of guaranteeing the tanned leather against subsequent color-change, render the actual tanning test unsuitable as a basis of contract, and still leave room for an optical method more accurate and intelligible in its results than that at present official. Attempts have been made from time to time to substitute for the Lovibond glasses some more scientific and less arbitrary scale, based on the actual spectrum, and measured by spectrophotometers, such as Hueffner's, described by Hough (*Collegium,* 1909, 417); but those who have gone carefully into the question will at once realize that the scientific measurement of a color, even if it can be executed with sufficient accuracy, can only be expressed fully by the form of a curve, and not in any way suitable for commercial requirements; and that any numerical expression must be based on arbitrary assumptions as to the component colors. It therefore seems unwise to leave the simple and well-known colored glasses of the tintometer for a more expensive, more complex, and for our purposes, probably less accurate method, although as will be shown later, the glasses have serious inherent defects; but while still retaining the color-standards now in use, I have sought to apply them in a more accurate and easier way, which I think also gives its information in a more comparable and clearer form.

To explain my meaning I may quote the results of a solution of a single (oakwood) extract in a solution of 20, 10, 5, and 2.5 grams per liter as measured by the tintometer and the new method (see Table I). While no intelligible relation exists between the tintometer results, those by the new method are simply proportional to the dilution of the solution, and when calculated back to terms of the original extract are identical within the limits of experimental error. The reason for the discrepancy of the tintometer results lies in the fact that the match between the glasses and the liquid, though perfect to the eye, is physically not a true one. The sum appears to be the same, but the individual constituents are different, as is at once obvious when both are dissected by the spectroscopic prism. The white unaltered light gives a band of infinite gradation of color, from red, through orange, yellow, green and blue to violet. If a colored glass or liquid is interposed, some portion of this band is shaded out, and the color which we see is the combined effect of that which remains. Thus an extract absorbs violet and blue, while the red, yellow and green which remain combine to produce orange or brown, and a blue liquid like ammoniacal copper sulphate absorbs red, yellow and green, leaving blue and violet. The absorption generally occurs as a broad band gradually shaded off, and if, the unshaded portion (Fig. 1) represents the entire spectrum of white light, Fig. 6 would represent that of an extract, the shaded curve indicating the proportion of light absorbed. If the depth of color is increased, the absorption widens; in the case of the extract, covering more blue and finally green. Thus the color of the extract usually becomes redder as it deepens, the degree of change depending on the form of the curves.

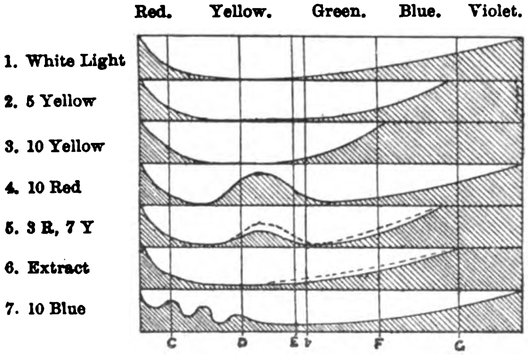

Fig. 1. Absorption-spectra.

If with these curves we compare those of the glasses, we shall find marked and curious differences. In the yellow glass (Figs.

2 and 3) the absorption somewhat resembles that of the extract, but the curve is more abrupt, so that there is little tendency for the color to become redder as it deepens; and when the whole of the blue is absorbed further addition of yellow glasses produce little change. On the other hand the red and blue glasses (Figs. 5 and 7) are marked by curious bands of selective color-absorption, so that by no possible combination can a curve be formed really similar to that of the extract. Fig. 5 for instance represents approximately the curve of 3R,7Y, which matches extract Fig. 6 in the tintometer while the dotted lines in Fig. 5 and 6 give an approximate idea of the relative effect of doubling both, which clearly shows that they no longer match, both the total depth of color and the proportion of red to yellow being varied.[1] This arises from the fact that doubling of a glass or of the depth of a layer of colored liquid does not double the color absorbed, but increases it in a proportion varying in its intensity. Thus if the first glass absorbs 50 per cent. of the total light and transmits 50, a second glass can only absorb 50 per cent. of the transmitted 50 and the total absorption will be 75 per cent. or 1½ times that of a single glass, while if the first glass absorbs 10 per cent. only, the second will absorb 10 per cent. of 90, or in all 1.9 times that of a single glass, and consequently a color consisting of bands of very different intensity will not vary in the same ratio as one evenly shaded. The conditions of color absorption being so complex that it is impossible to calculate actual color-strength from varying tintometer measurement, I have thought it preferable rather to measure the quantity of extract or tannin required to produce a definite standard color, than the color produced from a standard tannin-strength as at present; since under the proposed conditions equal arithmetical variations will always represent equal quantities of coloring matter. An instrument is therefore used in which the depth of extract-solution of known strength can be varied till its color is as dark as the color-standard. We are, however, still met by the difficulty that no single standard color will match all kinds of extract, since some are redder or yellower than others. I have therefore fallen

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[1] The curves are merely sketches and make no pretence of quantitative accuracy.

back on the arbitrary standards of the tintometer, and after considerable experiment have decided on 10 Lovibond units, red or yellow, as most suitable in intensity for accurate matching. This compound unit may contain any varying proportion of red or yellow from 9Y + 1R to 9R + 1Y, but for all ordinary tanning extracts it approximates to 7Y + 3R, and for approximate purposes, such as works control, it might be possible to adopt some average combination as a permanent standard and so greatly diminish both the cost of glasses and the trouble of making a measurement. For exact work, however, accurate match of color is essential. By keeping the standards in pairs running from 1Y + 9R to 9Y + 1R a first approximation is obtained by simply changing the pairs and varying the depth of the liquid till the nearest match is obtained. A red or yellow glass (according to whether the glasses are too red or too yellow) is then exchanged for the next lower unit, so that the standard is now of 9 units in all, and the 10 is made up by adding paired decimals equal to one unit till an exact match is obtained, the additional glass being balanced as in the tintometer by the addition of a plain glass on the side of the extract. Generally speaking no glasses on the extract side are required when one pair only of colored glasses is used, since the cylinder and liquid may be counted without sensible error as two glasses, but this will vary slightly with different instruments, and the exact compensation required must be determined by matching with plain glasses, with water on the measuring cell. The glass standard has, however, still one serious disadvantage depending mainly on the selective absorption of the red glass. For perfectly normal vision no difficulty is experienced in accurate measurement, but it is clear that an observer color-blind to the particular tract of green absorbed by the red glass would make quite a different match to the normal observer, and even slight difference of sensitiveness to this particular tract of light would affect the depth of extract solution required to match a given amount of red glass in the standard. In the tables it may be noticed that certain observers are normally higher or lower than the average, an effect probably due to the cause just named. If so, the error would disappear if the glass standard could be made a true spectrum match of the extract, and this might perhaps be accomplished by making most of its color depend on a brown-orange glass of suitable color, which has a spectrum very like that of an extract, and only employing the red and yellow glasses for minor correction.

We are now in a position to state the measurement for a given extract. The color-standard to be used is found, for example to be 7.5Y and 2.5R, or 25 per cent. red, and the depth of liquid in centimeters is 5.35. As, however, the diluted analytical solution may vary in concentration, the depth-measurement is not directly comparable for different extracts or different dilutions, and it is therefore best to calculate the theoretical concentration of extract in grams per liter (pounds per 100 gallons) required to produce the standard color in a depth of 1 centimeter (corresponding to the present 1 cm. cell). If the analytical solution after dilution was of 4 grams per liter, the required figure, obtained by multiplying depth by strength, would be 21.4 grams per liter, and again multiplying by the percentage of tannin found by analysis, (say 26.0) and dividing by 100 we should obtain 5.56 grams as the quantity of tannin present in a solution of standard color. Of course the greater these figures are the higher is the tanning strength in proportion to color, and the paler the extract.

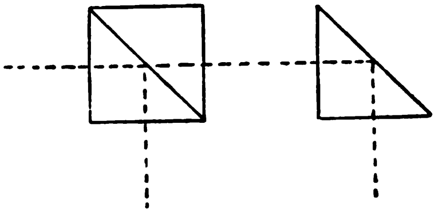

Fig. 2.—Arrangement of prisms in Schmidt andHaensch Colorimeter.

As regards instruments, the most accurate I know for the purpose is the Schmidt and Haensch colorimeter with a Lummer-Brodhun prism (Fig. 2) in which the color of the liquid appears as a stripe in the centre of the field of color from the glasses, and entirely disappears when a perfect match is obtained. Colorimeters of the Laurent and Dubosc type, in which the two colors are brought together in one field by rhombic prisms (Fig. 3) are also very good, but both are somewhat expensive (£9 or £10).

For those therefore who desire a cheaper instrument, Messrs. Reynolds and Branson are endeavoring to construct a modified form of their "chrometer" in which two separated patches of color are seen as in the tintometer, one through the colored glasses and one through a cylinder in which the depth of liquid can be varied by raising or lowering a tubular reservoir. The price of this apparatus will be about 35s. with a cylinder, but without glasses, and as only about 45 glasses are required will be much lower than that of the complete tintometer with which it is at least equal in accuracy.

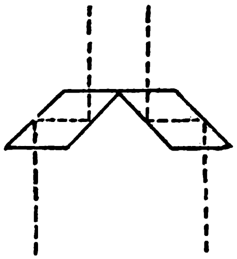

Fig. 3.—Arrangement of prisms in Dubosc Calorimeter.

In all these instruments, as in the tintometer, the use of blue glasses on one side or the other is occasionally needed to adjust the color of the glasses to that of an extract. This does not necessarily suggest any impurity of the extract, but may occur in one of very light color even more easily than in a dark one, if the color which remains is not vivid; or on the other hand an extract of deep but vivid color may require a shade of blue to reduce it to the standard glasses. In order to avoid complicating the measurement, it is proposed to state these small corrections, never more than a few decimals, as an addition to the standard (+ Blue), or a subtraction from it (— Blue) rather than vary the latter in red or yellow.

As regards the dilution of the liquor used for testing, it has been proved that under the prescribed conditions its effect, if any, is so small as to be negligible, and that most advisable will differ somewhat with the character of the extract, and the particular instrument used, as with dark solutions very small depths of liquor are needed, which cannot be measured with the same proportional accuracy as when about 5 cm. are required in the Schmidt and Haensch or 10 cm. in the chrometer. The analytical solution is always employed as soon as it is filtered, leaving the calculation of results till the analysis is completed, and in this way possible changes of color caused by time are avoided. For the Schmidt and Haensch a suitable quantity measured with an accurate pipette may be diluted to 50 cc. with colorless distilled water, while for the chrometer possibly dilution to 100 cc. will give more accurate reading, the quantity of solution taken being smaller for dark extracts and more for pale ones.

In order to overcome the uncertainty or absence of daylight it has been found desirable to employ artificial light, and the inverted incandescent gas burner with Bray or Welsbach mantle, and a globe transparent at least in its lower half, has proved most satisfactory of the lights easily available. The results differ little from good daylight, and approach it the more closely the brighter the light, so that it is found best to work with the burner slightly above the matt opal reflector of the instrument, and not more than 4 to 6 ins. distant from it. The light (and heat) should be suitably shaded, not only from the eyes, but from the cylinder of liquid and it is best to work in a darkened or dimly lighted room. Before using any colorimeter it must be ascertained that when the cylinder is filled with water and plain glasses are substituted for the standard, the brightness of the two fields is absolutely equal, and trifling differences may often be compensated by slightly moving the light towards one or other side of the instrument, or larger ones, due to the construction, with plain colorless glasses. When the instrument is accurately adjusted it is best to fix its position relative to the lamp with a clamping screw. Perfect cleanliness and brightness of the cells, glasses and opal reflector is essential to accurate work.

The advantages claimed over the present method are greater ease and accuracy of execution, closer concordance of different observers, and a much more intelligible statement of results, by which both the tint and depth of color of different extracts can be approximately compared. It is proposed that the Paris Conference of the International Association of Leather Trades Chemists should be asked to accept it as an optional method and familiarize the trade with its results by giving them for a time in addition to tintometer figures. To some extent the color standard as apart from the depth of color is characteristic for different materials.

The following tables give some idea as to the accuracy to be expected from the method, and its results as compared with ordinary tintometer-values.

TABLE I.—COMPARISON OF NEW METHOD AND TINTOMETER RESULTS ON SOLUTIONS OF CERYCH'S OAKWOOD EXTRACT OF VARIOUS DILUTIONS.

Tintometer.

Concentration	Red	Yellow	Blue
20 grams per liter	5.3	27.0	0
10 " " "	2.7	10.0	0
5.0 " " "	1.0	3.7	0
2.5 " " "	could not be measured		

TABLE IA.

Colorimeter.

Standard tint, 2.0 Red, 8.0 Yellow = 10 units.

	Depth of liquid			
Concentration	C. D. W.	H. B.	W. J.	
20 grm. per liter	.434	.424	.428 cm.	
10 grm. per liter	.890	.844	.860 cm.	
5 grm. per liter	1.818	1.710	1.796 cm.	
2.5 grm. per liter	3.620	3.458	3.498 cm.	
	Grm. per liter, for standard color in 1 cm.			
20 grm. per liter	8.68	8.48	8.36	
10 grm. per liter	8.90	8.44	8.60	mean 8.68 grm.
5 grm. per liter	9.04	8.55	8.98	per liter
2.5 grm. per liter	9.05	8.35	8.75	

The mean of 13 determinations of the same oakwood extract by five observers in various concentrations gave 8.72 grams per liter, with a mean error of ± 0.315 gram or 3.6 per cent. for a single determination and of ± 0.076 gram for the final result. Each determination was the average of five independent scale-readings. As the extract contained 23.4 per cent. of tanning matter the tanning strength of a solution of standard color would be 2.3 grams per liter.

THE BACTERIOLOGY OF THE LEATHER INDUSTRY.[1]

By J. T. Wood.

Perhaps the earliest paper dealing with the part played by

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[1] *Journal of the Society of Chemical Industry*, June 15, 1910.

bacteria in the leather industry in a scientific and practical manner was that of Eitner entitled "Antiseptics in the Tannery" (der Gerber, 1889) in which he deals with it from the point of view of the prevention of injurious fermentations. In 1894 I published a general paper entitled "Fermentation in the Leather Industry" setting forth what I knew of the subject up to that time, and indicating some of the problems which were awaiting solution.

Since that date much important work has been done, especially in the bacteriology of tan liquors by Andreasch, 1897, of drenches by Wood and Willcox, and of bates by Becker and Wood, and quite recently my friend, Dr. George Abt, has published a general paper on the part played by bacteria in the putrefaction of skin and in the bates.[1]

Since putrefaction is the most obvious danger to the raw skin it is necessary to say a few words about it. Nearly all bacteria can be cultivated on nitrogenous organic matter (the nutrient gelatine of the bacteriologist has become an article of commerce) so that there is scarcely any species of bacteria which cannot take some part in the putrefaction of skin. In an article on "Recent advances in the bacteriology of putrefaction"[2] I have given a short account of the researches of Tissier and Martelly on the putrefaction of meat, and it is probable that the putrefaction of skin follows much the same course. Abt (*loc. cit.*) gives the following table resuming the action of putrefactive bacteria.

Aerobic.	Mixed	Proteolytic:	*Micrococcus flavus liquefaciens*, *Proteus vulgaris*, White *staphylococcus*.
		Peptolytic:	*B. coli*, *B. filiformis*, *Streptococcus pyogenes*, *Diplococcus griseus*.
	Simple	Proteolytic:	*B. subtils*, *B. mesentericus*.
		Peptolytic:	*Proteus Zenkeri*.
Anaerobic.	Mixed	Proteolytic:	*B. perfringens*, *B. bifermentans sporogenes*.
		Peptolytic:	*B. bifidus*, *B. Lactopropylbutyricus nonliquefaciens* (*Tissier*).
	Simple	Proteolytic:	*B. putrificus*, *B. putidus gracilis*.
		Peptolytic:	*Diplococcus magnus anaerobius*, *B. facealis alkaligenes*.

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[1] (Le rôle des microbes dans la putrefaction des peaux en poils et en tripe dans les confits.)—Bull. Syndicat Gen. Cuirs et Peaux, Nov. 10, 1908, 416.

[2] *J. S. C. I.*, 1906, 109.

The simple ferments are those which are capable of fermenting nitrogenous matter only, the mixed ferments are able, not only to ferment nitrogenous bodies, or proteids, but also to act upon carbohydrates, such as sugars and starches, from which they produce organic acids.

The proteolytic bacteria which begin the action are those capable of liquefying, and afterwards decomposing the natural albumins. The peptolytic bacteria are those which are only able to attack the soluble products of the decomposition brought about by the former, so that it is clear the peptolytic organisms remain without action on a sound skin, but will be able to complete the attack begun by proteolytic organisms.

In a normal putrefaction the different groups of bacteria follow one another in regular order. At the beginning we find mixed aerobic organisms; first proteolytic, then peptolytic, they produce acids, principally amino-acids of the type of leucin, which are soon decomposed with production of amines and ammonia, so that the acidity is gradually neutralized. At the same time, the aerobic bacteria have used up all the oxygen of the material, and prepared the way for the mixed anaerobic bacteria. At this stage the putrefaction becomes rapid, and the production of ammonia is sufficient to render the mass alkaline. The simple anaerobic organisms now appear, *B. putrificus, B, putidus gracilis*, and *diplococcus magnus.* The complete cycle may take several weeks.

The most important putrefaction organisms are probably *B. putrificus,* and *B. Putidus gracilis,* which are anaerobic, and can only live in an alkaline medium.

It may be noted that the skins in their fresh state contain all the bacteria which develop later, and which cause putrefaction, but the putrefaction only begins when all the conditions are favorable. There is no doubt that the first stage—the solubilization and peptonization of the nitrogenous matter—is the most difficult, but once this has begun the fermentation soon reaches the stage at which ammonia is evolved. We see, therefore, that to preserve the skins it is necessary to prevent the presence of dissolved albuminous matter. The simplest method is that of drying the skins, and if this is properly done, it is quite effective in preventing bacterial decomposition, and in order to prevent the attacks of higher organisms such as mites, insects, and worms, the dry skins are strewn with naphthalene before being packed into bales. The other usual method of preserving skins is by means of salt. This also prevents the development of bacteria by dehydrating the fiber of the skin. There are some bacteria able to grow in the presence of salt, one species of which produces a coloring matter which it is impossible to remove from the skin, and which is one of the causes of the defect known as salt stains. The study of this defect, so far as I know, has not been made, and I might suggest this as an interesting and useful research.

There are very few poisons that actually kill bacteria, and at the same time are without action on skin. Corrosive sublimate, chlorine, and bromine, will kill them, but in practice the use of such substances is not possible, or even necessary, if due attention is given to the working. The use of a solution of arsenic in caustic soda has been tried, but has not been entirely successful in practice, owing to the fact that the main action is due to the soda; the arsenic has practically no detrimental action on the bacteria. Trotman found that *Bacillus subtilis* is not killed by arsenic solutions of the strength recommended. In some cases it actually continued to develop in the solution. Formaldehyde is a powerful and effective antiseptic but it has a tanning action on the skin which prohibits its use as a preservative. Since formic acid has become a cheap commercial product a good deal of attention is being paid to its use as a preservative for skins and Mr. Seymour-Jones has described its use in the pickling process.

At the present time the I. A. L. T. C. has formed a Committee under the presidency of Mr. A. Seymour-Jones, to deal with the preservation and curing of raw hides and skins with the object of reporting upon and standardizing various methods in use.

The chapter on antiseptics and disinfectants in Procter's "Principles of Leather Manufacture" is very complete as a reference to this subject.

I cannot leave the bacteriology of raw skins without saying something of anthrax, which is sometimes conveyed by bacteria contained in the skins and hair. This was one of the earliest diseases which was proved to be due to a specific organism (*Bacillus anthracis,* Davaine, 1863) growing in the blood of the animal infected, and capable of being cultivated on nutrient media outside the animal's body, such a culture inoculated into the blood of a healthy animal was found to produce the disease in all its virulence, and the bacteria were again found in the blood.

The anthrax bacillus is in the form of short rods very like *B. subtilis,* but as its characteristics may be found in any book on bacteriology, I shall not describe it further than to say that the chief reason it is so dangerous is its capability of forming very resistant spores, which remain capable of developing after years when again placed in favorable conditions. These spores are found in the dirt and dust of wool, horse hair, and hides of animals which have died of the disease. In this country anthrax among animals is rare, but in Russia, China, India, and many parts of the world the disease is common, and infected material is often shipped to British ports. Wet salted hides and greasy wools are free from dust, and little risk is incurred in handling them. The disease is communicated to man sometimes by breathing or swallowing the dust, but more usually by the poison lodging in some point where the skin is broken, such as a fresh scratch, or cut, or a scratched pimple, or even chapped hands.

Dr. B. A. Whitelegge, of the Home Office, from whom I have taken the above remarks, has prepared statistics of cases of anthrax caused by various industries, from which I have abstracted the following table for the five years, 1902-1906:—

Industries	Cases	Per cent.	Deaths	Per cent.
Wool sorting	15	5.7	4	5.6
Wool combing	87	33.5	24	34.0
Handling horse hair	46	17.5	12	17.0
Handling of hides, tanning, fellmongering	77	29.5	20	28.2
Other industries	36	13.8	11	15.2
Total	261	100	71	27 % of total cases.

It will be seen that the most dangerous cases are those occurring in wool combing, where there were 24 deaths in 87 cases. The next most dangerous occupations are handling of hides, tanning, and fellmongering, where there were 77 cases and 20 deaths.

It would seem from these figures that the breathing in of infected dust is more fatal than inoculation from a scratch.

In connection with this disease, Dr. Turnbull, of Liverpool, tells me that the gloves which are worn by the men handling hides are liable to become a source of infection if not disinfected or sterilized regularly, as the sweat from the hands causes them to become dirty and form a nidus for various kinds of organisms.

The Committee of the I. A. L. T. C. for the preservation and disinfection of hides and skins which I have previously mentioned has also this part of the subject under consideration, and Dr. C. Ponder, of Cambridge, has been appointed by the Leather Sellers Technical College to investigate anthrax. It may be of interest to mention that the anthrax cultures now being used by Dr. Jouan at the Pasteur Institute, are descended from the original culture isolated by Pasteur himself thirty years ago.

THE SOAKS.

The first process through which the raw skins go on reaching the tanner is the simple steeping or washing in water, known as the soaks. In the case of fresh skins coming from the markets a short immersion in cold, running water is sufficient to get rid of blood and dirt, and the skins have not time to undergo any putrefaction. In the treatment of salted skins the water quickly dissolves out the salt, and if mechanical means (paddle or drum) are used, there is little or no danger. It is in the soaking of the skins previously dried, which takes several days, that the danger of putrefaction arises. At one time the deliberate use of putrid soaks was in operation, but in the modern methods, where no chemicals are used, one fresh water is given to each pack of skins. Even in this case, considerable putrefaction (by putrefaction I do not mean actual damaged grain, but include simple solution of skin substance under this head), and consequent loss of skin substance, takes place where the soaking occupies seven days or more. The bacteria of the soaks are numerous and varied, and even at a temperature of 5° C. a single loop from a comparatively fresh soak will develop so many colonies of liquefying bacteria in a gelatine plate as to quickly liquefy the whole plate. A rise in temperature of a few degrees is sufficient to double the number of organisms, it is, therefore, imperative to keep the temperature of the soaks as low as possible; it should not exceed 10° C. So far as I know, the bacteria in the soaks have not been specially investigated except by Andreasch, who found the following species:—

Bacillus fluorescens liquefaciens (Flügge), *B. megaterium* (de Bary), *B. subtilis, B. mesentericus vulgatus, B. mesentericus fuscus, B. mycoides* (Flügge), *B. liquidus* (Frankland), *B. gasoformans* (Eisenberg), White bacillus (Manschek), *Proteus vulgaris, Proteus mirabilis, Bacillus butyricus* (Hueppe), White *streptococcus* (Maschek), Worm shaped *streptococcus* (Maschek) Grey *coccus* (Maschek). All these may be classed as putrefactive organisms, and some of them act energetically on the hide substance. From what has been said, it will be seen that the most suitable mode of preserving skins, by which the least risk will be run in subsequent operations, is the salting process, or some modification of it. We have seen that the species of bacteria developing in the soaks are mostly putrefactive, and, therefore, injurious bacteria, and I do not think that any useful purpose to the tanner would be served by a research as to the nature of the organisms developing. The line to be followed here is to work out the best method which will prevent the development of bacteria in this part of the work, that is, the soaking should be carried out, as far as possible, under antiseptic conditions.[1]

DEPILATING AND LIMING.

After soaking the hair or wool must be removed from the skins. This is usually done in the case of hides by immersion in lime water, or milk of lime, until the hair slips, and although lime is an antiseptic, we shall see that even in this process bacteria play an important part. I shall pass over the depilating of skins with sulphides, and sulphur compounds, which loosen the hair

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[1] The use of various substances in the soaks to prevent putrefaction has been tried. The best of these is a solution of caustic soda, one part per thousand, or of sodium sulphide 1½ to 3 parts per thousand. Forty-eight hours in either of these solutions is sufficient to soften most dried skins, while putrefaction is almost entirely prevented, and the soaking may be conducted without danger at temperatures up to 18° C. (*Vide* Procter, Principles of Leather Manufacture p. 114.)

by dissolving the epidermal tissue, because in this case bacteria take no part.

Both hides and sheep skins are frequently unhaired by the process known as sweating, in which the wet skins are hung in a moist chamber (the sweating stove) at a temperature of 15° to 20° C., partial putrefaction commences; ammonia is evolved, and in four or five days the hair or wool may be easily removed. Procter finds that the vapor of ammonia alone is sufficient to loosen the hair, but in sweating, the prime cause is the solution of the epidermal tissues surrounding the hair roots by bacteria, or rather, by digestive enzymes produced by bacteria.

Villon was the first to describe the organism which attacks the albuminous matter of the hair roots; he calls it *Bacterium pilline*, and describes it as an aerobic organism which decomposes pilline, transforming it into leucin, tyrosin, butyric and margaric acids, and sets free ammonia, which dissolves the coriin, and thus sets free the hair. From the description given it is very doubtful whether Villon's Bacterium was a pure culture, although he considered it to be so.

Villon's experiments have been criticised by Schmitz-Dumont (15) who describes the specific depilating organism as a streptococcus, which by decomposing the rete malpighi loosens the hair. Schmitz-Dumont's experiments are little more convincing than Villon's as to the sweating being caused by a specific organism, the difficulty being to sterilize the skins without injury. I have examined the bacteria from the roots of wool in a sweating stove used for depilating sheep skins, and have isolated several organism, among which are the bacteria described in a former paper[1] *as bacillus* D. & E. I also found *B. fluorescens liquefaciens*,[2] but I have not made an attempt to ascertain whether one of these alone, or all of them, are responsible for the unhairing process. I found a similar organism to *bacillus* D. in old limes; all of these produce ammonia from organic nitrogenous matter, and are capable of living in a strongly alkaline medium, even of higher alkalinity than a saturated lime water. Probably one of

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[1] *J. S. C. I.*, 1899, p. 990.

[2] **B. fluorescens is not invariably present, but there is some organism which produces a dark gray coloring matter, and which eventually overgrows the depilating organisms.**

these organisms is the same as the bacteria of Villon and Schmitz-Dumont, but in my opinion it will be found that the action is produced by a simultaneous growth of several different species of bacteria.

Procter states that an old lime becomes charged with ammonia and other products of the action of lime upon skin, such as tyrosin, leucin, and some caproic acid, but so far as I am aware the mode of production of these bodies is still unknown, and it seems doubtful whether ammonia is produced in the cold in a sterile lime. In the case of the sweated unlimed skin, we know that the ammonia and alkaline bodies are produced by the action of bacteria, on dissolved skin substance, and it is highly probable that the same kind of action goes on in the limes, and that it is produced by the same bacteria. The fresh lime dissolves the interfibrillar substance of the skin[1] bacteria obtain access from the air, then decompose the skin substance with the production of the bodies named. That this is so is supported by the statement that in Payne and Pullman's liming process, in which the skins are first treated with caustic soda, and afterwards placed in a solution of calcium chloride, they cannot be unhaired unless they have been previously acted upon by putrefactive bacteria, that is, the skin can be limed with the hair on, and this fact has been made use of in the preparation of fur skins.[2] This would seem to be an additional proof that the loosening of the hair in the limes is brought about by the same means as the unhairing in the sweating stove, though, in the latter case, real putrefactive bacteria are liable to attack the skin, whereas in the limes the skin is preserved from the action of these putrefactive organisms.

Payne, however, states that hydrosulphide of lime is produced by the action of caustic lime on the sulphur in the hair and that this has an unhairing action. In this case a sterile lime should unhair. I believe it will do so if time be given for the chemical action to take place. That this is a slow process is the

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[1] See the amount of skin substance dissolved in fellmongers' collecting limes. Wood and Trotman, *J. S. C. I.*, 1909, p. 1304. Where a lime was found containing 3.37 grms. skin per 100 cc.

[2] As a matter of fact, Payne and Pullman's process of liming sterilizes the skin, so that the depilating bacteria cannot grow.

probable explanation of the failure to unhair which has been observed in Payne and Pullman's process.

There is no doubt that the growth of bacteria in the limes is one of the principal factors in the "mellowing" as we call it. Griffith (J. Amer. Leather Chem. Assoc., 1910, 5, 109-129) states that the mellowness of the used lime liquor may be artificially produced by the addition of ammonium sulphate to the limes.

There is a form of damage, which principally affects sheep skins, known as "lime speck," and which is due to a colony of bacteria forming on the grain side of the skin just below the hyaline layer. When lime is applied to the skins by the fellmonger, in order to remove the wool, a portion of it becomes fixed in the colony in the form of carbonate, and partly as a combination with the fatty acids from the wool roots. Possibly there is also some combination of lime with the skin substance, which has been liquefied by the bacteria.

True lime speck, so far as I know, is never caused after the wool is removed, by sulphide or by lime only, although it is stated that it sometimes occurs in sweated skins. It may be classed as a putrefactive damage, and can be avoided by keeping the skin in a sterile condition until it is ready for painting. A further investigation of this defect is necessary, and would be very useful.

I have already suggested (J. S. C. I., Nov. 30, 1903, 1274) that the role of bacteria in the liming process should be worked out in our research laboratories in the same way as the bacteria in tan liquors, bates and drenches have been investigated by Andreasch, Becker, and myself. From what has been said it will be evident that the species to be isolated in this case are much less numerous than in most other parts of the tanning process and the work should demand a proportionately less time.

BATING AND PUERING.

The next process which the skins go through before passing into the tan liquors is to remove the lime, and give the desired character to the leather. Sole leather must be firm and dense, it is, therefore, usually sufficient for the surface lime to be removed by washing or handling in soft water, the natural acidity of the tan liquors dissolves the remainder of the lime.

Light leathers, which must be supple when tanned, require not only to be freed from lime before going into tan, but also require a portion of the interfibrillar substance to be dissolved out, and the fibers brought into such a condition that the resultant leather will stretch without springing back. The removal of the lime, and perhaps also some of the interfibrillar substance may be effected by means of acids used in a careful way, but as my object is to discuss the bacteriological problems of the bate, I shall pass over the purely chemical methods, and proceed directly to the fermentative processes which have been in use for this purpose since very early times. The skins are first washed to remove as much lime as possible, after which, hides for dressing or harness leather, are passed through a bate, consisting of an infusion of pigeon or hen manure. Skins for light leathers, such as goat and sheep, are treated with an infusion of dog manure in water at a temperature of 30° to 40° C. This somewhat disgusting process under normal conditions produces excellent results, and the great difficulty in finding an efficient substitute has been to combine in one bath the peculiar effects of the dung bate. Since the cause of the action in the two bates is very similar, I shall refer more particularly to the dog dung bate, which is usually known as a puer. Skins in the bate lose their plumpness and firmness, and become soft and slippery, or "fall," as we term it. The bating liquor has some osmotic effect, which causes the swollen fiber to give up its water. This falling also mechanically squeezes out a further quantity of lime, and at the same time a considerable chemical action takes place, so that the skin which originally contained 5 per cent. of lime will, on coming from the puer, contain only 0.7 to 1 per cent. of lime, calculated on the dry weight of skin. What is it in the dung which produces this extraordinary result? So far as our present knowledge goes, the causes are very complicated there is (1) the chemical action of various salts of organic acids which are contained in the dung. This is chiefly confined to the solution of lime, the reaction being similar to that taking place in a solution of ammonium chloride.

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

(2) The osmotic effect we have mentioned above; the interpretation of it is not yet quite clear, and I shall not therefore attempt to explain it.

(3) The action of bacteria and of enzymes produced by these organisms undoubtedly plays the greatest part in the "bringing down" of the skins, because, not only do they produce the acids, ammonia and amines which bring about the chemical reactions, but they also produce digestive ferments or enzymes, which have a solvent action on the fibers of the skin.

With the object of ascertaining the effect of the various species of bacteria contained in the dung upon skins, a large number of various species have been isolated, and the effect of pure cultures in different media has been tried.[1] A number of the results have been published in J. S. C. I. Professor H. Becker who has done a great deal of this part of the work, is of opinion that the principal organisms concerned in the bating exist in the dogs' intestines, and belong to the group of coli bacteria. These are very widely distributed bacteria, and are found in the large intestines of mammals, and, as a consequence, in almost all soils, and in the mud of rivers and lakes.

Lortet found it along with other organisms in the mud of the Lake of Geneva at a spot where the water was chemically very pure. Dr. A. C. Houston, the bacteriologist of the Metropolitan Water Board, enumerates sixteen varieties of this organism, 80 per cent. of which produced acid and gas in lactose peptone cultures, indol in peptone water cultures, and when grown in milk produced acid and clot. The bacterium coli resembles that of typhoid fever, and has frequently been mistaken for it. It is, however, much more resistant to destructive influences. It is

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[1] The subject is not so far removed from direct human interest as one might suppose. For many years Metschnikoff, in Paris, has been studying the bacterial flora of the human intestines. His theory is that old age is caused by the poisonous products of these intestinal bacteria, and he proposes to counteract the effects of these poisonous organisms by introducing into the system large quantities of lactic acid bacteria, either in the form of tabloids, or in the form of sour milk cultures.

a short bacillus, possessing flagellae by which it moves more or less rapidly.

Professor Becker's Bacterium No. 12, which he has named *Bacillus erodiens,* is undoubtedly a variety of *B. coli,* but has a more rapid motion, and does not coagulate milk, although it renders is somewhat thick. Cultivated in broth it gives off much gas, consisting of 12 per cent. carbon dioxide, 85 per cent. hydrogen, 3 per cent. oxygen. If glucose be added the quantity of carbon dioxide rises to 40 per cent. and acid is produced. The most rapid growth is at 37° C. and at this temperature a broth culture has a distinct reducing action on skin. According to the medium in which it is grown, it produces acid or alkali, and thus comes under the heading of mixed bacteria. In sugar[1] solutions acid is produced, and in proteid solutions ammonia compounds, indol and evil smelling gases are given off. Thus by varying the medium the effect produced may also be varied. I shall refer to this a little later.

I found in studying the bacteria of dog dung that the species existing in the *fresh* dung, which developed in ordinary plate cultures, appeared to belong to four or five species only, mostly bacilli. At the end of two or three weeks, the original species had given place to others, most cocci, in a very similar way to the change which takes place in putrefaction. It will be seen, therefore, that no single species produces the complex chemical and physiological changes which take place, or the bodies necessary for the bating of skin as some observers have supposed, but the various species succeed one another as the medium changes its reaction and composition until finally the organic portion is resolved into the simplest bodies such as carbon dioxide, ammonia and hydrogen. There is thus a moment when the dung is at its best so far as the bating action is concerned, and this moment is due to the vital activity of bacteria, and consequently varies according to the temperature, and some other influences (electrical condition of the atmosphere, etc.). One may say

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[1] Dr. A. C. Houston has been kind enough to make an examination of *B. erodiens*, and has ascertained its action on various sugars. It produces fluorescence in neutral red broth cultures, acid and gas in lactose cultures, indol, and acid and clot in milk cultures. It ferments dulcite, with production of acid, but *not* cane sugar, adonite, inulin, inosite, salicin, or raffinose.

it is at its best at about fifteen days in summer and one month or more in winter. Puer which has been dried is not as powerful in its action as that which is immediately made into a paste with water. It appears to lose its "nature," partly owing to irreversible dehydration processes, and partly because some of the bacteria are killed. I have here plate cultures on agar from fresh puer, and from a puer wheel in use. These show the number of bacteria in the puer wheel to be much greater than in the fresh puer. Many of the species of bacteria resemble one another very closely, and to show every species would weary you to no useful purpose. I shall, therefore, only throw on the screen the principal species existing in puer.

It will be noted that many of these organisms are identical with those which carry on putrefaction. The quantity of ammonia and volatile bases produced is very small, but non-volatile bases are produced in considerable quantity; the problem of the constitution of these, and of their mode of action on skin is one awaiting solution.

Another group of organisms which have some influence in the bating process are the class called by Beyerink *Granulobacter*. They produce butyric acid, and this acid combining with the ammonia compounds of the dung form salts which undoubtedly exert an effect on the lime in the skins, though its action on the fiber is not so great as the compounds of lactic and propionic acids.

I have pointed out previously the importance of the nutrient medium, or substratum, in which the bacteria grow, on the species surviving. In it one can see on a small scale the Darwinian process of natural selection. There is a great struggle for existence between the various species, and the circumstances determining the survival of this or that organism are extremely complicated, and we are yet very much in the dark as to the action of the various chemical compounds contained in the puer, so that it is unsafe to neglect even those which are present in the only small amounts. Very minute quantities of certain bodies, almost too small for detection by chemical means, are sufficient to cause large differences in the growth of certain organisms. For instance, Raulin found that the addition of a trace of zinc to his nutrient liquids increased the crop of the mould *Aspergillus niger* more than four times the weight of a crop grown in the same liquid free from zinc.

If we inoculate a nutrient material with a pure culture of bacteria, and the medium is not exactly adjusted to the needs of the particular organism, it will not thrive, and will speedily be overgrown by some other species obtaining access from the air. This fact very much discounts the use of pure cultures of bacteria which have been proposed for bating, although in the case of Erodin, where the medium has been adjusted to suit the organism, considerable success has been attained. The whole of the enzymes and chemical compounds essential for a perfect bate, are not present in the dung when it leaves the animal's body, but these compounds are produced by the continued action of these and other bacteria which obtain access from the air. The production of the enzymes depends, too upon the composition of the nutrient medium, since this exerts a selective influence on the species of bacteria obtaining access to it. Just as in the spontaneous souring of milk numerous bacteria have free access to it, yet the lactic ferment is generally so pure that it may be and is used as a pure culture on a large scale in the manufacture of lactic acid.

Seeing that the action of the dung varies in a great measure, according to the food on which the animals have been fed, and in the main a carnivorous diet is more effective than a vegetable diet, it was thought that the dung of an animal fed entirely on a meat diet would have a greater effect. I, therefore, procured some lion's dung, and puered skin with it, but it was found to have less action than the ordinary dog puer employed. The same result was obtained after keeping it for several weeks, and allowing the bacterial flora to develop.

The chemical composition of the lion's dung was as follows:—

	Per cent.
Water	59.2
Ash	21.1
Lime (CaO)	10.3
Phosphates (P_2O_5)	10.67
Organic matter	19.7

A bacteriological examination showed the presence of *B. coli* and a liquefying *diplococcus* not identified. A curious feature was a branching mould with extremely fine mycelium, in parts developing into yeast-like cells and which invaded the whole plate.

The recent researches of Tissier and Metchnikoff have shown that the flora of the intestines, both of men and animals, consist very largely of anaerobic bacteria. These have been overlooked in previous researches, owing to imperfect means of studying this class of organisms. Indeed, in one work on the microbes of the alimentary canal of the dog no mention was made of them, whereas they are all very active.

The following anaerobic bacteria have been isolated:—*B. bifidus, B. perfringens, B. bifermentans, B. funduliformis* (Veillon), *B. capillosus, B. sporogenes, B. ventriosus, B. Rodella III, Staphylococcus parvulus, Diplococcus orbiculus, Coccobacillus preacutus, Coccobacillus oviformis.* Most of these organisms, and the new methods by which they have been isolated, are fully described in a new work entitled "Les Anaèrobies" by M. Jungano and A. Distaso, of the Pasteur Institute, Paris.

Various bates have been patented based on the the above-mentioned researches, and in a recent patent it has been proposed to use an extract of the pancreas in conjuction with an ammonium salt.[1] Undoubtedly this will have a certain bating action, as I showed as far back as 1894, but I do not think from the evidence we have at present that the action of living bacteria can be dispensed with. Enzymes are of a colloidal nature, and consequently will not penetrate a semi-permeable membrane like skin, but the bacteria entering by means of the vessels and ducts into the interior of the skin produce their products in situ, and the action is thus greatly intensified.

Professor Procter, in his recent paper, to which I have referred above, says (page 331) "There is, however, no reason that all the necessary effects both of puering and bating should not ultimately be attained by purely chemical treatment without the risk and uncertainty which must always attach to bacterial and ferment action."

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[1] "Oropan," an artificial bate, manufactured by Röhm and Haas, of Darmstadt.

While I agree with him in this, still it is well to remember that in the case of one of the very oldest of the fermentation industries, that of the production of alcohol, a comparatively simple body, the natural process has not yet been replaced by a chemical one, and I believe this applies also to the manufacture of vinegar.

Chemical methods of bating may be used for leathers like chrome and alum leather, but even here natural processes like drenching, in which the acids are produced gradually during the working of the skins, give more beautiful results. With vegetable tanning materials the advantage is still on the side of the natural processes when these are conducted in a proper manner.

LIST OF BACTERIA WHICH HAVE BEEN FOUND IN DUNG, (MOSTLY DOG DUNG).

1. *Micrococcus ureae* (Cohn), (Pasteur).
2. " *fulvus* (Cohn) (Crookshank, p. 221, Macé, and Zopf.).
3. " *prodigiosus.*
4. " *ureae liquefaciens.*
5. *Bacterium sulphureum.*
6. " *coli commune.*
7. " *coli anindolicum.*
8. " *coli anaerogenes.*
9. " *furfuris* α.
10. " *furfuris* β.
11. *Bacillus fluorescens putridus.*
12. " *fluorescens putridus liquefaciens.*
13. " " *subtilis.*
14. " *saprogenes* (Herfeld, *J. S. C. I.*, May, 1895) three varieties.
15. " *butyricus* (Hueppe).
16. " *putrificus-coli.*
17. " *pyocyaneus.*
18. " *janthinus.*
19. " *coprogenes foetidus.*
20. " *pyogenes foetidus* (a variety of *B. coli*).
21. " *zenkeri.*
22. " *magnus.*
23. " *spinosus.*
24. " *liquefaciens* (Eisenberg).
25. " *amylobacter* (Van Tieghem).
26. " *acidi paralactici.*
27. " I.
28. " II. Isolated from horse manure by Severin, *Centr. Bl. f. Bakt.* (2). I., 97.
29. " III.

30. *Bacillus* from horse dung (anaerobic) Severin, *Central Bl. für Bakt.* (2). III., 708.
31. " from horse dung (anaerobic), No. 3.
32. " *oedematis maligni* Vibrion Septique, Pasteur).
33. " *mesentericus vulgatus.*
34. " *lactis aerogenes.*
35. " *cavicida* (Brieger).
36. " *albuminis* (Bienstock).
37. " *Bienstockii.*
38. " *tenuis.*
39. " *enteritidis sporogenes* (Klein).
40. " *lactis acidi* (Ankerschmid, 1905).
41. " *megatherium* (Ankerschmid, 1905).
42. " *cadaveris sporogenus* (Klein) said to be identical with No. 16.
43. " *thermophilus* (Houston).
44. " *a.* from puer. Wood. p. 8, *J. S. C. I.*, 1898, p. 1012.
45. " *b.* from puer. Wood, p. 8, *J. S. C. I.*, 1898, p. 1012.
47. " *mycoides.*
48-61. 14 species isolated from dog and pigeon dung by Prof. H. Becker. *Zeit. f. Öffentlich. Chemie*, Heft 23, Jahrgang X, p. 447.
62. *Sarcina fimentaria* (Lehmann and Newmann).
63. *Streptococcus* from Sewage. Houston, 7 p. 104, 114.
64. " *brevis.*
65. " *longus.*
66. " *-pyogenes.*
67. " *liquefaciens coli.* (Gamgee. Phys. Chem' 2).
68. *Streptothrix* from stable manure. Severin, 6.
69. *Spirillum serpens* (Kutscher).
70. " *tenue* (Kutscher).
71. " *undula* (Kutscher).
72. " *volutans* (Kutscher).
73. " from pig dung. Smith, *Centr. Bl. f. Bakt.*, **16**, (1), 124.
74-76. *Vibrio*, three species isolated by Kutscher.
77. *Clostridum butyricum* (Prazmowski) said to be identical with No. 25.
78. *Streptococcus faecalis.* Sidney Martin, 37 and 38. *Anh. Rep. Loc. Gov. Board*, 1907-9.

DRENCHING.

After bating the skins go through a simpler fermentative process known as drenching. An infusion of bran is generally used at a temperature of 35° C. to 10 grams per liter or half to one lb. per gallons. The skins from the bate, after washing in water, are placed in this liquid. It ferments vigorously for 18-24 hours. A considerable quantity of gas is evolved, and weak organic acids are produced, which are absorbed by the skins, and swell them slightly. In a drench taken in actual work, but without skins, the acids produced per liter were:—

Lactic acid	0.7907
Acetic acid	0.2402
Formic acid	0.0306
Butyric acid	0.0134
Total acids	1.0749

The composition of the gases was:—

Carbon dioxide	25.2%
Hydrogen	46.7%
Nitrogen	26.0%
Oxygen	2.1%

A small quantity of trimethylamine was also found. The nature of this fermentation was very thoroughly investigated by the author and Dr. W. H. Wilcox from 1892 to 1897, and was found to be due to the specific action of bacteria, which we have called *Bacillus furfuris*. There are two varieties of this organism, α and β, which are very similar in form, and differ only in the shape of the colonies when grown in glucose gelatine, and also that when grown together, they produce more acid than when growing separately. They are sensitive to acids, which inhibit their growth, and when the acidity reaches N/50, their growth ceases, and being non-sporing organisms, they soon die. They are present in the puer used for bating the skins, and consequently there is no difficulty in starting a fermentation.

The mode of action of the drench on skins may be summed up as follows:—

1. The solution of the last traces of lime which has not been removed by the bate, by the organic acids produced by the fermentation, and the subsequent swelling action of these on the skin fibers. The acids also dissolve a small amount of skin substance.

2. Simultaneously with (1) the distention and floating of the skins by gases produced by the fermentation, so enabling them better to take up the acids.

3. The mechanical absorption of dirt by the particles of bran or flour in the drench.

I do not know of any further investigation of the drenching process since the above research was made, but in practice, meal is now frequently used instead of bran, and consequently a smaller quantity may be employed. The mechanical effect of meal in removing dirt is not so great as with bran, but where the adherence of the bran to the skin is objectionable, no doubt the use of meal is to be preferred.

With regard to the production of acids by bacteria, Jordan[1] points out that there is no fundamental difference between the formation of acid, and alkali by bacteria, since ammonia is just as much a true decomposition product of nitrogenous bodies, as are the amino acids which are produced by the digestion of gelatine, and in lactic acid and sugar fermentation. Both processes go on simultaneously, and the reaction of any culture medium, in which bacteria are growing, depends not only on the capability of these organisms of attacking certain substances or even on their chemical constitution, but also on the exact moment of growth when reaction is ascertained.

BACTERIA OF TAN LIQUORS.

We owe most of our knowledge of the fermentation processes going on in tan liquors to Professor F. Andreasch, of Vienna (born April 29th, 1867), who published the result of his work in "Der Gerber" in 1895-6. I had the privilege of knowing Andreasch personally, and can testify to the thoroughness with which his work was done. His death, June 14th, 1899, at Pörtschach in Carinthia was a great loss to the tanning world.

Andreasch found that neither yeasts nor bacteria ferment the tannin itself, but that they attack the non-tannins of the liquors with production of alcohol and acids. Some moulds, such as *Penicillium glaucum,* decompose the tannin, especially in those materials which contain only a small amount of non-tannin in comparison with their tannin, such as quebracho and knoppern.

It would be impossible in a short lecture to give details of Andreasch's work,[2] but the more important results of his researches may be briefly summarized thus:—

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[1] Koch's Jahresbericht über Gährungsorganismen, 1906, p. 102.

[2] See abstract, *J. S. C. I.*, 1896, 910; 1897, 340, etc.

1. Putrefactive bacteria from the hides, bates, etc., accommodate themselves to the acid reaction of tan liquors; they dissolve certain nitrogenous constituents of the hide, and thereby furnish the chief nutriment for the more specific acid-producing bacteria. In liquors which are in use, the production of acid is proportional to the hide substance present, provided sufficient quantity of carbohydrates are present.

2. Acetic acid, which in fresh tan liquors is the chief acid, is always formed by two separate processes:—(1) the production of alcohol by yeasts from the glucoses of the non-tannins, and (2) the fermentation of the alcohol by acetic bacteria. In tan liquors it is never formed directly from carbohydrates.

3. Lactic acid is produced by several species of bacteria both from the sugars and other carbohydrates of tan liquors, and from the sugars alone by a yeast. A good supply of nitrogenous nutriment is necessary for its production, the greater part of which is furnished by the hides.

4. Butyric acid occurs in traces only in sound tan liquors.

A practical application of the results, is the preparation of sour liquors from materials poor in fermentable matter, by addition of glucose and alcoholic yeasts. A proper lactic fermentation is best induced by the sowing of the lactic yeast in the liquors.

I have given a list of the organisms isolated by Andreasch, which may be of use to workers on this subject.

Recently Von Schroeder (Zur Kenntnis des Gerbprozesses. Koll. Chem. Beihefte, Dresden, 1909, p. 21) found that, when a tannin solution was kept in contact with hide powder for 20 days gallic acid was formed, but that when the hide powder and the tannin solution were sterilized, no gallic acid was produced. He ascribes the formation of the gallic acid to the action of bacteria, but he makes no attempt to demonstrate their presence, although, in order to have the effect described by him, the microscopic demonstration of the bacteria should have been easy. It may be possible that there exists a specific organism capable of converting gallotannic acid into gallic acid.

LIST OF ORGANISMS TAKING PART IN THE FERMENTATION OF TAN LIQUORS. ANDREASCH.

A. *Yeasts.*
  1. *Saccharomyces pastorianus.* Hansen.
  2. *S. ellipsoideus.* Hansen.
  3. *S. apiculatus.* Reess.
  4. *S. ellipsoideus.* I. Hansen.
  5. *S. acidi lactici.* Grotenfeld.
  6. A rose colored *torula.*
  7. An orange-yellow *torula.*
  8. *Mycoderma.*

B. *Acetic acid ferments.*
  9. *Bacterium aceti.* Hansen.
  10. *B. Pasteurianum.* Hansen.

C. *Lactic acid ferments.*
  11. *Bacillus acidi lactici.* Hueppe.
  12. *Bacterium acidi lactici.* Grotenfeld.
  13. *Bacterium lactis acidi.* Marpmann.
  14. *Bacillus* XIX. Adametz.
  15. *Bacillus* α. Freudenreich.
  16. Lactic acid *tyrothrix.* Duclaux.
  17. Lactic acid *bacterium* I. Andreasch.
  18. Lactic acid *bacterium* II, Andreasch.
  19. Lactic acid *Bacillus* α. Andreasch.
  20. Lactic acid *Bacillus* β. Andreasch.
  21. Lactic acid *micrococcus* α. Andreasch.
  22. *Bacterium acidi lactici.* Pasteur.
  23. *Bacillus lactis viscosus.* Adametz.
  24. Gas forming liquefying lactic acid bacillus. Andreasch.
  25, 26, 27. Lactic acid yeasts of tan liquors α, β and γ. Andreasch.

D. *Butyric acid ferments.*
  28. *Clostridium butyricum.* Prazmowski.

E. *Other organisms causing viscous or ropy fermentation.*
  29. *Bacillus viscosus.* Frankland.
  30. *B. mesentercus fuscus.* Hueppe.

NOTE.—*B. viscosus* is identical with *B. fluorescens liquefaciens.* Numerous other bacteria were found in the liquors but did not take part in the fermentation.

F. *Moulds.*
  31. *Penicillium glaucum.*

LEATHER.

It is not possible to say much about the bacteriology of leather, and I do not know of anyone who has worked at it. Many of the bacteria of the bates and tan liquors remain in the empty spaces of the leather from which the glands have been removed by scudding, etc., and Dr. G. Abt has been able, by suitable staining methods, to demonstrate these *in situ*. A photo-micrograph prepared by Dr. G. Abt, of the Pasteur Institute, shows a section of calf skin tanned with sumac, and is interesting as being one of the first preparations of leather showing the presence of micro organisms *in situ*. They are in all probability merely the dead organisms, and it is uncertain whether any are capable of further growth. I have not heard of any case of anthrax being conveyed by leather tanned from an infected hide, notwithstanding the very resistant nature of the spores of this organism.

Mycoderma vini and *M. cerevisiae* have also been found in the interstices of the leather. Everyone knows that moulds grow very readily on damp leather, as may be seen in the case of a pair of boots left in a damp cupboard, and sometimes this is the case with leather in the drying rooms under certain conditions. The commonest variety met with is the green mould *Penicillium glaucum,* but there are cases in which *Aspergillus niger,* a black mould has developed in spots during the drying of the leather, thus causing considerable damage.

I have also met with a case in which American shoulders stored by a Railway Co. had become damaged owing to a discoloration, caused by a mould. Other leather in the same store was not affected. It was found that the difference in behavior was due to the presence of glucose and Epsom salts in the American leather, which, being hygroscopic, gave the moulds a very favorable nutrient medium. In some cases moulds grow upon colored leather, and in so doing discharge the color, causing light colored spots. Quite recently Trotman J. S. C. I., 1909, 1238) has found a mould causing a pink coloration on skivers. He also found a variety of pink torula, which produced a brownish pink growth on the same goods.

An investigation of the various species of moulds growing upon leather would be very interesting.

It is impossible to give more than a general outline of a subject like this in one paper, and I must make this my apology for a very inadequate treatment of it.

In conclusion I should like to urge upon the Directors of the Leather Industries Department of the Leeds University, and of the new Technical College of the Leatherseller's Company, the necessity of taking up the bacteriology of leather manufacture in a manner worthy of the subject. It is impossible for this work to be taken up as part of a course by the present teachers. It requires continuous work in attending to the cultures, etc., and, therefore requires a special room set apart for the work and a bacteriologist to give it attention. The work for such a man might well be combined with the microscopic study of skin and leather, the preparation and staining of sections of which demand a special technique, but which in my opinion is of equal importance with chemistry in helping us to understand what goes on in the process of making skins into leather.

THE WORLD'S HIDE AND SKIN SUPPLY.

Alfred Seymour Jones in an article with the above title in the *Leather Trades' Review*, quotes the opinion of Mr. Augustus H. Vogel of Milwaukee, that the supply of hides is decreasing because the per capita consumption of meat is diminishing. Mr. Jones thinks this an insufficient explanation of the gradual rise in the price of hides. As texts for a somewhat extensive review of the situation he proposes the following two questions:

1. Have cattle and sheep meat supplies kept pace with increase of population? If not, why not?

2. Is the demand for leather increasing and why?

As to the first, he thinks the answer is negative. In support of this view he quotes Mr. R. H. Hooker's paper of May, 1909, on the meat supply of the United Kingdom, and Mr. Vogel's address before referred to. Both gentlemen point out the increased use of butter, milk and cheese accompanying the increased raising of cattle for dairy purposes and corresponding decrease in beef-raising. This change in the cattle industry is largely due to the cutting up into farms of so many of the great western ranges.

The writer reviews the sheep situation at length, showing that sheep-raising is stationary or declining in all countries except Australia. The first question is thus answered negatively.

As to the second question, Mr. Jones thinks that the demand for leather is increasing, and that therefore prices will in the long run tend to rise. He suggests as a partial remedy that means should be taken to prevent injuries to hides from branding and disease, and hopes that Chinese and other hides now shipped in the dry-salted condition may be eventually wet-salted, so as to prevent the danger of anthrax infection from them, and thus to bring them into competition with domestic hides.

ABSTRACTS.

Action of Lime, Salt and Acetic Acid upon Green, Sweated, Limed or Bated Hide. GEORGES ABT AND EDMUND STIASNY. *Collegium*, 1910, Nos. 410-11, pp. 189-99, 205-12.—The systematic experiments here described were made with a view to determining the loss of hide by solution at various stages of leather making and also to ascertain whether the nitrogenous substances extracted were derived from the hide fiber itself or the interstitial substance, the "coriine" of Reimer. The mucoidal substance extracted by van Lier (abstr. this JOURNAL, 1909, (4), 302) appears in liming, hence is not considered here.

For the material, fresh cow-hide (1) was used and given the following preliminary treatments in separate 100 grm. strips: (2) sweating de-hairing, washing; (3) same followed by a dog dung bate; (4) sweating, de-hairing. washing, liming, superficial deliming with acetic acid; (5) same, followed by dog dung bate; (6) liming, de-hairing, washing; (7) same, and superficial treatment with acetic acid; (8) as in (6), followed by bran bate; (9) as in (6), then deliming, bran bate; (10) liming, de-hairing, dog dung bate; (11) liming, de-hairing, superficial de-hairing, dog dung bate.

The sweating was carried out in closed vessel containing weak ammonia water; in 2½ days the epidermal layer was liquefied and the hair roots loose. The liming lasted 6 days, 100 grms. lime to 2 liters water. For the dog dung bate, 50 grms. dry dung were digested over night at 60° and the filtered extract (1 liter) applied to the hide 6 hours at 34° C. For the bran bate, a liter extract of 10 grms. bran to 100 grms. hide was employed for 24 hours.

For the principal experiments, 3 portions from each of the above were taken, corresponding to 30 grms. green hide and treated as follows: The first with 300 cc. of lime water (N/24), the second with 10 per cent. salt solution, the third with N/10 acetic acid, a few cc. of chloroform and toluene being added in each case as antiseptic. After 7 days the liquor was removed for analysis and the residual hide treated a second time for 23 to 25 days and a third time for 25 to 26 days. In each of the resulting liquors, the nitrogen was determined by Kjeldahl and reckoned into hide (17.85 per cent N). In the tables, the percentage of dissolved hide represents dried hide; the real loss in moist hide would be at least + 3.5 times greater.

Percentage of hide dissolved by

I. Lime Water

	1st ext.	2d ext.	3d ext.	Total
1. Green hide	0.964	0.618	0.423	2.005
2. Sweated	0.858	0.594	0.444	1.896
3. Sweated, puered	0.818	0.557	0.422	1.797
4. Sweated, limed	0.218	0.589	0.324	1.131
5. Sweated, limed, puered	0.339	0.331	0.271	0.941
6. Limed	0.316	0.482	0.414	1.212
7. Limed, acid	0.316	0.452	0.452	1.220
8. Limed, bran bate	0.226	0.429	0.361	1.016
9. Limed, acid, bran	0.241	0.452	0.346	1.039
10. Limed, puered	0.346	0.414	0.361	1.121
11. Limed, acid, puered	0.323	0.346	0.437	1.106
II. 10 *Per Cent. Salt.*				
1. Green hide	0.796	0.203	0.055	1.054
2. Sweated	1.862	1.507	0.663	4.032
3. Sweated, puered	2.027	1.575	0.633	4.235
4. Sweated, limed	0.090	0.067	0.120	0.277
5. Sweated, limed, puered	0.196	0.135	0.090	0.421
6. Limed	0.045	0.080	0.040	0.165
7. Limed, acid	0.165	0.060	0.045	0.270
8. Limed, bran bate	0.090	0.075	0.067	0.232
9. Limed, acid, bran	0.090	0.075	0.075	0.240
10. Limed, puered	0.263	0.128	0.090	0.481
11. Limed, acid, puered	0.233	0.135	0.113	0.481
III. Acetic Acid.				
1. Green hide	0.470	0.305	0.190	0.965
2. Sweated	0.422	0.241	0.150	0.813
3. Sweated, puered	0.467	0.271	0.165	0.903
4. Sweated, limed	0.105	0.060	0.075	0.240
5. Sweated, limed, puered	0.165	0.150	0.105	0.420
6. Limed	0.105	0.095	0.077	0.277
7. Limed, acid,	0.075	0.075	0.052	0.202
8. Limed, bran bate	0.090	0.090	0.060	0.240
9. Limed acid, bran	0.083	0.090	0.090	0.263
10. Limed, puered	0.165	0.105	0.090	0.360
11. Limed, acid, puered	0.165	0.105	0.105	0.390

Action of Lime Water.

The amount of nitrogenous substance dissolved varies little in the different extractions, a marked contrast with the action of salt or acetic acid. It is evident that there is a constant action of the lime upon the fibers; the collagen it attacked with formation of alkali-albumins, albumoses, peptoses and acid amines. The highest numbers are with the green hide and the sweated hides (2), (3); this is due to putrefaction which is finally arrested by the lime and the antiseptics in the third extract. The antiseptic action of the lime upon the fermentation developed during sweating is much greater than that of salt. The sweated hide after liming gives much the same extract as if not sweated. The total loss is doubtless greater but the loss in the lime liuqor was not included in this study.

In discussing the character of the substances dissolved, the authors give a detailed table of titrations with alkali after formaldehyde addition (abstract, ante p. 345), before and after hydrolysis with H_2SO_4. The ratios of cc. alkali used are fairly constant, being approximately ½, showing that the lime had completed the hydrolysis to that extent.

Action of Salt.

The amounts taken up with each extraction decrease more rapidly than with the lime solution. There is no solvent action on the fiber but on the decomposition products resulting from fermentation or liming. The highest extracts are with the green and sweated hide. 16 to 20 times as much as with the limed hides. This is largely due to continued putrefaction during extraction in spite of the salt and antiseptics. This same fermentation ensues during the soaking of sheepskins which have been sweated, de-wooled and dried. It would therefore be preferable to pickle these or put them in lime direct after pulling the wool.

Action of Acetic Acid.

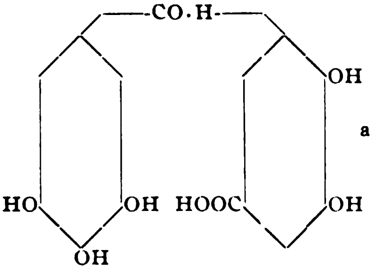
The amount of extracted is 4 to 5 times less than by lime water. The action is different, the fibers being greatly swelled. The substance in solution gives scarcely any acid reaction after the formaldehyde treatment, being in the state of acid-albumin. With the sweated hides the extract is also less than with lime showing the higher antiseptic power of the acetic acid.

Nature of the Dissolved Substance.

It is difficult to identify the compounds contained in these extracts; they represent various stages of hydrolysis of the primitive material which cannot again be precipitated unchanged. The solution in acetic acid differs from that in salt or lime; the product precipitated by neutralization does not dissolve in lime or salt solutions and even with difficulty in soda. The authors regard the interstitial substance as a hydrolyzed decomposition product of collagen produced by liming or bacterial actions. The result of titrations of the formaldehyde condensation after complete hydrolysis of the extracted substance with H_2SO_4, seems to show that the substances in solution are of variable composition. It has been previously found that for completely hydrolyzed gelatine, 1 cc. N/5 NaOH corresponded always to 5.8 mg. nitrogen. Here the ratios were found fairly constant for the lime solutions, being 4.27 to 4.92, but varied from 5 to 7 for the salt and acetic acid extracts.

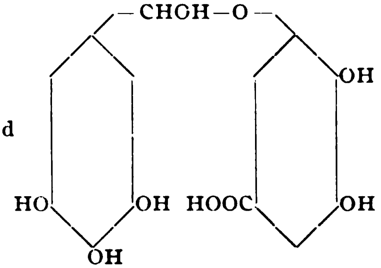
The authors also determined the amount of lime and acetic acid taken up by the hide during these extractions. The total quantities employed were 4.44 per cent. of lime and 18.26 per cent. of acid. Of these about 3 per cent. lime was absorbed in the three extractions, the first giving the least. Of the acid, 1.6 to 2.5 per cent. was absorbed, the most during the first extraction. With both the lime and the acid, the highest result was obtained with hide which had been puered.

Constitution of Tannin. M. Nierenstein. Ber. deutsch. chem. Ges., 1910, (43), 628.—As in preceding papers, the author supports the view that commercial tannin (leviss, pur. Schering) is a mixture of



Digallic acid (tannin)

and



Leucotannin

in which the leucotannins only is optically active, the upper carbon atom of the formula being asymmetric. This excludes the theory that the activity of tannin is due to sugar and moreover the author (confirmed by Sisley) has shown that tannin free from sugar is still active. In confirmation of the above formula, the author has finally succeeded in isolating pure inactive digallic acid by Emil Fischer's method. Tannin was treated with alkali and ethyl chloroformate, yielding after acidulation, pentacarbo ethoxydigallic acid,

$$(C_2H_5OOCO)_3C_6H_2 - COOC_6H_2(OCOOC_2H_5)_2 - COOH,$$

(melting-point 194-5°). This product on saponification by pyridin reverts to digallic acid. By repeating the process 3 or 4 times, the purified digallic acid on recrystallization from dilute alcohol was found to melt at 268-270°, to be optically inactive, to give the characteristic gelatine precipitate and to be quantitatively absorbed by hide-powder. On oxidation with hydrogen peroxide, it gives luteoic and ellagic acids and on hydrolysis forms gallic acid.

The Present State of our Knowledge of Emulsions. L. Meunier. *Collegium,* 1910, No. 413, pp. 222-8.—In this paper the author outlines the principles of this branch of physical chemistry which "deserves attention for its industrial importance." A true emulsion contains its elementary particles or granules permanently separated without tendency to reunite in an intergranular medium. Some so-called emulsions, like milk for instance are dilutions of true emulsions with excess of the intergranular liquid. From these the true emulsions can be separated.

Dimensions of Emulsionized Particles. A. SOLIDS. M. J. PERRIN, (Ann. chim. et phys., 1909, Sept.) has recently studied emulsions of the solids—gutta percha and gum mastic obtained by precipitating their methyl alcohol solutions with water. These crude emulsions, containing particles of various sizes were assorted into emulsions containing granules of uniform or limited diameters by a process of repeated fractional centrifuging analogous to fractional distillation. The dimensions of the granules in these homogeneous emulsions were then determined by 3 different methods with fairly concordant results, their radii being from 14 to 54 100ths of microns. B. *Liquids.* In the case of liquid, especially fat or mineral oil emulsions, the ultra-filters of Bechold may be employed. These are prepared by saturating filter paper with acetic acid solution of collodion or aqueous solution of gelatine and precipitating the colloid with water or formaldehyde respectively. Bechold determined the dimensions of the pores of these filters as used under pressure; with 5 per cent. colloid ions, their diameters were 21 to 24 $\mu\mu$, and with the 2½ per cent. collodion, 170-930 $\mu\mu$. Hatschek (Jour. Soc. Chem. Ind., 1910, (29), 125) found that with filters prepared as above, the first kept back emulsified oil while the second at times allowed the oil globules to pass. This is consistent with the diameters of oil globules, 400 $\mu\mu$ as found by Lewis.

The foregoing shows that the elementary granules of most emulsions are larger than those of colloids. A paper is promised later with practical considerations bearing upon the emulsified oils used in tanning.

Study on the Impermeability of Leathers. U. J. THUAN AND P. DE KORSAK. *Collegium*, 1910, No. 414, pp. 229-32.—The impermeability of sole-leather to water is one of its most essential properties and its determination should receive more attention. It is an error to guage this by the amount of solubles extracted by water, an entirely independent matter. The authors have devised the following method for directly measuring the resistance to penetration. The sample of leather is applied to the base of a bell jar or inverted funnel which is exhausted by a pump, the leather being meanwhile immersed in water. The time is noted required for the passage of 10 cc. of water through the leather into the funnel. The portion of leather outside the circle of the bell jar is protected from the water by a coating of paraffine and varnish. The glass rim is at the outset made to adhere to the moistened grain of the leather by greasing with tallow and applying the suction.

We condense the detailed results given in a table:

Make of leather	Thickness mm.	Vacuum cm.	Time	Cc. water per min. to 1 sq. cm.	Cc. water per min. to 1 cu. cm.
1. Rapid, laboratory	2.7	52	30″	1.600	5.924
2. Mixed, central, low yield	4.1	53.2	3′30″	0.229	0.571
3. Mixed, Breton	2.0	54.4	4′30″	0.177	0.888
4. Same, horny part	2.0	55.4	31″	0.026	0.129
5. Smooth, mixed, north	5.5	59.6	28′	0.028	0.052
6. Rapid	3.5	50	2′	0.400	0.142
7. Same, laid away 4 mos	3.5	51	29′	0.027	0.092
8. Extra rapid, vats	3.4	51	30″	1.600	4.704
9. Rapid, retanned	5.7	52	13′	0.061	0.109
10. Quebracho and oak, conc., pits	4.5	51	18′	0.044	0.098
11. Chestnut ext., very conc., pits	4.5	53	2h. 27′	0.005	0.012
12. Oxhide, pits	7.8	55	2h. 23′	0.005	0.007

This is considered but preliminary—the work being yet incomplete; the relative figures thus obtained enable one to compare the qualities of the leathers.

Leather Analysis (Concl.). U. J. THUAN. *Le Cuir* 1910, (3), Nos. 9, 11; pp. 217-8, 281-3.—The determination of dermal substance is the most important element of a leather analysis, and involves the determination of the nitrogen present. The dry dermal substance of the hide of kine, horse and pig contains 17.8 per cent. N, the corresponding figures for goat and deer skin being 17.4 per cent. and 17.1 per cent. for sheep. Reciprocally, 1 per cent. of N corresponds to 5.62, 5.75 and 5.83 per cent. dermal substance in each. The determination is made by the Kjeldahl method using mercury in the digestion with H_2SO_4. L. Meunier recommends heating 1 grm. leather with 5 grm. of anhydrous $CuSO_4$, 25 cc. conc, H_2SO_3, and 1 grm. K_2SO_4. The French section of the International Association has recently appointed a commission on leather analysis to establish an official method for French use, hence the author defers further discussion until later.

Extract Guarantee in Germany. *Ledertechn, Rundschau,* 1910, No. 22, p. 172.—The Union of German dye and tanning extract makers announces that in consequence of the varying reports in analysis from different laboratories, that new rules go into effect after May 1, 1910. Weak chromed hide powder of the Frieberg Station must be used according to the filter methods and only the following are recognized as guarantee laboratories, (1) Dr. Louis Allen, Hamburg (2) Freiberg Versuchsanstalt, (3) Drs. Hundeshagen and Philip, Stuttgart, (4) Dr. L. Maschke, Berlin.

Report of Meeting of Austrian-Hungarain Section of I. V. L. I. C. FR. NEUNIER. *Collegium,* 1910, No. 415, pp. 245-9.—The meeting was held at Vienna, June 18, 1910. Director F. K. Kopecky was elected chairman, succeeding Dr. Wilh, Eitner, incapacitated by illness. The Section voted a protest against the decision of the German Extract makers to accept only the guarantee of German laboratories and to prescribe the filter method. Prof. Kohnstein quoted the following limiting values of tan percentages by the shake method, resulting from many analyses at the Vienna Station.

Oak bark	9.36-12.3
Pine bark	12.13-15.68
Trillo	37.07-45.81
Valonia	26.73-32.06
Knoppern	28.60-31.80
Divi	37.20-41.13
Sumac	22.66-26.7
Mimosa	31.30-36.0
Quebracho wood	20.37-20.71
Myrabolams, hulled	41.60-50.50
Maletto	32.73-45.93
Algarobilla	45.30-53.00

Fundamental Rules of Practice; Extraction. (Cont.). L. Manstetten. *Ledertechn. Rundschau,* 1910, Nos. 18, 19; pp. 137-8, 145-6.—As previously shown extraction is best made in a battery, gradually increasing the heat, the easily soluble tans being extracted at the lower temperatures. Reversed, the hot liquors are always brought in contact with cooler bark and finally so far cool off on fresh material as to acquire the temperature suitable for direct use. This permits a rational precept to be followed, namely; utilize to the utmost the heat used for extraction. In general a special cooling arrangement for extract liquor is unnecessary, or at the most, in summer. If a liquor is to be cooled it is best passed through pipes surrounded by the cooling liquors and not the reverse, since there is loss of tans by oxidation on exposing hot liquor to the air.

Parker and Procter's tables (ante p. 320) show the lowering of yield by continued boiling in the case of oak and even by heating above 60° for sumac.

This loss is doubtless due to decomposition of the dissolved tannin by heat, and also to oxidation during the protracted agitation in contact. A good precept is therefore in pumping or pressing hot liquors, not let them fall or be sprayed a considerable distance in contact with air. The darkening of tan stuffs by oxidation was shown by experiments with a 2° B. liquor made at 70° from 2 parts quebracho, 1 part pine bark, 1 part oak bark. Of this, 2 liters were boiled one hour in the open air with replacement of the water and another 2 liters heated the same time at an over pressure of 1-8 atmospheres. The liquid boiled in the open air was much darker than the other and gave a dark leather while the leather obtained from the overheated liquor differed little from that obtained from the original liquor.

When it was found that extraction at high temperatures and pressures in closed vessels resulted in loss of tannin, many tanners rejected this form of apparatus as unsuitable. This is an error, for if a closed extractor be kept down to the proper temperature, as good results may be obtained as in open vats and with much less consumption of steam. By insulating the copper vessels, the difference in fuel consumption may be made still greater.

Leather Dressings. FERDINAND KOHL. *Ledertechn. Rundschau,* 1910, No. 16, pp. 121-4.—These may be classed according as applied to the grain or flesh and also as protective and gloss dressings. For protective dressings, the coating must not be so thick as to have the appearance of a lacquer and is best colored to the tone of the leather. Shellac is one of the most important materials for both classes of dressing. It is soluble in alcohol and in water containing alkali like borax, ammonia, etc. It comes in different shades of color and is often adulterated with rosin which is detected by its solubility in petroleum ether which only dissolves 1 to 2 per cent. shellac. In making the alcoholic solutions, some water may be added; turpentine is also used. Spirit soluble dyes are employed to color. To dissolve in water ammonia or borax is used equal to ¼ the weight of shellac, with gentle heating. Such solutions are used in dressing flesh spits to imitate grain. Cracking of the shellac coat is prevented by addition of glycerin which should be moderate, else the gloss suffers. Acid and diamine dyes (Cassella) are used for coloring. The "gold beetle" lacquer is made from 1 liter alcohol, 200-250 grms. shellac and 100-150 grms. Fuchsine 1a. (which can be substituted by methyl violet or brilliant green). The metallic effect is due to undissolved dye and the mixture must be shaken before each application; also the leather is best grounded black in advance.

Celluloid or Zapon lacquers are much used under fanciful names. They are solutions of nitro cellulose in acetone, amyl alcohol or ether, with or without addition of camphor, castor oil, linseed oil, turpentine, etc. They are water-proof and compete well with patent leather. They are also used to protect dyed leather from fading. When used for colored coats, finely ground mineral pigments are incorporated, shaking well before application.

Cerasin dyes (Cassella) are also used. The more oil used in the lacquers, the thicker the coat may be without cracking.

Casein is a similar dressing; it is first mixed with water to a thin paste and 1/10 ammonia or borax added, gradually diluting with water. By treatment with formaldehyde, casein becomes insoluble and this may be taken advantage of.

Besides the above, decoctions of linseed, gum tragacanth, Irish (Carragheen) moss, gelatin, dilute milk, etc. are used, applied after cooling. For gloss dressing, polished by the machine, albumin is well suited, prepared from white of egg or blood. The last is dark but can be bleached by ozone. Albumin can be dissolved in cold water (heat coagulates it) best with addition of a little ammonia. For grain dressing, leather cremes are important. Soap creme is an emulsion prepared by melting in a kettle carnauba, montan or other wax and stirring this until cold with hot soap solution in which the desired dye has been previously dissolved.

Turpentine creme is prepared by melting the wax with addition of the desired cerasin dye at 85-90°, and then stirring in warm, clear turpentine oil. For flesh dressing, wax and soap "smears" are used for greased leather and glaze dressings for saddler's leather. The waxes (Wichse) are fine ground mineral colors in tallow and oil often mixed with starch and wax. A glue glaze is applied to prevent the above from rubbing off. Soap "smears" are emulsions of tallow, linseed oil, etc., with soap, united with a decoction of Irish moss.

Spots on Leather from Hard Water. *Werkm. Ztg.* through *Ledertechn. Rundschau,* 1910, No. 18, p. 140.—In a case from actual practice in the manufacture of russet leather, this on softening showed spots. Chemical examination of the leather failed to explain the trouble, but finally it was found that the water was high in lime and contained traces of iron. On using distilled water, the leather remained clear.

The Cure of Anthrax. E. DESTRANGES. *La Halle aux Cuirs,* 1910, (54), No. 26, pp. 409-10.—This is a contagious malady which especially attacks herbivorous animals caused by the presence in the blood of fili form corpuscles. Pasteur devised a system of vaccination which has given excellent results but is expensive and is only a preventive. Dr. Louis Fortineau of Nantes has recently discovered a cure which "promises to revolutionize veterinary practice." It consists in the injection of pyocyanase, a culture derived from bacilli present in the pus of boils on the human subject. Trials on infected sheep were successful and the recovery of a woman affected with malignant pustule appeared to be favored by the treatment.

PATENTS.

Cutter Guard for Leather Skiving Machine. U. S. Patent No. 959,830. A. B. ALDEN AND L. W. REINHARDT, assignors to Chas. S. Pierce, Brockton, Mass.

Leather Skiving Machine. U. S. Patent No. 961,736. JACOB R. SCOTT, Boston, Mass.

Leather Folding Machine. U. S. Patent No. 962,034. R. H. LUFKIN, Medford, Mass.

Device for Boarding Leather. U. S. Patent No. 962,157. A. M. MARX, Germany.

Machine for Surfacing Leather. U. S. Patent No. 963,303. CHARLES A. LOMBARD, Boston, Mass.

Leather Cutting Machine. U. S. Patent No. 964,061. JOSEPH SCHWABER, Baltimore, Md.

Manufacture of Artificial Rubber. U. S. Patent No. 964,304. ARVID NILSON, Chicago. Hydrochloric acid and alcohol are added to a hot solution of bichromate of potash; then to the still hot liquid are added in order, glycerine, caustic soda and glue.

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ELECTIONS.

ACTIVE.

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Walter H. Dickerson, c/o Muskegon Extract Co., Muskegon, Mich.

ASSOCIATE.

Stuart Hall Frank, Redwood City, Cal.
George H. Tousey, Muskegon, Mich.

COUNCIL MEETING.

A meeting of the Council was held in New York City, July 29th, those present being, Messrs. Wilson, Reed, Small and Alsop.

The principal business to come before the meeting was the report of President Wilson in reference to the arrangements for the Annual Meeting.

The list of names from which to choose candidates was selected to be presented to the members in accordance with Section 6 of the By-Laws.

ANNUAL MEETING.

The Seventh Annual Meeting of the American Leather Chemists Association will be held in conjunction with the convention of the National Association of Tanners at the Hotel La Salle, Chicago, Ill., October 6th, 7th and 8th.

The headquarters of the Association will be the Hotel La Salle. A room has been reserved at the hotel, in which the meetings will be held.

The program so far as completed at the present time is as follows:

THURSDAY, OCTOBER 6TH.

Morning Session:

Opening remarks by the President.

Report of the Secretary-Treasurer.

Committee reports.

Afternoon Session:

Address by Dr. Allen Rogers, "Trade School for the Leather Industry."

Address by Mr. George A. Kerr, "Manufacture of Extracts in the United States."

Address by Mr. F. C. Rose, "Leather Oils."

Address by Mr. John H. Yocum, subject to be announced.

FRIDAY, OCTOBER 7TH.

Morning Session:

Meeting of the National Association of Tanners. Members of the A. L. C. A. are invited to attend this meeting.

Afternoon Session:

Visit to the Stock Yards of Armour & Company.

Evening:

Joint Banquet at the Hotel La Salle. The National Association of Tanners have cordially invited the active members of the A. L. C. A. to attend this banquet as their guests.

SATURDAY, OCTOBER 8TH.

Morning Session:

Address by Mr. F. P. Veitch, subject to the announced.

Address by Mr. F. E. Atteaux, "The Proper Bating of Hides."

Address by Mr. J. H. Russell, "Tannage of Heavy Leather in California."

Afternoon Session:

Address by Mr. R. C. Jacobsen, subject to be announced.

Committee reports.

Election of officers.

This program may be subject to some rearrangement and there will probably be two more papers to be presented

The rates at the Hotel La Salle are as follows:

One person, room with detached bath	$2 to $3	per day
One person, room with private bath	$3 to $5	" "
Two persons, room with detached bath	$3 to $5	" "
Two persons, room with private bath	$5 to $8	" "
Two persons, two connecting rooms with bath	$5 to $8	" "
Four persons, two connecting rooms with bath	$8 to $15	" "

NOTICE.

Stamford, Conn., Aug. 3, 1910.

All those desiring accomodations reserved for the Annual Meeting of the American Leather Chemists Association, in conjunction with the meeting of the National Association of Tanners, in Chicago, on October 6th, 7th, and 8th, are requested to communicate direct with the Hotel LaSalle, Madison St., Chicago, Ill., which hotel has been selected as headquarters for the Association.

H. C. REED,
Secretary.

INTERNATIONAL ASSOCIATION OF LEATHER TRADE CHEMISTS.[1]

FORTHCOMING CONFERENCE IN PARIS.

The bi-annual Conference of the I. A. L. T. C. will open in

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[1] From *Leather Trades Review.*

Paris on September 18th next, and will conclude on the 22d. The preliminary business agenda includes the opening of Conference by the President; welcome to delegates and guests; award of "Seymour-Jones" prize; minutes of last Conference for signing; treasurer's report; reports of corresponding secretaries; report of hon. editor of *Collegium*; place of next Conference; election of officers, President, hon. treasurer, hon. secretary; proposed enlargement of Executive Committee; revision of rules as to voting, etc.; rules as to election and conduct of general and sectional commissions; rules as to appointment of referees; publication of amended statutes and rules for analysis.

THE TECHNICAL AGENDA.

Report of International Commission on Tannin Analysis, Professor H. R. Procter. Results of German Sectional Commission, Zeuthen's Method, Professor Dr. Paessler. Results of French Sectional Commission, A. de la Bruère. Report on Commission on Preservation of Hides and Skins, A. Seymour-Jones. A New Method of Color Determination, Professor H. R. Procter. Proposed Changes in Rules of Sampling, Dr. J. G. Parker. Proposed Appointment of Referees on Acidity Determination in Liquors, Professor H. R. Procter. Proposed Appointment of Referees on Control of Lime Liquors and Wetwork, J. T. Wood and Dr. J. Gordon Parker. Proposed Appointment of Referees on the Practical Testing and Detection of Mixture in Extracts, Professor Dr. E. Stiasny. Formation and Properties of Emulsions, Professor Dr. Meunier. Determination of Breaking Stress in Belting Leather, Professor Dr. Paessler. New Method for Estimation of Nitrogen in Skins and Leather, U. J. Thuau. Proposed Official Method for Analysis of Leather, Messrs. Meunier, Paessler, Parker.

SOME NOTES ON CHROME TANNING.

By William M. Norris.

It is much to be regretted that most leather trade chemists have devoted their attention almost exclusively to tannin determinations. An immense amount of literature has been created and controversies waged, sometimes warmly, for the last 20 years. Very probably before a system of tannin determinations has been developed which will suit everybody, the chemists, tanners, and vendors of tannin materials, it will cease to be a matter of much importance how much tannin the various vegetable products on the market contain, as by that time all hides and skins of every kind and description will be tanned with chrome. The process of chrome tanning as conducted to-day is almost entirely empirical. It has been developed and brought to its present high state of efficiency by the glazed kid manufacturers of this country, an exceptionally energetic and progressive body of men. Starting with the process of Schultz, through long experimenting and trying out of different quantities of the various chemicals employed, they have succeeded in producing a leather far superior to anything heretofore made, and fame and fortune have rewarded their efforts. Still they have been severely handicapped from a lack of theoretical knowledge as to what they were doing, the difficulty arising with dealing with undesirable results as they frequently developed from unknown causes and the difficulty in producing just the leather desired by their customers to suit the ever varying, ever changing demands of the market. Much time and money also have been wasted on experiments which by no possible chance could yield any useful result, but even so, the results they accomplished have proved magnificent. A goat skin tanned in the good old fashioned way would be of no value. Chrome tanned glazed kid is the only thing; not only does it command the domestic market, but the foreign one as well. This year glazed kid will be sent abroad to a value of nearly $20,000,000.00, but reliable statistics as to exports are wanting.

Mendeleeff, in his Principles of Chemistry, says:—"It must be observed that the chromates have not been sufficiently investigated." It also must be remarked that the chrome process of tanning has hardly been investigated at all.

When the manufacturer has his skins ready for tanning, they are weighed and this weight constitutes the basis of his subsequent operations, as all chemicals are used on a percentage basis as to the weight of the skins.

In the first place he is confronted with the question as to whether or not it is advisable to pickle his stock before tanning. In a prolonged contention over patents, one prominent and successful manufacturer testifies—"it is our regular custom to pickle all our skins previous to tanning." While an equally successful one states—"skins if pickled will be practically spoiled for chrome tanning." The pickle referred to consists of sulphate of alumina. I have seen stock about as near perfection as could be conceived of which was pickled before tanning and stock equally good which had no pickle. At the present time pickle is rather in favor; say for 100 pounds of skins, 4 pounds of sulphate of alumina and 4 pounds of salt. Stock is treated to this for about an hour, then horsed up over night and placed in chrome bath the following day. This pickle is merely a preparation of the stock for the chrome bath. The alum does not remain in the skin and forms no part of the tanning process. The next step is the preparation of the chrome bath. This consists of about 6 per cent. of the weight of the skins, of bichromate of potash, or bichromate of soda, and 3 per cent. of muriatic acid, 20° Baumé. The chrome is dissolved in boiling water and added to the water in the reel, about 650 gallons of water for 1,000 pounds of skins. We thus have 60 pounds of bichromate to 650 gallons of water, a little over 1 per cent. solution; 30 pounds of muriatic acid is added, and the bath is ready for the stock. It is immaterial whether bichromate of potash or soda is used. Bichromate of soda contains two molecules of water of crystallization and the corresponding potash salt is anhydrous. This difference is nearly made up by sodium, being a much lighter metal than potassium; 299 parts of bichromate of soda contains the same amount of chromic acid as 295 parts of bichromate of potash, a difference so trifling that it may be ignored. Bichromate of soda is a deliquescent salt which makes its use somewhat troublesome; still the manufacturers of this article have a much drier product on the market now and it cost 1¾ cents less a pound than the potash salt. The reactions in this first step of the process probably take this course: $Na_2Cr_2O_7 + 2HCl = 2NaCl + 2CrO_3 + Aq$, although by no means complete. Now when the skins are introduced, they absorb this CrO_3 and remove it from the bath, destroying the equilibrium of the solution. More CrO_3 is formed and this goes on until all the HCl is exhausted by liberating the CrO_3 from the bichromate. About enough acid is employed to break up one-half of the bichromate used so that an analysis of the liquor after the skins have been removed show it contains 30 pounds of bichromate, considerable salt and no acid, although spent liquors are by no means uniform. Acting upon this fact some manufacturers have restored this bath by adding 30 pounds of bichromate and 30 pounds of muriatic acid, thus bringing it back to what it was at the start, and saving one-half of the bichromate usually employed. After restoring the bath a few times, there is a large accumulation of salt and also of dirt, brought over by the stock from the beam-house, and as the bath was never exactly alike from day to day, the accumulation of salt making the stock too soft and spongy, this restoring process did not commend itself. Many manufacturers place the skins in this weak spent bath for a few hours and then in the freshly prepared one afterward, acting upon the well-known practice of vegetable tanners where stock is always placed in weak liquors first and then gradually in stronger ones. But the chemical characteristics of this spent liquor are such that it cannot be considered as a weak solution of the first bath. There is little or no acid present and the skins have the power to absorb but very little of the chromium compound present. Their appearance and feel indicate this; they are only slightly colored and somewhat swollen and tripey. If it is desired to use this bath, some acid should be added, say 1 per cent. of the weight of the stock. Then in the fresh bath use 5 per cent. of the bichromate and 2½ per cent. of acid, in this manner saving 1 per cent. of the bichromate and one-half of 1 per cent. of acid. This saving, however, is somewhat offset by the labor of entering and removing stock from this liquor and as it does not run uniform from day to day by any means, practical men conclude that all these spent liquors should be rejected and there is much to commend this view. Some tanners will dissolve the bichromate in a comparatively small amount of water, then add the muriatic acid and this mixture is then poured into the large amount of water in the reel. Others after dissolving the bichromate in the reel and adding acid, will let the solution stand for some time before placing the skins therein—all this to have some, or as much as possible, reaction between the bichromate and acid before coming in contact with the skins. The reason for always using twice as much bichromate as the skins take up is obscure, although long experience has proved its necessity. Hydrochloric acid ionizes very freely in dilute solutions, and in such a very weak solution it would not exist as HCl but as H ions and Cl ions, and the activity or acidity of the acid would be very great, and severe on the skins. It is a well-known fact that the presence of a neutral salt in the solution reduces the tendency of the acid to ionize and we must conclude that the excess of bichromate performs the function in this case of a neutral salt. We must make our theories fit the actual process in use and not indulge in crude criticism of a process which has taken years and a large expenditure of money to produce. Stock is run in this first bath for several hours, then allowed to remain at rest over night. In the morning skins are removed from reel, struck out and then dipped in a weak solution of hyposulphite of soda to which a little muriatic acid is added. After dipping, stock is thrown on a horse and allowed to remain for a short time before being placed in the second bath of the process. This bath consists of hyposulphite of soda in water, to which muriatic acid is added. The proportion for many years was 20-5, but recently the amount of hypo used is somewhat less, say 18-5, thus for 1,000 pounds of stock, 180 pounds of hyposulphite is dissolved in 650 gallons of water; the paddles in reel allowed to revolve, 50 pounds of acid added and the stock at once thrown in. The reactions here are somewhat complicated; the acid would at once attack the hypo, liberating hyposulphurous acid (thiosulphuric) which would be converted in a short time to sulphurous acid and sulphur. This reaction is apparent; the liquor remains clear momentarily after adding the acid but shortly a cloud of sulphur appears and the pungent odor of sulphurous acid is noticed. Now while there is enough water present to hold the sulphurous acid in solution, it does not do so, owing doubtless to the mechanical action of the skins and the rapidity of its evolution, an abundant discharge of SO_2 is at once given off. This cannot be prevented, as a rapid reduction of the chrome is necessary at the start to prevent undue bleeding of the chrome from the skins. The sulphurous acid would act upon the chromic acid in this manner—$CrO_3Aq + SO_2Aq$ form at first CrO_2 and H_2SO_4Aq. Now we must have in the solution something to take care of the H_2SO_4 (sulphuric acid) formed as otherwise it would combine with the CrO_2 and form chromic sulphate $Cr_2(SO_4)_3Aq$. That is to say, an aqueous solution of sulphurous acid acting upon chromic acid produces at first sulphuric acid and chromium dioxide and finally these last two combine to form chromic sulphate a soluble compound which would wash out of the stock and leave it in a raw condition. The sulphuric acid formed is readily taken care of by having always a considerable excess of hyposulphite of soda present in the solution. Then the sulphuric acid will preferably unite with the soda in the hypo, rather than with the chromic dioxide, and liberate more sulphurous acid which will continue the reduction of the chromic acid in the skins until finally all the interaction between the chromium compounds and the reducing agent has ceased and the desired insoluble compound, chromic oxide, is formed in the stock.

So the action of this step of the process is automatic and continuous. Stock is usually run for several hours in this solution, and then allowed to remain over night. Some chromic acid will wash out of the stock and be reduced in the bath to some greenish chromic compound, but after all the reduction process is over, the skins will take up the chromium compound from the liquor if allowed sufficient time to do so. The color of the liquors is quite a dark green at the end of the reduction, but the next morning much lighter, showing the stock must have absorbed considerable of it. The large amount of sulphur present in this bath is somewhat objectionable and efforts are made to effect the reduction with as little liberation of sulphur as possible. Some tanners having the requisite amount of hypo dissolved in reel, take skins from the horse and drop in convenient sized piles, then while one man adds the acid from one side of the reel, two men throw the skins in from the other side, hoping that the thiosulphuric acid first liberated from the hypo will act immediately on the stock before going over to sulphurous acid and sulphur. Others will use in connection with hypo, sulphite of soda, which is quite effective in reducing the amount of sulphur developed, while some do not use any hypo or acid at all, but rely upon a solution of bisulphite of soda to accomplish their work; in this last case no sulphur at all is formed. In adding acid to hypo solutions some successful manufacturers do not add all at once; where 50 pounds is the amount usually required, 35 pounds is used at first, then more, a little at a time—as the stock requires it, usually ending up by using less than 50 pounds. A workman examines the skins in the reel from time to time and judges from the feel and appearance of the stock as to when they require more acid, and how much. This man must have long experience and good judgment, as much responsibility is thrown upon him. This is the correct principle, give the skins what they require and no more. Set arbitrary formulas will not work in chrome tannage owing to the great diversity of raw stock which the tanner is obliged to work. An examination of the spent hypo liquor will show about 80 pounds of hypo with an undetermined amount of salt, sulphur, basic chrome compounds, etc., but no muriatic acid. About 50 pounds of the hypo would be decomposed by the 50 pounds of muriatic acid used, so we must assume that 50 pounds of the hypo has been used up by the sulphuric acid which as long as the reduction proceeds is being constantly formed in this bath.

When stock is removed from this bath, the tanning operation is complete and after being washed thoroughly in warm water is shaved and then subjected to the usual coloring and finishing operations. Owing to the fact that chrome tanned leather will stand any amount of washing with water without injury, being unique in this respect, some have hastily presumed that it would stand most anything except fire, but it is quite sensitive to the action of both alkalies and acids. In order to avoid too prolonged a washing, some use a small amount of alkali in the water. This is unwise, but in some cases necessary, as there is not sufficient apparatus available in some factories to continue this washing long enough to free the stock from acid. Skins should come from hypo bath as nearly neutral as possible and this reduction process should be so conducted to produce this result. As bichromate of soda and hyposulphite of soda are used in large excess, a few pounds more or less does not make much difference, nor need the tanner concern himself as to the strength or purity of these articles. The quality of these goods furnished the trade is good and well adapted to the purpose for which they are used. The strength of the muriatic acid, however, is a matter of the greatest importance as it first renders the chrome available and secondly breaks up the hypo liberating the reducing gases. The article of commerce is pure enough; traces of iron and other impurities present are of no consequence to the tanner. The carboys are marked 20° Baumé; this seems to mean that it does not run under 20°. Among the many hundreds of carboys of muriatic acid I have examined in only one or two cases I have found acid under 20° in strength and this was doubtless due to the stopper of the carboy being displaced and some gas allowed to escape. Most of them run from 20.3° to 21.5°; now this means quite a difference in strength. The muriatic acid of commerce is HCl gas held in solution by water, at 20° Baumé 31.8 per cent. of HCl would be held in solution, at 21° 34.6 per cent. a difference of nearly 9 per cent. Tanners should insist upon obtaining muriatic acid of a uniform strength as many troubles might arise from using too much acid. Having determined the proper amount of acid to use, say on carboys running 20.3°, the next lot comes along 21° over 6 per cent. stronger and the tanner wonders what makes his stock inclined to "spue" or to crack. It would be an easy matter for the manufacturers of this article to produce a uniform product. Water is usually abundant and cheap. It is not practical for the leather manufacturer to test every carboy of acid and use it in the proportion of the HCl it contains.

Doubtless the manufacturer thinks that as he only guarantees acid of a strength of 20° Baumé anything more is a gift to the purchaser and he is in the position of giving, not only good measure but more. But this gift to the tanner is most unwelcome and undesirable.

The chemistry of the process as set forth—The saturation of a skin with chromic acid as the first step, and as a second and final step the reduction of this chromic acid to chromic oxide is rather crude to conform to our present conceptions of solutions and reactions. It would also be difficult to prove what the final chromium compound contained in the skin really is. It has been suggested that we form a chrome gelatine, or colloid, compound as the result of the first step, and as the result of the second step a reduced, insoluble, chrome colloid compound which constitutes leather—a theory which sounds well but no evidence whatever has been produced to support such a contention.

VARIETIES AND ANALYSES OF THE VIRGINIA SUMACS

By C. R. Delancy.

Owing to the increased demand in rceent years for the thinner and finer grades of leather, the use of Sumac has been very greatly extended. There are, as is well known, two varieties of Sumac used for tanning, the Rhus coriaria of Sicily, and the Rhus glabra of the United States. As there are various varieties of Rhus which are ground in along with the Sicily Leaf, so also are there several varieties of the Domestic Sumac which are used for tanning, and the manufacturer of the extract has generally been in ignorance of which variety he was getting. As it has always been our aim to manufacture standards which will be as nearly unvarying in their composition as it is possible for any vegetable extract to be: and as it was impossible with the various types of leaf coming in, to secure anything like precision in uniformity, it was found necessary to separate the varieties of leaf. Consequently whole cars of various types were very carefully sampled by taking two whole bags and grinding up every part, then separating the leaves and the stems by hand, which was a tedious and long winded process, getting the weight of both and then fine grinding, quartering and sampling down to about 5 pounds, drawing the sample for the final analysis from this. By this means it was possible to ascertain the general proportions of leaves, stems, tannin, non-tannin and extract, although of course, the amount of tannin varies widely in the different regions where the same type of sumac grows. The following analyses were made in duplicate and represent types, some of them being the means of a great many cars.

	Total solids	Soluble solids	Insolubles	Non-tannin	Available tannin	Stems	Leaves
[1]1—R. Typhina, Va..	48.2	46.6	1.6	17.3	29.3	14	86
2— " W.Va.	36.6	35.5	1.1	23.6	11.9	..	72.2
3— " "	23.1	22.3	0.8	17.6	4.7	27.8	..
[1]4—R. Glabra, Va....	41.8	40.2	1.6	21.6	18.6	67.9	32.1
5— " ".....	49.1	47.0	2.1	25.3	21.7	..	62.9
6— " ".....	19.9	19.4	0.5	15.1	4.3	37.1	..
[1]7— " ".....	46.5	44.5	2.0	18.2	26.3	19	81
8— " ".....	56.7	55.8	0.9	20.1	35.7	..	71
9— " ".....	23.6	22.8	0.8	13.3	9.5	29	..
10— " ".....	55.1	53.7	1.4	18.8	34.9	..	63
11— " ".....	24.1	22.8	1.3	14.0	8.8	37	..
12— " W. Va.	30.9	29.9	1.0	19.8	10.1	..	75.0
13— " "	19.1	18.6	0.5	12.3	6.3	25	..
14— " "	50.2	48.9	1.3	26.5	22.4	..	41.3
15— " "	23.9	23.1	0.8	19.1	4.0	58.7	..
16—R. Copallina, Va.	51.8	50.5	1.3	19.0	31.5	..	78.4
17— " ".....	28.3	26.7	1.6	15.8	10.9	21.6	..
18— " W. Va.	54.5	52.9	1.6	21.2	31.7	..	61.2
19— " "	24.0	23.5	0.5	17.7	5.8	38.8	..
[1]20— " "	37.4	36.9	0.6	19.3	17.6	29.9	70.1

[1] Numbers 1, 4, 7 and 20, were made on the stems and leaves combined. The different analyses represent mean averages of different places in the same states. All analyses made with the special soxhlet described in this Journal for August, 1910.

The difference between the domestic sumac and the foreign is solely on account of reddish color of the domestic leaf. There is a little more tannin generally speaking, in the domestic leaf of the best quality, than there is in the Sicilian such as ordinarily comes to the United States, and owing to the greater difficulty in extracting and higher price of the Sicilian leaf, it is a great wonder that the tanner is not even more larger interested in the American sumac than at present. Extracts are made of American leaf containing not over 20 per cent. more coloring matter than the best Sicilian but with absolutely the same analytical figures at three-fifths the price, so that it would much more than pay the tanners to use the domestic leaf extract and do their own bleaching if necessary rather than to use the more expensive leaf.

BUTYRIC ACID IN THE TANNERY.[1]

By Urbain J. Thuau.

It often happens in industrial chemical processes, that certain

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[1] Translated from *Le Cuir*, Aug. 1, 1910.

substances or products are substituted for those formerly employed. Each substance or product does not possess a set of properties which make its use indispensable, and the choice is often dictated by commercial custom or vogue.

The acids most employed in the tannery for deliming, plumping, and coloring the hides, have been up to the present, formic, lactic, and acetic acids. Why have not other organic acids also been used which form soluble lime salts, and whose properties are, perhaps, of more value in the tannery? The cost of production, the essential factor in industrial technology, eliminates these other acids.

Dr. Effront, of the Institute of Fermentation at Brussels, has within a few months perfected a process by which butyric acid may be obtained by bacterial treatment of distillery residues, at a price such that it is believed that it will be cheaper for equal acidity than formic or lactic acid.

Butyric acid was discovered in 1814 in butter, where it exists in the form of glycerol ester. It is in the irritant liquids excreted by insects, in the muscular juices, and in many secretions and excretions of the human body, and also occurs frequently in plants. The acid is a colorless oily liquid, having the disagreeable odor of rancid butter. It is soluble in water, alcohol, and ether, and forms with lime a water-soluble salt.

Up to the present butyric acid has not been made at a price permitting its industrial use; (it could not be bought for less than 7 or 8 francs per kilo) but thanks to Dr. Effront's process it may now find practical application.

By trial in the laboratory and the tannery we have learned the remarkable properties of butyric acid in contact with hides. In spite of the disagreeable odor of this substance, we can easily see the importance which such an acid may have, as well for its deliming properties, in no respect injurious to the hide, as for its plumping properties. On the one hand, the hides delimed by butyric acid are much clearer than others, and on the other hand, on adding to a tanning liquor a small quantity of butyric acid, there is communicated to it an odor of old oak liquor which pleasantly recalls the good old times.

Let us now examine somewhat in detail the process of Dr.

Effront which permits the production at such a favorable price of this acid so valuable to the tanner.

Fermentation, whenever it is possible to employ it, is almost always the most economical and indeed the only possible process for effecting the transformation of organic substances. Fermentation processes are complex, and are less understood than reactions which are purely chemical, and for this reason discoveries in this field are more rare.

There are many albuminoid materials among waste products, of which we may mention residues from distilleries and sugar refineries, water from which wool-grease has been recovered, etc., also other substances without much industrial value, such as peat. The quantity of organic nitrogen which they contain is enormous. This fact has escaped no specialist, and many and various are the methods proposed for the recovery of the nitrogen. But no one of the specialists has arrived at the result sought, which consists in the extraction in a commercial form, (that is, concentrated and available for agriculture or commerce) of the organic nitrogen of the residues.

These residues have been up to the present without value. The distilleries which make alcohol from molasses recover by calcination the mineral salts contained in the residues, the other products being lost. As for the residues from other materials employed in the manufacture of alcohol, such as the beet-root residues, liquids from the filtration of malt, etc., these are even a source of expense to the distilleries, which are obliged to dispose of them as they can. They are either thrown into rivers or canals where they are a nuisance, or they are evaporated in pits, where they become a serious menace to health.

For the first time, Dr. Effront has succeeded in solving this problem and given in his process a practical solution based on the action of special diastases which decompose the complex molecule of the albuminoids into simpler parts, in which the nitrogen appears in the form of ammonia and amines, economically recoverable.

It should be mentioned that this dissociation affects only the organic matters and does not at all modify the composition of the mineral salts, so that, for instance, the potassium salts in the molasses residues remain as they were and may be recovered in the way already mentioned, independently of the nitrogen. Experiment has even shown that after the residues from molasses have been treated for the recovery of the nitrogen by the Effront process, they burn better in the potash furnaces.

The Effront process, as we have briefly shown, permits the entire recovery of the nitrogen of the residues in an economical manner, and this would suffice to justify its universal use; but its advantages are not limited to the production of useful nitrogenous substances. The fermentation does not destroy the albuminoid molecule in extracting ammonia and amines, but divides it, and gives on the one hand these ammoniacal products, and on the other carbon compounds of the series of volatile fatty acids, whose importance as to both quantity and value, surpasses that of the nitrogenous products. These are mainly acetic, propionic and butyric acids. It seems then, to be an ideal process, for it makes possible the conversion of substances not heretofore utilized nor utilizable, (including especially betaïne, asparagin and glycocoll) into products of great value and of prime necessity.

The application of the process has been worked out in the following manner:—

The residues, distillery refuse, waste water after the recovery of wool-grease, etc., are subjected to a special fermentation induced by means of a bacterial culture and carried on in a manner similar to alcoholic fermentation.

As soon as the albuminoids are decomposed into ammoniacal products and volatile fatty acids, the fermented liquors are subjected to two successive distillations. The first distillation, in alkaline medium, has for its object the recovery of the ammoniacal bases in the form of sulphates or other salts. The residues which result, now free from nitrogen compounds, are then concentrated by evaporation, and after the addition of sulphuric acid, are subjected to a second distillation which sets free the volatile fatty acids.

The crude acids thus recovered are subjected to various processes of concentration, purification, rectification, etc., and give as final products acetic, propionic and butyric acids in the different degrees of purity and concentration demanded by industrial uses, and even, when the manipulations have been carried far enough, chemically pure acids.

The Effront process permits the recovery in this manner, for each cubic metre of distillery refuse from 25 to 35 kilos of sulphate of ammonia and almost as much of the organic acids.

When one considers that in Europe alone the yearly production of alcohol reaches 18,000,000 hectoliters (450,000,000 gallons), and if we diminish these figures one-half by deducting the alcohol made by the distillation of such materials as potatoes, for which the Effront process is not available because of the poverty of the residues, there yet remain 9,000,000 hectoliters of alcohol, the residues from which are actually lost and ought to be recovered. The Effront process permits the production for agricultural purposes of a large additional tonnage of ammonium sulphate, and besides this, will furnish for industrial uses, acetic, propionic and butyric acids. This last acid is of especial importance to the tannery.

As we have said above, the distillery refuse is subjected to a special fermentation. This fermentation is due to an enzyme, which Dr. Effront has named amydase, and which transforms the compound diamides into ammonia and fatty acids. This amydase exists in brewers' yeast (barm) and in garden soil. If the yeast is employed, it is permitted to digest in a yeast room for 3 days, becoming alkaline, being aerated, and being rendered coherent by means of salts of alumina. If garden soil is used, it is kept at 70° to 80° C. for an hour: all the ferments are then destroyed except those which produce ammonia. The refuse is inoculated with these ferments. The distillery refuse leaves the still at a temperature of 45° C. This is rendered alkaline: 2 kilos of the prepared ferment are added per hectoliter of refuse, and it is then maintained at the same temperature. During the first two days the fermentation is active, then the liquid settles and the formation of the ammonia begins. Three days having elapsed, the decomposition of the compound diamides is complete.

The ammonia is collected in sulphuric acid, and the sulphate of ammonia sold as fertilizer. The fatty acids remain in the residue, from which they are easily extracted.

Molasses refuse which has furnished 100 liters of alcohol yields

35 kilos of ammonium sulphate and 35 kilos of fatty acids. Beet-root refuse which has furnished 100 liters of alcohol yields 16 kilos of ammonium sulphate and 12 to 14 kilos of fatty acids. These acids are acetic, propionic and butyric.

The importance of the discoveries of Dr. Effront of Brussels is considerable, when one considers the immense service which the products of recovery may render to industry, those products which he has learned how to extract from the albuminoid residues, in particular butyric acid, which could not formerly be used in the tannery, in spite of its important properties for deliming and plumping. We should also pay our respect to the knowledge of this learned inventor whose reputation is universal in matters of fermentation.

CERIUM AS A TANNING MATERIAL.[1]

The principal source of cerium is the material known as Monazite sand, found extensively in Brazil. Cerium is the most abundant metal in this substance, but in the manufacture of Welsbach gas mantles the proportion of thorium used is much larger than of cerium. Thus a large quantity of cerium compounds comes into the market as a by-product from the gas mantle industry.

Another important source of cerium is the mineral cerite, a complex silicate found in Sweden. By its place in the periodic table, cerium, whose atomic weight is 140.2, is seen to be related to carbon and silicon, and like them it combines with two atoms of oxygen. Beside this oxide, CeO_2, it also forms a lower oxide,C_2O_3. This lower oxide is analogous to the oxides formed by aluminum and chromium, Al_2O_3 and Cr_2O_3. Compounds of aluminum and chromium are used for tanning, and while both combine readily with the hide substance, those formed by chromium are much less soluble in water than those formed by aluminum. Chrome leather is therefore much more serviceable for general purposes than alum leather.

It is probable that the anology of its oxide to those of aluminum and chromium first suggested the use of cerium compounds

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[1] Abridged from the article by Alan A. Claflin in *Shoe and Leather Reporter* for July 21, 1910.

as a tanning agent. Little can be predicted, however, from this similarity, and much remains to be done before we can know whether cerium leather is a practical possibility. If it is found to have important advantages for particular purposes, and if the price of the cerium residues does not rise because of the discovery of new uses to which they may be put to better advantage, then cerium leather may be made commercially at some time in the future.

ABSTRACTS.

Meeting of the German Section, I. A. L. T. C. Frankfurt, June 12, *Collegium,* 1910, No. 416, pp. 261-4.—It was voted to urge at the Paris Congress that the Zeuthen method of tannin analysis be tested by the Analysis Commission. The subject of discrepancies in determination of insolubles was discussed. Dr. Jablonski proposed centrifuging instead of filtration. Dr. Paessler preferred to dissolve the extract at room temperature with continued shaking, the resulting solution being readily filtered and the insolubles left in an entirely different form from that produced by precipitation from a hot solution on cooling. Dr. Paessler reported that he had observed that repeatedly each year for a short time at the beginning of the warm season, the non-tan determinations were abnormally high, although temperature prescriptions were carefully followed. Others reported the same. Dr. Paessler reported the frequent adulteration of sumach with the leaves of *Pistacia lentiscus* and *Tamarix africana,* which not only lowers the tannin content but gves a color to the leather which darkens by action of light. The other topics presented will appear in full in the *Collegium.*

Report of the French Commission on Tannin Analysis. MM. DE LA BRUERE, SCHELL, THUAN AND DE KORSAK. *Le Cuir,* 1910 (3) No. 13, pp. 341-5.—Detailed comparative analyses of a chestnut extract of 39 per cent. total solids, 7 per cent. non-tans, are reported. The official method was strictly followed, using American hide powder; full details of operations, dimensions of apparatus, etc., are given. For total solids, the maximum difference was 0.3 per cent.; for non-tans, 1.3 per cent. The discrepancies in non-tans are considered as largely due to the washing of the hide powder which the commission proposes to study specially.

New Method for Determination of Acids in Tan Liquors (preliminary note). A. SEYMOUR JONES. *Collegium,* 1910, No. 419, pp. 298-300.—This depends upon direct titration with alkali, using fluorescein as indicator. Fluorescence first appears when the acids present are neutralized; tannic acid is too weak to influence the indication. Some have stated that acetic acid will produce a fluorescence. This is, however, very slight, but for certainty alkali is added sufficient to produce a maximum effect. Two Nessler glasses of equal dimensions are covered within 1 cm. from the bottom with black glazed paper, (black inside). In one, 10 cc. of the liquor and 5 drops of 2 per cent. alcohol. sol. fluorescein are placed and excess N/10 NaOH run in to give maximum result. This is the standard and remains permanent over an hour. The actual titration is then carefully made in the other glass, matching the standard for end point. It is best to previously filter the liquor examined.

Glucose Determination with Fehling's Reagent. F. MAYEZIMA. *Pharm. Zentralh.* (49) No. 34.—(1) Copper sulphate solution, 39.2704 grams cryst. salt to 1 liter; 1 cc. = 0.01 grams cu. (2) Fehling's copper sulphate solution, 69.278 grams in 1 liter; 25 cc. = 0.441 grams cu. (3) Allihn's alkali solution, 346 grams Rochelle salt, 250 grams KOH to 1 liter. (4) Potassium cyanide solution; 10 cc. should exactly decolorize 10 cc. of sol. (1) after addition of 10 cc. of ammonia water. For the analysis, a mixture of 30 cc. of Fehling's sol., 30 cc. Allihn's sol. and 60 cc. H_2O are boiled in a 300 cc. stand. flask and then 25 cc. of the sugar sol. added. After 2 minutes boiling, cool and fill to mark. After settling and filtering if necessary, 50 cc. are pipetted off, weakly acidified with HNO_3, then made alkaline with NH_3 and then titrated with the KCN sol. till colorless.

WILH. MENGERT *Pharm. Zentralh.* (49) No. 44.—The end point of the titration is recognized by spotting on filter-paper previously moistened with acetic acid and potassium ferrocyanide and dried. The ring ceases to appear when all the copper is reduced.

Preparation of Alcoholic Potash Solution. L. RABE. *Pharm. Zentralh.* (49) No. 45.—To avoid the formation of the yellow aldehyde resin due to heating of the alcohol with the alkali especially when carbonate is present, the author dissolves 29 (or 58) grams KOH in an equal amount of water, and after cooling pours the solution into 900 cc. 95 per cent. alcohol, fills to 1,000 cc. and lets stand. The solution is cautiously poured off from the separated oil as soon as possible, and then left stand 1 to 2 days until the carbonate has settled and then decanted into reagent bottles.

Fat Emulsions. L. MEUNIER AND M. MAURY. *Collegium,* 1910, Nos. 418-9, pp. 277-87.—In this study, the authors attempt to determine the principles controlling the formation of the emulsions used in currying. The principal factor in the emulsionizing of neutral oils is the surface tension of the oil which opposes its division into globules and tends to reunite these when divided; the greater the tension, the less easily is the oil emulsified. The authors have made relative determinations of this constant in various oils by noting the number of drops produced by 1 gram issuing, from a small burette, the tip of which had been finely drawn out, bent upward and immersed in a fixed depth of water. All experiments were made under the same conditions. The surface tension was considered to be inversely proportional to the number of drops.

Thus neatsfoot oil gave 18 drops, olive oil 20, castor oil 9, linseed oil 18, and mineral oil (sp. gr. 0.934) 9. The results were not much affected by temperature.

When salt was dissolved in the interglobular liquor (water), the emulsion was promoted; neatsfoot oil which in pure water gave 18 drops, gave with 1, 5 and 10 per cent. salt solutions, 19, 24 and 31 drops. The influence of alkaline ricinoleates was still greater. The number was raised from 29 to 122 drops progressively with solutions of 5 to 55 per cent. commercial ammonia ricinoleate and from 44 to 104 drops with 5 to 20 per cent. of the sodium salt. When these upper limits were passed, the oil issued in an unbroken stream in both cases. This marked diminution of tension is explained as caused by the saponifying action of the sulpho-compound analogous to the reaction in Twitchell's industrial process for saponification of fats. As a result of the hydrolytic action, the oil becomes coated with a minute pellicle which reduces the surface tension. This action was found to be much less with sulphuric acid and aromatic sulpho-acids Pure olive oil giving with water 20 drops, in H_2SO_4 of 0.1 to 10 per cent. gave 21 to 33 drops; with benzene sulphonic acid 1 to 10 per cent., 23 to 33 drops; with sodium salt of same, 1 to 5 per cent., 21 to 24 drops; with sodium benzene disulphonate, 1 to 5 per cent., 22 to 28 drops; with sodium α naphthol disulphonate, ½ to 10 per cent., 21 to 62 drops. The production of permanent emulsions by prolonged agitation with water is likewise due to hydrolysis.

The presence of colloids greatly favors the formation of emulsions, the colloidal particles which are much smaller than the oil globules, forming a protective sheath which prevents their union. Milk and egg yolk represent such emulsions favored by colloidal albumin. In technical emulsions, gelatine, gum, Irish moss, etc., act similarly.

Another condition producing very stable emulsions is the employment of a fine emulsion as the intergranular liquid. An example of this is afforded by the free fatty acids in rancid oils which have notable emulsifying powers. These form an intimate emulsion with water which protects the oil globule. Besides this, the superficial tension of neutral oil is greater than that of acid oils. A neutral neats-foot oil gave 30 drops in water; the same oil, containing ⅓ free fat acid, 40 drops; ½ acid, 44 drops; 2/3 acid, 60 drops; pure acid, 62 drops.

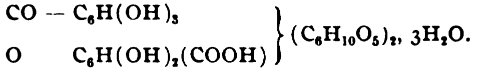
If an alkaline solution be used for the intergranular liquor, the tension of the contact surface is greatly lowered. Neats-foot oil giving 13 drops in pure water, gave 21 to 57 drops on addition of 0.02 to 0.055 per cent NaOH.

The general conclusion is that any substance precipitated or emulsified in fine granules may act as an emulsifying agent, especially if its surface tension is less than that of the oil in question. By employing both colloids and emulsions in the intergranular liquor, a very active agent is obtained. A soap solution may be considered colloidal. As to the favorable proportion of alkali in the soap used, the authors find this increases wih the dilution. For making such emulsions, the soap should be dissolved in the smallest amount of water possible and not diluted until the oil has been emulsified. The presence of salt in a soap is unfavorable to emulsions, as it coagulates the colloid. For the same reason egg yolk preserved by salt is less suitable than the fresh article for the emulsion used in currying chrome leather.

Fermentation of oils, as in chamoisage, promotes emulsification by the liberation of free fatty acids.

Ellagotannic Acid. M. NIERENSTEIN. *Ber. deutsch. chem. Ges.*, 1910 (43) 1267.—This acid according to Löwe occurs in several plants and differs from ellagic acid in solubility in water and alcohol. It has been considered to be a glucoside of ellagic acid or a condensation product of the last with gallic acid. Procter (Laboratory Book) considers it to be merely colloidal ellagic acid.

The author has first succeeded in crystallizing this substance. Ellagotannic acid prepared from myrobalams according to Löwe and purified by dialysis was further purified by Emil Fischer's carbo-ethoxylizing method. The alkaline solution was treated with excess ethyl chloroformate and the condensation product saponified by pyridine. On repeating this several times, the pure acid was obtained, crystallizing from pyridine and acetic acid in pale yellow needles, m.p. 329-336°; formula



$$\left.\begin{array}{l}\mathrm{CO} - \mathrm{C_6H(OH)_3}\\ \mathrm{O}\qquad \mathrm{C_6H(OH)_2(COOH)}\end{array}\right\}(\mathrm{C_6H_{10}O_5})_2,\ 3\mathrm{H_2O}.$$

It is considered to be a diglucoside of luteoic acid (this JOURNAL (4) 62). It is precipitated by gelatine and quantitatively absorbed by hide powder. With nitric acid it gives the characteristic reaction for ellagic acid. It is optically active; boiled with dilute sulphuric acid it gives ellagic acid.

The Nature of Tanning. W. FAHRION. *Collegium*, 1910, No. 415, pp. 249-59.—The substance of this article has been presented in the author's previous reviews and accounts of his researches. Physical chemistry has greatly developed but has not yet led to the expected improvements in chemical technology. Especially in colloidal chemistry, the scientists are by no means agreed as to the distinction between the colloidal condition and chemical equilibrium. Finally the author asserts that there is no proof of the physical nature of the tanning process. While he no longer maintains that leather is a salt of hide and tannin, he claims that chemical action is necessary to tannage, since it has been shown that formaldehyde, quinone and unsaturated fatty peroxy-acids are genuine tanning agents. His theory in brief is: "Every form of tannage depends upon a condensation between hide and tannin; in genuine tannage, this takes place directly, in pseudo-tannage, the tannin condenses first with itself, and then with the hide."

The Testing of Belting. B. KOHNSTEIN. *Collegium*, 1910, No. 419, pp. 287-92.—The degree to which a belt may be stretched depends upon many factors. Among these are the nature of the original hide, time of soaking and bating, use of stale limes, variations in plumping and tannage. Rapid drying of unstretched leather produces shrinkage, and consequent proneness to stretching, likewise freezing of wet leather. A table of tests is given showing the influence of fats upon the stretching.

	Per cent. fat	Kilos resistance to tearing	Per cent. stretching
A. Pine and mimosa tannage	0.0	3.0	21.5
Same, stearin burnt in	16.8	3.33	25.25
B. Pine and extract tannage	0.0	1.88	24.6
Same, greased with stearin	15.0	1.92	25.5
C. Pine-valonia-myrabalams	28.0	2.7	32.3
Same, degreased petroleum ether	2.0	2.4	31.1
D. Pine and oak tannage	12.0	3.28	35.0
Same, degreased petroleum ether	1.5	2.72	31.7
E. Chrome, two-bath	0.0	3.0	57.2
Same, paraffine burnt in	41.0	3.4	70.0
F. Chrome, two-bath	0.0	2.1	44.0
Same, greased, burnt in	71.0	2.5	56.0
G. Chrome, two-bath, soaped	2.5	3.4	50.0
Same, paraffine	25.0	3.9	74.0
H. Chrome, two-bath	14.0	3.73	84.1
Same, degreased, petroleum ether	1.6	2.74	76.9
J. Chrome, one-bath	6.0	3.1	54.0
Same, degreased petroleum ether	0.3	2.8	44.0

The above shows that the breaking strength and stretching increase on greasing. There is a final limit in each case but these do not fall together and diverge especially when fats of different melting-points are used; while the resistance to tearing remains much the same, the stretching increases with the softer fats.

	Per cent. fats	Resist. to tearing	Per cent. stretching
K. Chrome leather, one-bath	0.0	2.42	27.8
Same, paraffine, m.p. 58° C. burnt in	18.0	3.75	32.0
Same, paraffine, m.p. 54 burnt in	18.0	3.8	41.5
L. Chrome, one-bath	0.0	2.59	37.0
Same, greased with paraffine and vaseline, m.p. 51	18.0	3.8	56.6

Another important factor which is usually overlooked is the elasticity which enables the belt to cling to its pulley and tends to oppose the stretching. This is very great in rubber belting but slight in vegetable tanned leather; in chrome leather it is more marked. This elasticity factor may be measured in testing by the space left on the rebounding of the leather after tearing. The following tests were made upon belting leathers of Austrian manufacture:

	Per cent. fat	Kilos resist. tearing	Per cent. stretching	Per cent. elasticity factor
M. Chrone, one-bath	12.0	3.4	68.0	21.0
Same, degreased	0.0	2.91	61.4	17.4
N. Chrome, one-bath	8.6	2.85	64.0	24.0
Same, degreased	0.0	2.62	61.1	18.2
O. Chrome, one-bath	20.0	8.5	60.0	11.0
Same, degreased	0.0	8.27	48.5	10.0

The Composition of Linseed Oil. W. Fahrion. *Zeit. angew. chem.*, 1910, (23), 1106-8.—The details of the experimental work employed in the analysis are described, the final results being: unsaponifiable 0.8, saturated fatty acids 8.6, oleic acid 17.5, linolic acid 30.0, linolenic acid 38.0, glycerol radical C_6H_2 5.3 per cent. His earlier analyses, questioned by Lewkowitsch, are substantially confirmed.

Japan Wax. G. Weigel. *Pharm. Zentralh.*, (49) No. 45.—A variety has been lately sent from China apparently identical with the Japanese article. The constants are; melting-point 49° C., (ordinary Japan wax, 52 to 54°), saponification No. 222.4, iodine No. 12.1. Japan wax is usually bleached naturally; it is boiled and poured into water and then exposed, 3 to 5 weeks in summer, 7 to 8 weeks in winter, to the action of sunlight.

PATENTS.

Waterproof Leather Board and Process of Preparing the Same. U. S. Patent No. 965,152. Edgar S. Buffum, Newton, and William W. Carter, Needham, Mass.

The leather board is made from a pulp consisting in part of leather fibers.

Reinforced Leather and Process of Manufacturing the Same. U. S. Patent No. 965,261. Emil Weinheim, New York, N. Y.

Leather of unequal thickness is filled in with a paste and a layer of woven fabric laid on. The paste is then so treated as to render it insoluble, or, in effect, to tan it, thus producing a composite reinforced leather of uniform thickness.

Journal of the

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Vol. V OCTOBER, 1910 No. 10

W. K. ALSOP . . . . Editor and Manager
LLOYD BALDERSTON . . . . Associate Editor

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ELECTIONS.

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Harrison L. Clough, c/o W. H. McElwain Co., Merrimack, N. H.

ASSOCIATE.

Thomas P. Durell, c/o Marden, Orth & Hastings, 1030 North Branch St., Chicago, Ill.

CHANGES OF ADDRESS.

Dr. I. Dreyfus from 106 E. 82d St., New York, to 239 Mason St., Milwaukee, Wis.

ANNUAL MEETING.

The Seventh Annual Meeting of the American Leather Chemists Association will be held in conjunction with the convention of the National Association of Tanners at the Hotel La Salle. Chicago, Ill, October 6th, 7th and 8th. Convening at 9.30 A. M. on the 6th.

The headquarters of the Association will be at the Hotel La Salle. A room has been reserved at the hotel, in which the meetings will be held.

The program is as follows:

THURSDAY, OCTOBER 6TH.

Morning Session:

Opening remarks by the President.

Report of the Secretary-Treasurer.

Committee reports.

Afternoon Session:

Address by Dr. Allen Rogers, "Trade School for the Leather Industry."

Address by Mr. George A. Kerr, "Manufacture of Extracts in the United States."

Address by Mr. F. C. Rose, "Leather Oils."

Address by Mr. John H. Yocum, "The Disinfection of Hides."

FRIDAY, OCTOBER 7TH.

Morning Session:

Meeting of the National Association of Tanners. Members of the A. L. C. A. are invited to attend this meeting.

Afternoon Session:

Visit to the Stock Yards of Armour & Company.

Evening:

Joint Banquet at the Hotel La Salle. The National Association of Tanners have cordially invited the active members of the A. L. C. A. to attend this banquet as their guests.

SATURDAY, OCTOBER 8TH.

Morning Session:

Address by Mr. F. P. Veitch, subject to be announced.

Address by Mr. F. E. Atteaux, "The Proper Bating of Hides."

Address by Mr. J. H. Russell, "Tannage of Heavy Leather in California."

Afternoon Session:

Address by Mr. R. C. Jacobsen, subject to be announced.

Committee reports.

Election of officers.

This program may be subject to some rearrangement.

A paper is also promised by Mr. George A. Riker on "Extraction of Leather by Various Solvents," and one by Mr. Thomas A. Faust on "The Necessity of Proper Sampling."

The rates at the Hotel La Salle are as follows:

One person, room with detached bath	$2 to $3	per day
One person, room with private bath	$3 to $5	" "
Two persons, room with detached bath	$3 to $5	" "
Two persons, room with private bath	$5 to $8	" "
Two persons, two connecting rooms with bath	$5 to $8	" "
Four persons, two connecting rooms with bath	$8 to $15	" "

NOTICE.

Stamford, Conn., Aug. 3, 1910.

All those desiring accommodations reserved for the Annual Meeting of the American Leather Chemists Association, in conjunction with the meeting of the National Association of Tanners, in Chicago, on October 6th, 7th, and 8th, are requested to communicate direct with the Hotel La Salle, Madison St., Chicago, Ill., which hotel has been selected as headquarters for the Association.

H. C. REED,
Secretary.

PARIS MEETING OF THE I. A. L. T. C.

Our Association was represented at the International Convention by two members of the Council, Messrs. Alsop and Griffith. We hope to publish an account of the meeting in our next issue.

CHROMING OF HIDE POWDER.

By Charles R. Oberfell.

Certain lines of investigation for the 1910 Committee on Chroming of Hide Powder were suggested by a review of the researches published in this JOURNAL since its inception in 1905.

In 1905 Alsop[1] as Chairman of the committee deduced the following as a result of his investigation:—"The results do not warrant changing the method so as to shorten the time of chroming to the extent tried," *i.e.*, 30 minutes and 1 hour with constant stirring. In this investigation the hide powder was wet with 25 times its weight of water.

Small[2] as Referee in 1906 said; "From the collaborative results of the committee the referee could see no sufficient reason for changing from the official chromed powder (light) to a heavier chromed powder."

In 1907 there was no committee report on this subject but Small[3] in reporting the results of his committee on the acidity of hide powder said; "It would appear, ..., that the heavily chromed hide powder gives uniformly lower non-tannin values and in so far is inferior to the hide powder chromed by the official A. L. C. A. method."

Reed[4] as Chairman of the 1908 committee compared the present official method of chroming against the official method of the I. A. L. T. C. to the detriment of the latter.

There seems to be a satisfied feeling among the members of the A. L. C. A. regarding the efficiency of the present method of chroming. The subject has been under investigation for several years, and at each succeeding annual meeting they steadfastly refuse to increase the amount of chroming or to substitute chromium chlorid (basic) for chromium potassium sulphate. Basic chromium chlorid apparently holds no advantage over chrome alum, as has been repeatedly shown by American chemists,[5] but if a suitable substitute for chrome alum could be found which would eliminate the "sulphate factor" doubtless it would receive attention. The only substance of any promise which has been proposed as a substitute is a basic chromium formate by Reed.[6] This investigation yielded promising results, but it can be assumed that later Reed found an objection to its

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[1] Com. Report, 1905, this J., I, 25, 26.

[2] Referee's Report, this J., I, 338.

[3] This J., II, 347.

[4] This J., III, 326.

[5] This J., III, 326.

[6] This J., II, 426.

use, inasmuch as he failed to give it a trial in 1908 when Chairman of this committee.

At the same time there is a well defined desire among American Leather Chemists to shorten the time of chroming. As has been shown by Alsop in 1905 this cannot be accomplished by using the official amount of water to wet the hide. Recent developments have suggested the use of less water than prescribed in the official method. This amount of water must not be too small since very acid powders swell greatly on becoming wet and hence decrease the fluidity of the magma, which is undesirable. Water to the amount of ten times the weight of the hide powder being chromed has been suggested and found convenient.

With these considerations in mind it becomes desirable to definitely settle the point as to whether or not the hide powder can be chromed to the same degree as by the official method, with chrome alum, but within a short time, *eg.*, one hour. This point was touched upon in 1908, but very little was accomplished, and again by the 1909 committee,[1] but nothing conclusive can be drawn from the report.

This question, then, of the length of time necessary to chrome powder is the one most needful of settlement, and the Chairman set the committee to this task.

Samples of extract representative of three classes; *i.e.*, low, medium and high percentage of non-tans were prepared and sent to the committee accompanied by the following set of directions.

"Analyze the materials sent to you according to the official method, using hide powder prepared as follows:—

(A) As per official method.

(B) Wet the hide powder by using ten times its weight of water. Allow it to become thoroughly soaked and add 3 per cent. of chrome alum in solution. Agitate continuously for one hour, then wash as per the official method.

"If possible use different varieties of hide powder.

"By reviewing the work which has been done on determining the proper acidity of hide powder it is found that hide powder which consumes 1 cc. 0.1 N NaOH for one gram of dry hide

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[1] This J., IV, 310.

gives the best results. It becomes necessary therefore to reduce the acidity of all hide powder used on this investigation to this definite acidity. This is best accomplished by adding the calculated amount of alkali or acid to the soaked hide powder before the chrome alum is added.

"In order to check the hide powder as chromed in A against B by some other value than the non-tannin figure you are requested to prepare sufficient hide powder each time to make the following determination of the amount of chromium trioxid absorbed by the hide.

"Weigh in a closed tube 7-8 grams of absolutely dry chromed hide powder and transfer to a platinum crucible. Incinerate carefully and then ignite completely. (It may be necessary to add the hide powder in two or three successive amounts, due to its disposition to swell exceedingly during incineration.) Mix intimately with the ash two grams of a mixture containing equal parts of sodium carbonate (anhydrous) and magnesium oxid. Heat with the ordinary bunsen flame for 30 minutes and then in blast flame five minutes. Occasionally allow air to enter the crucible and at no time allow the flame to completely envelope same. Wash the melt into a glass stoppered bottle, 400 to 500 cc. capacity, using as little water as possible. Add 10 cc. of a 15.0 per cent. potassium iodide solution (free from iodates) and then 10 cc. of concentrated HCl. Agitate until all solid particles are dissolved and then titrate with 0.1 N sodium thiosulphate (recently standardized) using starch paste indicator.

Report in duplicate as follows:—

1. Weight of dry chromed hide powder taken for determination.
2. Cubic centimeters sodium thiosulphate solution consumed.

An answer to each of the following questions will greatly aid when comparing the results of all the members of the committee.

1. How do you make chrome alum solution? Give weight of chrome alum and weight of water you use.
2. The moisture in air dry hide powder which you used for chroming?
3. Do you measure or weigh the chrome alum solution to be added to the hide powder?

"Please make the non-tannin figure the corrected figure for solubles introduced from soluble matter in the kaolin.

"Use the following approximate amounts of extract sent to you in making solutions for analysis:—

Sample A. Chestnut wood extract, 15.00 grams to the 1000 cc.
Sample B. Blended " " 22.00 " " " " "
Sample C. Quebracho " " 6.00 " " " " "

In an investigation of this kind comparable results are not expected unless the details of manipulation are very similar. The report asked for from the committee was framed so that it would be possible to determine just how much each collaborator varied from the other. A study of the accompanying tables will show how closely the members worked and it will also tend to determine the value of this investigation.

TABLE I.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER OFFICIAL METHOD.

	Chestnut wood extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	38.16	37.88	13.13	12.55	74.90	0.3764	Clear
C. C. Smoot, 3d	37.88	37.52	13.04	12.51	72.19	0.3893	Clear
F. B. Shields	93.02	37.60	13.89	13.10	73.80	0.3643	Slight Greenish Cast
W. F. Wilson	38.13	37.78	13.30	12.37	72.50	0.3657	——
W. P. Maxwell	37.70	37.36	12.86	13.09	70.90	....	Clear
Average	37.98	37.63	13.22				

TABLE Ia.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER RAPID METHOD.

	Chestnut wood extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	38.18	37.95	12.90	12.87	74.25	0.3799	Clear
C. C. Smoot, 3d	37.88	37.52	13.05	12.14	73.03	0.3894	Clear
F. B. Shields	38.02	37.60	13.46	13.40	73.20	0.3722	Slight Greenish Cast
W. F. Wilson	38.12	37.78	13.19	11.92	73.50	0.3677	——
W. P. Maxwell	37.69	37.45	12.80	13.44	70.14	....	Clear
Average	37.98	37.66	13.08				

TABLE II.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER OFFICIAL METHOD.

	Blended extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	44.88	43.91	23.56	12.55	74.90	0.4500	Clear
C. C. Smoot, 3d	44.62	43.62	23.64	12.51	72.19	0.4261	Bril.
F. B. Shields	44.62	42.50[1]	23.80	12.10	73.80	0.4147	Opalescent
W. F. Wilson	44.50	43.40	23.10	12.37	72.50	0.4465	——
W. P. Maxwell	44.82	43.82	23.40	13.09	70.90	——	Clear
Average	44.69	43.69	23.50				

[1] Not included in average.

TABLE IIa.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER RAPID METHOD.

	Blended extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	44.98	43.90	23.39	12.87	74.25	0.4527	Clear
C. C. Smoot, 3d	44.62	43.61	23.24	12.14	73.03	0.4347	Bril.
F. B. Shields	44.62	42.50[1]	23.62	13.40	73.20	0.4184	Opalescent
W. F. Wilson	44.50	43.40	23.00	11.92	73.50	0.4449	——
W. P. Maxwell	44.93	43.98	23.44	13.44	70.14	——	Clear
Average	44.73	43.72	23.34				

[1] Not included in average.

TABLE III.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER OFFICIAL METHOD.

	Ordinary solid quebracho extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	84.79	78.28	6.00	13.05	73.90	0.4401	Clear
C. C. Smoot, 3d	84.64	78.32	6.05	12.51	72.19	0.4252	Bril.
F, B. Shields	86.27[1]	79.86[1]	6.08	13.50	73.00	0.4319	Colorless
W. F. Wilson	85.46	78.53	6.41	12.37	72.50	0.4344	——
W. P. Maxwell	84.69	77.22	5.63	13.09	70.90	——	Clear
Average	84.89	78.09	6.03				

[1] Not included in average.

TABLE IIIa.—AMERICAN STANDARD HIDE POWDER (1910), CHROMED AS PER RAPID METHOD.

	Ordinary solid quebracho extract						
	Per cent. total solids	Per cent. soluble solids	Per cent. non-tannin	Gms. dry hide	Per cent. moisture in hide	Gms. tannin per 100 cc. sol.	App. N. T. filtrate
Chas. R. Oberfell	84.79	78.28	5.71	13.38	73.25	0.4427	Clear
C. C. Smoot, 3d	84.64	78.32	6.15	12.14	73.03	0.4246	Bril.
F. B. Shields	86.27[1]	79.86[1]	6.41	14.30	71.40	0.4289	Colorless
W. F. Wilson	85.46	78.53	6.43	11.92	73.50	0.4342	——
W. P. Maxwell	84.18	77.39	5.76	13.44	70.14	——	Clear
Average	84.77	78.13	6.09				

[1] Not included in average.

It may be assumed that if two hide powders are chromed with the same solution to the same degree they will act similarly when brought into contact with portions of the same tan infusion. By determining the amount of chromium absorbed we have a basis for comparison and in the case of the work at hand, we can determine accurately how closely the hide powder chromed by the rapid method resembles that chromed by the official method.

Only two members besides the chairman participated in this part of the work and the results in Table IV indicate that the hide chromed by the rapid method contains less chromium as chrome alum, but the difference in chromium as such is very small.

TABLE IV.

	A. Per cent. chrome alum not absorbed. Official method.	B. Per cent. chrome alum not absorbed. Rapid method.	Per cent. A. over B.
W. P. Maxwell	20.29	17.59	—2.70
C. C. Smooth, 3d	15.60	17.18	+2.58
Chas. R. Oberfell	7.17	10.01	+2.84

In regard to the general subject before the committee the following opinions were expressed:—

F. B. Shields—"The results in our laboratory by the quick method do not very well agree with, nor vary concordantly from, those by the official method. Neither do I find it more convenient."

C. C. Smoot, 3d, prefers to see other results than his before expressing an opinion of the two methods.

W. F. Wilson—"The quick method would often have a great advantage over the present method on account of the difference of time it takes and if we would have an optional as well as an official method I would be in favor of making the quick method optional, provided my results are found to check with the other chemists."

Charles R. Oberfell, Chairman—It is certain that the only advantage of the rapid method over the official method is a saving of time, and this can not be taken advantage of in extract analysis unless a rapid cooling of the analysis solution is adopted.

The hide used in this investigation was from the same source, but undoubtedly from different lots, giving about an average of hide used by the American chemists.

With the exception of the ordinary quebracho extract the results show that lower non-tannin values are obtained by the rapid method. The difference is not great but consistently in one direction. This is in line with an opinion by Small[1] expressed as a member of this committee in 1908.

There is a decided advantage in the rapid method when the analysis of liquors is considered and this with the other work of the 1910 committee is respectfully submitted to the consideration of the Association.

England-Walton Chemical Laboratory,
Harrisonburg, Va.

REPORT ON METHODS FOR THE ANALYSIS OF LEATHER.

By F. P. Veitch.

Two samples of greased leather, one a fair and the other a blackened harness leather, were sent out, accompanied by the following directions:—

DIRECTIONS OR LEATHER WORK A. L. C. A., 1910.

Moisture.—Dry 15 grams of ground sample in a water oven for 15 hours at a temperature of from 95-98° C. The sample should be placed in a glass weighing bottle, about 2½ inches high, and 1⅞ inches in diameter, and the cover should be put in place

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[1] This J., III, 326.

when the sample is removed from the oven. Or the samples may be placed in a regulation tannin dish and covered with a small watch glass when removed. Desiccate over sulphuric acid and weigh when thoroughly cooled.

Fats.—Extract 15 grams of water free sample in a Soxhlet extractor for 16 hours or until free from grease, using petroleum ether distilling between 50-80° C. Evaporate ether, dry and weigh.

Water Extract.—(Method A. L. C. A.). Digest 30 grams of fat free leather in a percolator over night, then extract with water at 50° C. for 3 hours, the total volume of solution to be two liters and determine the soluble solids and non-tannins by the official method.

Water Extract.—(Method of Bureau of Chemistry.) Extract 15 grams each of the original and of fat free sample with water in a Soxhlet, the cylinder of which is surrounded by a water-bath kept at 50° C. The extraction is continued for 14 hours, and the extract obtained is made up to one liter. At the beginning of the extraction 300 cc. of water are poured into the Soxhlet and allowed to syphon over, then the boiling is begun. At the end of one hour, the flame is removed and the extract transferred to a one liter graduated flask, 150 cc. of water are then added and the extraction continued two hours, extract removed, 150 cc. of water added and extraction continued for three hours, and extract removed. Two more extractions are made in each of which 150 cc. of water is added and the extraction is continued for four hours. This gives 14 hours extraction and an extract which does not exceed one liter in volume. (A small piece of cotton is placed in the bottom of the Soxhlet and another on top of the leather to prevent small particles of leather from being carried over.)

Determine the soluble solids and non-tannins by the official method.

Nitrogen.—Determine by the straight Gunning and Kjeldahl method as laid down in Bulletin 107, Revised, Bureau of Chemistry, boiling with acid for at least four hours.

The results reported are given in the succeeding tables.

MOISTURE.

	No. 1.		No. 2.	
	15 hours at 95-98° C. Per cent.	1 hour at 100°. Per cent.	15 hours at 95-98° C. Per cent.	1 hour at 111°. Per cent.
John Seltzer	7.7	..	8.0	..
W. A. Fox	7.6	8.1	8.3	9.1
G. A. Riker	7.9	..	8.5	..
" after fat extraction	7.3	..	7.8	..
J. S. Rogers and C. F. Speh	7.6	..	9.2	..
Covered weighing bottles	3.9[1]	..	4.3[1]	..
Covered tannin dishes	3.7	..	4.4	..
Open tannin dishes	3.6	..	4.2	..
Vacuum oven, 4 hrs. 98-100°				
Covered weighing bottles	4.5	..	4.7	..
Covered tannin dishes	4.5	..	4.8	..
Distillation with toluol	3.5	..	..	..
H_2O oven, 15 hrs. 95-98° C.				
Residue from fat extraction	3.3	..	4.3	..

[1] These and following results obtained on samples placed in glass stoppered bottles immediately after grinding, and before they reached air dry condition.

GREASE.

	No. 1.		No. 2.	
	Basis original sample. Per cent.	Basis moisture free sample Per cent.	Basis original sample Per cent.	Basis moisture free moisture Per cent.
John Seltzer.				
Moisture free sample extracted 16 hrs	14.1	15.3	8.6	9.3
W. A. Fox.				
Moisture free sample dried 15 hrs., extracted 16 hrs	13.0	14.1	8.0	8.8
Moisture free sample dried 1 hr., extracted 6 hrs	13.2	14.4	8.3	9.1
Moisture free sample dried 1 hr., extracted 16 hrs	13.2	14.4	8.2	9.0
G. A. Riker.				
Moisture free sample	13.5	14.7	8.4	9.2
Original sample	13.6	14.8	8.5	9.3
J. S. Rogers and C. F. Speh.				
Original sample	14.2	14.8	8.9	9.5
	14.3	..	9.3	..
Moisture free sample	14.2	14.5	8.9	9.1
	13.9	..	8.7	..

WATER EXTRACT, NON-TANNINS AND TANNINS.

	No. 1.						No. 2.					
	Solubles.		Non-Tannins.		Tannin.		Solubles.		Non-Tannins.		Tannin.	
	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.
John Seltzer.												
A. L. C. A. method	7.0	7.6	3.7	4.0	3.3	3.6	22.8	24.7	17.2	18.6	5.6	6.1
Bur. Chem. method	8.5	9.2	4.5	4.9	4.0	4.3	24.4	26.5	19.0	20.7	5.4	5.8
G. A. Riker.												
A. L. C. A. method	10.4	11.3	4.1	4.4	6.3	6.9	23.9	26.1	18.5	20.2	5.4	5.9
Bur. Chem. method orig. sample	11.5	12.5	4.4	4.8	7.1	7.7	23.5	25.7	18.7	20.4	4.8	5.5
Bur. Chem. method fat free sample	10.5	11.4	4.1	4.4	6.4	7.0	24.0	26.2	18.5	20.3	5.5	5.9
J. S. Rogers and C. F. Speh.												
A. L. C. A. method orig. sample	8.3	...	4.8	..	3.5	..	25.3	...	19.3	...	6.0	..
	8.3	...	4.5	..	3.8	..	25.3	...	19.4	...	5.9	..
	8.8	8.8	4.6	4.8	4.2	4.0	24.8	26.2	20.0	20.5	4.8	5.7
	8.4	...	4.8	..	3.6	..	24.9	...	19.8	...	5.1	..
A. L. C. A. method fat free sample	9.0	...	4.1	..	4.9	..	24.1	...	19.1	...	5.0	..
	9.0	9.4	4.0	4.2	5.0	5.2	24.0	...	19.1	...	4.9	..
	...	...	..	..	..	..	24.4	25.3	19.3	25.3	5.1	5.2
	...	...	..	..	..	..	24.4	...	19.2	...	5.2	..

WATER EXTRACT, NON-TANNINS AND TANNINS.—Continued.

	No. 1.						No. 2.					
	Solubles.		Non-Tannins.		Tannin.		Solubles.		Non-Tannins.		Tannin.	
	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig. sample. Per cent.	Basis moisture free sample. Per cent.	Basis orig sample. Per cent.	Basis moisture free sample. Per cent.
J. S. Rogers and C. F. Speh. A. L. C. A. method moisture and fat free sample	6.2	...	3.3	..	2.9	..	19.2	...	15.4	...	3.8	..
	6.2	6.5	3.3	3.4	2.9	3.1	19.1	...	16.6	16.8	3.9	3.9
	...	...	..	..	..	..	20.5	20.7	16.8	...	3.6	..
	...	...	..	..	..	..	20.4	...	...	...	..	..
Bur. Chem. method orig. sample	11.0	...	4.0	4.1	7.0	7.3	28.8	...	18.8	...	10.0	..
	11.0	11.4	3.9	..	7.1	..	28.9	30.2	19.0	19.8	9.9	10.4
	11.4	...	4.1	..	7.3	7.6	28.7	...	19.3	...	9.4	..
	11.5	11.9	4.1	4.3	7.4	..	28.8	30.1	19.0	20.0	9.8	10.1
	9.3	9.7	4.3	4.7	5.0	5.0	28.2	29.5	19.3	20.2	8.9	9.3
	9.2	9.5	4.5	4.7	4.7	4.8	28.2	29.5	19.0	20.2	9.2	9.3
Fat free sample	5.7	6.0	3.2	3.3	2.5	2.7	27.3	22.5	19.0	19.9	8.3	8.6
	5.8	6.0	2.9	3.1	2.9	2.9	20.4	27.6	18.7	19.5	7.7	8.1
Moisture and fat free sample	7.5	7.8	4.5	4.7	3.0	3.1	24.6	25.7	17.7	18.6	6.9	7.1
	6.8	7.1	3.4	3.5	3.4	3.6	...	...	...	...	..	..
Moisture free sample	9.9	10.3	4.3	4.5	5.6	5.8	27.8	29.1	18.9	19.7	8.9	9.4
	9.8	10.2	3.9	4.1	5.9	6.1	26.7	27.9	18.0	18.8	8.7	9.1

HIDE SUBSTANCE.

	No. 1.		No. 2.	
	Original. Per cent.	Moisture free. Per cent.	Original. Per cent.	Moisture free. Per cent.
John Seltzer.				
Original sample	37.8	40.9	31.7	34.4
W. A. Fox.				
Original sample	39.77	43.0	32.4	35.3
Fat free sample	38.44	41.6	32.1	35.0
J. S. Rogers & C. F. Speh.				
	41.0	43.3	34.7	35.2
	41.6	..	34.7	..
	41.6	..	34 7	..

COMMENTS OF ANALYSTS.

W. A. Fox.—You will notice that the moisture runs a trifle high by our method (dried one hour in hot air oven at 110° C. and then extracted six hours for fat) and the fat obtained from this leather was higher than that obtained by 15 hours drying, probably due to the oxidation of the fatty oils present by the longer heating, and the fact that the products of oxidation are only partially soluble in petroleum ether. There is practically no difference in the results obtained by six or sixteen hours extraction.

G. A. Riker.—I favor the determination of grease first in preference to the moisture first. I also favor the A. L. C. A. method of water extraction. If moisture is determined before grease, on leather containing considerable quantities of fats and oils, such as belting, upper chrome and harness leather, great difficulty is experienced in determining accurately the moisture and fats because of the fats melting out of the leather and retaining considerable of the moisture in the fatty matter at the bottom of the dish. Also, a great deal of it sticks to the sides and bottom of the dish used in drying the leather. The method I have been pursuing has been to weigh out 15 grams, extract in a Soxhlet with petroleum ether at 50-80° C. to free from grease. Evaporate ether and weigh. Dry the fat free leather at 100° C. for 10 hours, desiccate, cool and weigh. The difference between this weight and the original is the amount of moisture and grease. The difference between the loss of weight after drying and the grease is the moisture. This is the only method I have found to give concordant duplicate results.

Messrs. Rogers and Speh.—We prefer to make moisture, fat and water soluble on original sample, as time and amount of manipulation are decreased.

DISCUSSION OF RESULTS.

The moisture determination on the samples as sent out are fairly good, there being but one result, on sample No. 2, that is decidedly different from the average. The results of Messrs. Rogers and Speh below the line were obtained on the same sample, put in glass stoppered bottles immediately after grinding and before they had returned to normal air dry condition. These results cannot, therefore, be compared with the other results given, but may be considered comparable among themselves. It will be observed that covered dishes give higher results than uncovered and that vacuum-drying at 98-100° gives decidedly higher results than drying in the water oven at normal pressure. Moisture determined after fat extraction is lower than when determined before. It will be observed also that the fat results are lower after determination of moisture than before and also that water soluble material is less when made on samples which have been extracted with petroleum ether and much less when made on samples which have been also dried at 95°. The effect of previous drying on the fat determination is not as great as the effect of previous extraction on the moisture or of previous drying or extraction, or both on water solubles.

Several more or less plausible explanations may be offered for the above-mentioned facts; the results, however, do not warrant theorizing at this time. The water soluble material is most affected by previous treatment of the leather and gives the most discordant results in the tests of the several analysts. It is quite evident, that more work is needed at this point, particularly on greased leather. Of the two methods used this year, that of the Bureau of Chemistry has given, as a rule, the higher results. The increase obtained by this method is largely tannin, which apparently is not destroyed, by boiling the extract as is done by this method. A great deal of work done in this laboratory leaves me firmly of the opinion, that the tannin obtained by this method is not "combined tannin" but is rather the more difficultly soluble tannin, such as is found in all tanning materials.

The results on nitrogen and hide substances are not as concordant as they should be. The question whether nitrogen should be made on the original sample or on the fat free sample, needs investigation.

Summarizing the work, the indications are that, moisture, fat and water solubles each made on the original sample, will probably give the most concordant and accurate results. The error, if it is an error, introduced by making fat after moisture is small, but the difference in water soluble results obtained on original and a dried and extracted sample are certainly too great to pass, and as the indications are that changes in solubility are occasioned by drying or extracting the present association procedure of using the original sample for the water soluble determination should be adhered to, until it is definitely proved to be wrong. The Association's methods for moisture and fat are satisfactory and should be adhered to, though future work should be done with a view to shortening the time of fat extraction.

No work was called for on the determination of ash or glucose. The methods for ash need no further work, though I would recommend that the following be added to the ash method: cool and weigh. The ash may be examined for mineral loading materials, by standard methods.

The present method for glucose is known to give erroneous results, owing to the use of lead sub-acetate. It has been definitely shown that normal lead acetate gives accurate results, and the statement of the method should be corrected accordingly. With this correction made, the method for glucose needs no future work.

RECOMMENDATIONS.

Work on shortening the time of fat extraction.

Work on the extraction of water soluble, with particular reference to the effect of previous heating or treatment with fat solvents on extraction.

Work on the determination of nitrogen in the original and fat free leather.

Add, to the method for ash, the following:—

Cool in desiccator and weigh. The ash may be examined for mineral loading materials by standard methods.

Substitute normal lead acetate for sub-acetate in the method for glucose.

DETERMINATION OF ACIDITY OF TAN LIQUORS.[1]

W. K. Alsop.

The work done by this committee consists principally in testing the method proposed by J. H. Yocum, T. A. Faust and G. A. Riker (this Journal, Vol. 5, No. 6, Pages 292-295).

Their method is a modification of the Gelatine-Hematin one, the radical difference being that the addition of a gum arabic solution to the liquor when precipitating with gelatine is advocated. The claim is made that gallic acid, which may be present in some liquors, is precipitated and that the results will indicate more correctly the "plumping" acids present.

Samples marked No. 1, 2, 3 and 4 were sent out for collaborative work, and were as follows:—

No. 1, strong oak bark liquor.

No. 2, strong oak bark liquor to which had been added 0.5 per cent. of gallic acid.

No. 3, rocker liquor to which had been added 0.5 per cent. gallic acid.

No. 4, identical with No. 3, except that gallic acid was not added.

Some dissatisfaction being expressed as to the character of the samples, three additional ones were sent to collaborators:—

No. 5, liquor containing 50 per cent. or more chestnut to which was added 1 per cent. gallic acid.[2]

No. 6, identical with No. 5, except that gallic acid was not added.

No. 7, 37° barkometer liquor made in the laboratory from chestnut extract.

All the samples except No. 7 were tannery liquors.

The following experiments were asked for:—

"Ridgway, Pa., Aug. 3, 1910.

Dear Sir:—

I am sending you by express 4 samples of liquor and request acid determinations in order to test the Gelatine-Gum

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[1] Report of 1910 Committee.

[2] This percentage was carefully calculated from the tested strength of the acid.

method proposed by John H. Yocum, T. A. Faust and G. A. Riker, which was published in the June 1910 number of our JOURNAL. The results from any other experiments than those outlined will be welcomed.

Solutions Required.—1 per cent. water-gelatine solution; 1 per cent. alcoholic-gelatine solution; 2 per cent. solution of gum arabic; hematine for indicator; standard sodium hydroxide; (10th Normal preferred).

Experiment No. 1.—(a) To 25 cc. of liquor add 50 cc. of water gelatine solution and 25 cc. of gum arabic solution, (these two solutions should be mixed before being added to the liquor). Make up to 250 cc. add 10 grams kaolin, shake, let stand fifteen minutes and pipette 30 cc. of the supernatant liquor for titration.

(b) Repeat, using alcoholic-gelatine solution.

(c) Proceed as in (a) and(b), except omit the gum arabic solution. The titration for these experiments may also be made on a filtered solution, but if this be done, please report results on both unfiltered and filtered solution.

Experiment No. 2.—(a) To 15 cc. of liquor add 50 cc. of water-gelatine solution and 20 cc. of gum arabic solution, (mixing these before adding to liquor). Make up to 200 cc., add about 5 grams of kaolin. Throw on filter and titrate 40 cc. of filtrate.

(b) Proceed as in (a), using an alcoholic solution.

(c) Same as in (a) and (b), omitting addition of gum arabic solution.

Please send full report of results giving cc. of soda used and percentage of acid found. Also please give full expression as to your opinion of this proposed method."

Results are shown in the table expressed in terms of per cent. of acetic acid. No comment on the results shown in the table seems necessary.

Several other matters were referred to this committee, as follows:—

1. Further work on indicators. Nothing has been done in regard to this.

Liquor	Observer	Experiment 1.								Experiment 2.			
		Wat'r Gel. + Gum	Wat's Gel. + Gum filtered	Alc. Gel. + Gum	Alc. Gel. + Gum filtered	Water Gelatine	Water Gelatine filtered	Alcoholic Gelatine	Alc. Gel. filtered	Wat'r Gel. + Gum	Alc. Gel. + Gum	Water Gelatine	Alcoholic Gelatine
No. 1	C. M. Emery	0.72	0.71	0.76	. .	0.74	0.74	0.74	. .	0.64	0.62	0.64	0.64
	L. Balderston	0.76	0.67	0.79	. .	0.74	0.71	0.74	. .	0.68	0.69	0.69	0.68
	W. K. Alsop	0.75	. .	0.78	. .	0.76	. .	0.76	. .	0.68	0.69	0.69	0.72
	T. A. Faust	0.72	0.58	0.74	0.56	0.66	0.68	0.68	0.63	0.53	0.52	0.56	0.59
	Reed & Wisdom	0.78	. .	0.74	. .	0.75	. .	0.77	. .	0.71	0.70	0.78	0.72
	C. R. Oberfell	0.87	. .	0.92	. .	0.81	. .	0.89	. .	0.74	0.79	0.76	0.77
	T. J. Mosser	0.64	. .	0.66	. .	0.76	. .	0.74	. .	0.64	0.66	0.68	0.70
No. 2	C. M. Emery	0.88	0.85	0.89	. .	0.88	0.86	0.88	. .	0.76	0.77	0.74	0.74
	L. Bladerston	0.89	0.80	0.90	. .	0.89	0.87	0.88	. .	0.78	0.79	0.79	0.77
	W. K. Alsop	0.88	. .	0.91	. .	0.90	. .	0.89	. .	0.82	0.84	0.82	0.82
	T. A. Faust	0.90	0.64	0.90	0.66	0.86	0.73	0.87	0.74	0.67	0.70	0.72	0.73
	Reed & Wisdom	0.92	. .	0.91	. .	0.89	. .	0.88	. .	0.83	0.88	0.84	0.84
	C. R. Oberfell	0.99	. .	1.06	. .	1.00	. .	1.07	. .	0.92	0.95	0.90	0.91
	T. J. Mosser	0.76	. .	0.80	. .	0.90	. .	0.90	. .	0.82	0.80	0.82	0.80
No. 3	C. M. Emery	0.60	0.60	0.60	. .	0.68	0.66	0.66	. .	0.52	0.50	0.54	0.55
	L. Balderston	0.61	0.56	0.63	. .	0.65	0.60	0.64	. .	0.55	0.56	0.60	0.60
	W. K. Alsop	0.62	. .	0.62	. .	0.67	. .	0.67	. .	0.55	0.58	0.62	0.60
	T. A. Faust	0.56	0.51	0.57	0.50	0.57	0.50	0.57	0.53	0.52	0.51	0.49	0.50
	Reed & Wisdom	0.60	. .	0.62	. .	0.66	. .	0.63	. .	0.58	0.57	0.66	0.65
	C. R. Oberfell	0.66	. .	0.66	. .	0.67	. .	0.70	. .	0.61	0.61	0.64	0.66
	T. J. Mosser	0.50	. .	0.50	. .	0.64	. .	0.64	. .	0.58	0.60	0.60	0.60
No. 4	C. M. Emery	0.48	0.46	0.48	. .	0.54	0.51	0.51	. .	0.42	0.40	0.46	0.40
	L. Balderston	0.50	0.44	0.50	. .	0.51	0.49	0.50	. .	0.45	0.44	0.46	0.47
	W. K. Alsop	0.51	. .	0.49	. .	0.52	. .	0.51	. .	0.46	0.45	0.48	0.47
	T. A. Faust	0.44	0.38	0.42	0.40	0.44	0.39	0.44	0.40	0.36	0.36	0.38	0.37
	Reed & Wisdom	0.50	. .	0.48	. .	0.52	. .	0.52	. .	0.47	0.46	0.50	0.52
	C. R. Oberfell	0.52	. .	0.52	. .	0.54	. .	0.56	. .	0.50	0.50	0.50	0.54
	T. J. Mosser	0.50	. .	0.50	. .	0.54	. .	0.52	. .	0.46	0.46	0.48	0.50
No. 5	C. M. Emery	0.73	0.70	0.76	0.705	0.735	0.715	0.74	0.715	0.635	0.615	0.64	0.65
	L. Balderston	0.75	0.735	0.78	0.75	0.72	0.73	0.72	0.73	0.62	0.63	0.60	0.67
	T. A. Faust	0.69	0.54	0.75	0.49	0.67	0.63	0.67	0.60	0.55	0.56	0.61	0.61
	Reed & Wisdom	0.76	. .	0.76	. .	0.75	. .	0.745	. .	0.685	0.68	0.66	0.675
	T. J. Mosser	0.82	. .	0.82	. .	0.80	.	0.78	. .	0.70	0.70	0.70	0.70
No. 6	C. M. Emery	0.40	0.39	0.41	0.38	0.415	0.39	0.415	0.385	0.33	0.325	0.33	0.335
	L. Balderston	0.395	0.375	0.445	0.39	0.37	0.37	0.42	0.39	0.325	0.335	0.33	0.31
	T. A. Faust	0.35	0.21	0.37	0.19	0.32	0.27	0.34	0.25	0.20	0.20	0.23	0.25
	Reed & Wisdom	0.42	. .	0.425	. .	0.405	. .	0.40	. .	0.345	0.375	0.345	0.345
	T. J. Mosser	0.42	. .	0.42	. .	0.42	.	0.40	. .	0.36	0.34	0.36	0.34
No. 7	**C. M. Emery**	0.485	0.46	0.485	0.46	0.490	0.475	0.49	0.48	0.345	0.355	0.36	0.36
	L. Balderston	0.465	0.445	0.50	0.52	0.48	0.445	0.46	0.49	0.375	0.405	0.36	0.40
	T. A. Faust	0.46	0.26	0.48	0.30	0.42	0.32	0.43	0.34	0.20	0.18	0.26	0.30
	Reed & Wisdom	0.52	. .	0.525	. .	0.50	. .	0.47	. .	0.365	0.41	0.385	0.395
	T. J. Mosser	0.54	. .	0.52	. .	0.48	. .	0.48	. .	0.42	0.44	0.42	0.42

2. The question of the preservation of liquors and alterations in the method of sampling.

No collaborative work has been done on this subject, but experiments under the direction of the chairman seem to show that under ordinary conditions 0.02 per cent. of thymol, or 0.1 per cent. naphthylamine hold the acid in open vessels for two weeks and do not affect the analyses of the liquors.

3. Measurement of the plumping effect of liquors.

A series of experiments on this subject was carried out under direction of the chairman, but no collaborative work was done, and the results obtained are not yet ready for publication.

Comments on the gelatine-gum acid method by several of the collaborators follow:—

NEWARK, N. J., Aug. 12, 1910.

Mr. Wm. K. Alsop,

Dear Sir:

The results of my titrations lead me to believe that there is very little gallic acid present in these liquors.[1] The liquors gave a green black with ferric alum, showing them to consist principally of catechol tannins which do not form gallic acid.

I am not in favor of titrating the supernatant solutions, as they are always very cloudy, the end point is not clear and results are invariably high. Using the same proportions and filtering, I got very good results, although I do not think 50 cc. of gelatine sufficient for 25 cc. of liquors, Nos. 1 and 2. I believe this is the reason of getting higher results on liquors Nos. 1 and 2 in experiment No. 1, than on the same liquors in experiment No. 2.

On experiment No. 2 I get lower results when using the gum solution, indicating the presence of a slight amount of gallic acid. I ran all experiments with water alcoholic and denatured alcoholic gelatine solutions and found the variations within the limit of error.

Personally, I favor using the denatured alcoholic gelatine so-

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[1] The first four.

lutions on account of its being less expensive than the grain alcohol and not as liable to decomposition as is the water gelatine.

In liquors where gallic acid is present, I am firmly convinced that the addition of gum to the gelatine will effect the removal of the gallic acid which the gelatine alone only partially removes. I believe that by the gelatine-gum filtration method, only the plumping acids are reported, and are the acids which the tanner desires to know of.

T. A. FAUST.

NEWARK, N. J. Sept. 3, 1910.

Under date of September 3d, Mr. John H. Yocum reports the results of some experiments on the effect of gum arabic in precipitating gallic acid. He reports that gallic acid which has been repeatedly re-crystallized from water is much more completely precipitated by gelatine and gum than is the acid as obtained from the dealers. He thinks that this indicates the presence of impurities and decomposition products in the C. P. gallic acid of the manufacturing chemist.

He also found that the alcoholic gelatine-gum solution precipitated gallic acid better than the solution made wholly with water, and that if the liquor was shaken for ten minutes after the addition of the gelatine and gum, the precipitation was more complete.

In order to avoid the loss of acid caused by absorption on the part of the filter-paper, he suggests that the first part of the filtrate be thrown away.

He notes that because of the much greater solubility of gallic acid in hot than in cold water, the quantity of gallic acid present in a saturated solution is very different for solutions of different temperatures.

STAMFORD, CONN.

MR. W. K. ALSOP, Chairman Acid Committee,
Ridgway, Penna.

DEAR SIR:—Enclosed you will find results upon the Gelatine-

Gum method for determining the acidity of tan liquors, as per your request by communication of August 3d.

Commenting upon the results as shown in the table we would say that by Experiment No. 1, there is apparently no difference of any moment between determinations made with or without the presence of gum. In the case of Experiment No. 2, where the solutions are filtered, there seems to be a slight reduction in the acidity found with liquors Nos. 1, 3 and 4, where gum is present and more notably in liquor No. 3.

Some tests that may be of interest, were run upon a solution of gallic acid.

Gallic acid Solution.

	Cc. N/10 soda.
Titrated without addition of gelatine or gum	2.8
Titrated after addition of 50 cc. water-gelatine kaolin and filtering	2.2
Titrated after addition of 50 cc. alcoholic gelatine kaolin and filtering	2.2
Titrated after addition of 50 cc. water-gelatine 25 cc. gum, kaolin and filtering	1.9
Titrated after addition of 50 cc. alcoholic-gelatine 25 cc. gum, kaolin and filtering	1.9

From these tests it appears that the gelatine solution itself throws out a certain amount of gallic acid and that the addition of gum throws out but little more than gelatine alone. As the tests were run by diluting the solutions immediately after the addition of the gelatine and gum, tests were run to ascertain whether by standing for some time prior to dilution and filtering a greater precipitation of gallic acid would result.

Gallic Acid Solution.

Allowed to stand one hour before dilution and filtering.

	Cc. N/10 soda.
Water gelatine only	2.2
Water gelatine plus 25 cc. gum solution	1.8
Water gelatine plus 50 cc. gum solution	2.0
Water gelatine plus 75 cc. gum solution	2.0

It would appear from this that not only does standing produce little, if any, further precipitation of gallic acid, but that the addition of more gum solution tends rather to a re-solution of the gallic acid.

It is our opinion that the precipitation of gallic acid in the presence of gum is to some considerable extent dependent upon the concentrations of the solutions and the relative proportions of gallic acid, gelatine and gum. It seems certain from our results, that these relative proportions as prescribed by Experiments Nos. 1 and 2, are not so adjusted as to throw out the gallic acid in anything but an approximation of the total quantity present.

The original article proposing the Gum-Gelatine method (JOURNAL A. L. C. A., Vol. V, No. 6, p. 295) does not specify that the gelatine and gum solutions should be mixed before adding to the tan liquor. Thinking that perhaps the addition of the gelatine solution to the liquor, followed by the gum solution might produce results other than those from following the method suggested by the Chairman, we tested the four samples of liquor using water-gelatine solution, which was added before the gum solution. The experiments were conducted otherwise as in the Chairman's Experiment No. 2, which we note to be exactly similar to the method originally proposed (see reference above) with the possible exception noted. Our results were as follows:

TABLE II.

	Liquor No. 1		Liquor No. 2		Liquor No. 3		Liquor No. 4	
	cc. N/10 Soda	% Acid	cc. N/10 Soda	% Acid	cc. N/10 Soda	% Acid	cc. N/10 Soda	% Acid
Water-gelatine	3.4	0.68	4.15	0.85	3.1	0.62	2.35	0.47
Water, gelatine and gum	3.4	0.68	4.2	0.84	2.75	0.55	2.2	0.44

It would appear from the results that the addition of the gum solution after the gelatine solution throws out no more gallic acid than by the method as proposed by the Chairman.

We hesitate to condemn the method without further trial than the limited time permits, and believe that further investigation should be made.

Yours very truly,

H. C. REED,
R. H. WISDOM,

HARRISONBURG, VA., Aug. 13, 1910.

MR. W. K. ALSOP,
Ridgway, Pa.

DEAR SIR:—

Enclosed are acid results on samples recently received from you.

I have had no opportunity to make a study of the chemistry involved. If there is a question on gallic acid being precipitated by gelatine in the presence of a gum I can not see how the work prescribed for the committee will clear up this point. Assuming that lower percentages of acid are found, on these samples which you sent out, by the Gelatine-Gum method, how does this prove that the difference is gallic acid *not determined?* To determine this point would require some very painstaking and accurate scientific work; mere comparison will surely not do it.

I have used the Water-Gelatine method on hundreds of samples with satisfactory results, but I do not use the same amount of gelatine solution on every liquor regardless of the amount of tannic acid it contains. For this reason I find fault with Experiment No. 2; the ratio of liquor to gelatine solution, *i.e.*, 15: 50 is entirely too great in the case of the weaker liquors. Since a constant volume of liquor is used in both methods, and as the gelatine solution is added to precipitate the tannic acid I can see no argument in favor of using the same quantity of gelatine solution for a liquor which contains 4.50 per cent. of tannin as for one containing but 1.00 per cent.

I trust my results will be in agreement with your own and other members of the committee.

Yours very truly,

CHARLES R. OBERFELL.

P. S.—As to the end-point on the titrations of which results are enclosed; I always, when using hematine, carry the titration along until I get fully developed coloration.—C. R. O.

NEWBERRY, PA., Aug. 17, 1910.

MR. W. K. ALSOP,
Ridgway, Pa.

DEAR SIR:—

Enclosed find report of work done on the Acid Committee

In regard to the gum method I would not like to express any opinion on the merits as claimed for it until I had tried it on liquors whose effects have been observed under tannery conditions. It seems to give lower results on several of the sample liquors. The working of the method presents some difficulties in that precipitate does not settle as readily as in the alcoholic or water-gelatine method: in fact it was impossible in the case of liquors 1 to 2 to get anything like a clear solution either by settling or filtration.

I hope to do some more work on this method before the convention and will then be better able to give a more intelligent opinion.

Yours truly,

THOS. J. MOSSER.

RIDGWAY, PA., Sept. 6, 1910.

In addition to the work whose results are shown in the table, page 436, several other experiments were tried in this laboratory on the gelatine-gum method. Two samples of gum arabic were tried. One gave a neutral solution, the other slightly acid. After neutralizing the latter, the two were compared in precipitating gallic acid and gave identical results. The effect of adding the gelatine and gum separately and mixed was also tested out, and the results found to be identical.

A solution was made up with 5 grams gallic acid, C. P. (E. and A.) to 500 cc. of water. Gallic acid has a molecular weight of 170, and one molecule of water of crystallization. Assuming that the acid is really C. P., this would give 4.52 grams of acid to 505 grams of solution, almost exactly 0.9 per cent. A blank was run by taking 25 cc. of this solution, filling up to 250 cc., adding 10 grams of kaolin and filtering. 30 cc. of the filtrate took 1.5, 1.4, 1.5. 1.5 cc. tenth normal soda. This corresponds to 0.295 per cent. acid (as acetic), or 0.836 per cent. as gallic.

Other 25 cc. samples were treated with 50 cc. water-gelatine, 50 cc. alcoholic-gelatine, 50 cc. water-gelatine plus 25 cc. gum solution and 50 cc. alcoholic-gelatine plus 25 cc. gum solution.

Another solution was made up of equal parts of the 0.9 per cent. gallic acid solution and a 2 per cent. solution of tannic acid, and a third one was a 2 per cent. solution of tannic acid. Both of these were treated with water-gelatine, with and without gum, in the same manner as the gallic acid alone. The results are shown in the table, in which values are given as per cent. of gallic acid.

	Water-gelatine not filtered	Water-gelatine filtered	Water-gelatine and gum not filtered	Water-gelatine and gum filtered	Alcoholic-gelatine filtered	Alcohol gelatine and gum filtered	Blank not filtered	Blank filtered
Gallic acid solution..	0.79	0.76	0.62	0.62	0.72	0.64	——	0.84
Gallic & tannic acid.	0.56	0.51	0.51	0.46	——	——	0.75	0.66
Tannic acid.........	0.37	0.28	0.35	0.21	——	——	——	——

The tannic acid evidently contains some gallic acid. In the mixed solution we have in effect ½ per cent. gallic and 1 per cent. tannic acid. The sum of one-half of 0.79 and one-half of 0.37 is not very far from 0.56 (see first column of table). It would seem that gelatine alone throws out a part of the gallic acid, and filtration, (through Swedish paper), throws out an additional part.

The gum seems to be responsible for throwing out from a fourth to a tenth part of the gallic acid present, and does not work perceptibly better in the presence of tannic acid than in its absence.

An average of all the values in the table (page 436) for liquor No. 5, taken by method 1 without gum and unfiltered, is 0.733 per cent. An average taken in the same manner for No. 6 is 0.391 per cent., giving a difference of 0.342 per cent. The actual difference between these liquors was 1 per cent. of gallic acid, whose acidity is equal to 0.333 per cent. of acetic acid. An average of No. 5 by method 1 with gum unfiltered is 0.762 per cent., nearly 0.03 per cent. higher than without the gum. The average value for this liquor by method No. 1 filtered without gum is 0.687 per cent., and with gum 0.653 per cent., the difference (0.034 per cent.) being about one-tenth of the gallic acid.

An average of all the values for the acidity of No. 5, by method 2, without gum, is 0.652 per cent. With gum the average is 0.637 per cent., a difference of 0.015 per cent., about one-twentieth the amount of gallic acid actually present.

Taking the results altogether, it appears to me that the claims made for the gelatine-gum method are thus far not proven.

It will be observed that in the table (page 436), the acid values obtained by all the collaborators are less by the second method than by the first, in which a larger quantity of liquor is taken. In order to test which of the two methods gives nearer the true result, two experiments were tried.

First, three 25 cc. samples of liquor No. 1, were taken and quantities of soda sufficient to neutralize 0.75, 0.80, and 0.85 per cent. of acetic acid, respectively, were added to them. In like manner to three samples of No. 4 quantities sufficient to neutralize, 0.50, 0.55 and 0.60 per cent. were added. The six samples were then diluted to 100 cc. and 80 cc. distilled over. The distillates from liquor No. 1 took 2.35, 1.85 and 1.30 cc. tenth normal soda to neutralize them, indicating that the acidity was in excess of 0.85 per cent., as Mr. Oberfell found it. Liquor No. 4 seemed to have at least 0.55 per cent.[1]

The second experiment was tried with liquor No. 4. To 50 cc. of this liquor 50 cc. of gelatine were added and diluted to 250 cc. This was filtered, 30 cc. of the filtrate titrated and 150 cc. distilled. After 135 cc. had come over, the residue was made up to 115 cc. and 100 cc. distilled over. The three distillates took 11.7, 4.1 and 1.5 cc. of tenth normal soda, giving a total for volatile acid in terms of acetic of 0.34 per cent. The residue showed 0.15 per cent. acid, making a total acidity of 0.49 per cent. The titration of 30 cc. of the filtrate gave 0.50 per cent. This would certainly seem to show that 0.50 per cent. is more nearly correct for liquor No. 4 than 0.38 per cent.

The second experiment was also tried with liquor No. 7. In this case the first two distillates took 2.8 and 0.5 cc. respectively, and it did not seem worth while to carry it any further. These two added give a volatile acidity of 0.066 per cent. The residue gave 0.42 per cent., and the total acidity shown in the filtered liquor was 0.50 per cent. The 0.42 per cent. non-volatile could hardly be lactic acid, and if it is gallic acid, certainly not nearly all of it is thrown out by the gelatine-gum method in the hands of any of the collaborators.

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[1] This experiment is based on the belief, supported by a number of careful experiments, that when alkali is added slowly to liquors containing volatile and non-volatile acids, the non-volatile are neutralized first; so that if nearly all the acid is neutralized, the remaining acidity is all due to volatile acid.

It is certainly surprising that the results for filtered and unfiltered liquors should be so widely different in the work of some of the collaborators. In the work done in this laboratory the paper used was Munktells No. 1 F., and in the case of most liquors the acid was not reduced by filtration more than 0.05 per cent.

Certainly the most obvious conclusion from a study of the table of results on page 436 is that we need a better method of determining total acidity than any now in use.

L. BALDERSTON.

NEWBERRY PA., Sept. 10, 1910.

W. K. Alsop,
Ridgway, Pa.,

DEAR SIR:—

Enclosed please find reports on liquors Nos. 5, 6, 7.

The gelatine-gum method does not seem to eliminate the gallic acid as is claimed for it. Furthermore it was almost impossible to obtain a clear solution for titration either by filtration or settling. It does not seem right to me to filter with any method as there is some absorption of acid by the paper. In experiment No. 2 Swedish 1 F paper was used and in experiment No. 3 Prat and Dumas white paper and in both cases absorption of acid is shown, the latter showing the more.

	Water-gelatine + gum Swedish	Water-gelatine + gum Prat-Dumas	Alc.-gelatine + gum Swedish	Alc.-gelatine + gum Prat-Dumas	Water-gelatine Swedish	Water-gelatine Prat-Dumas	Alc.-gelatine Swedish	Alc.-gelatine Prat-Dumas
Liquor 5....	0.70	0.66	0.70	0.68	0.70	0.68	0.70	0.68
Liquor 6....	0.36	0.32	0.34	0.30	0.36	0.30	0.34	0.32
Liquor 7....	0.42	0.36	0.44	0.38	0.42	0.38	0.42	0.38

I also have done some work on the fluoresceine method published by Seymour-Jones using these same liquors and found that it was not as ideal as one would suppose from reading the article. The fluorescence appears soon after beginning to add the alkali and continues to become more intense until a maximum is reached.

The following are the results obtained, the minimum figures are those for the first appearance of fluorescence and the maximum the final end point.

Liquor 5		Liquor 6		Liquor 7	
Min. per cent.	Max. per cent.	Min. per cent.	Max. per cent.	Min. per cent.	Max. per cent.
0.24	0.90	0.15	0.48	0.24	0.69

Yours truly,

THOS. J. MOSSER.

THE PRINCIPLES OF TANNING[1]

By Dr. J. Gordon Parker.

Innumerable new methods have been proposed and patents have been taken out during the last century for the acceleration and improvement in tanning leather, mostly by those but remotely connected with the trade. In spite of this the general outline in process of tanning sole leather is much the same to-day as carried out a thousand years ago. In short the changes which have taken place between the tanning of sole leather even 1000 years ago and to-day consist not so much in principle as in a more intelligent method of carrying out the process.

The raw material for the British tanner is the hide of oxen and cows, and is drawn from practically all parts of the globe. From the Argentine, Uruguay, China, and Africa come hides which have been dried in the sun; from America, from all parts of Europe and the Colonies, come hides in what is known as the salted condition—the hides are piled, a sprinkling of salt between each, and gradually the salt draws out the water, becomes dissolved, and diffuses into the interior. After lying in pile for some time, the excess water is thrown off, and the hides are re-salted; in this condition they frequently contain as much as 30 per cent. of salt on the original weight of the hide. From the home market the hides are usually obtained "green" or "fresh." The first process, therefore, is the soaking and cleansing to soften the fibres, remove extraneous matters, salt, blood, dirt, etc., and to bring the hide back to its natural state. In bygone days this was done by suspending the hides in a running stream by the tan-yard, but now the common custom is to soak the

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[1] From the *Journal of the Society of Chemical Industry*, Aug. 15, 1910.

hides in pits containing water. The hides are usually given a change of one or two waters; salted hides receive a longer treatment and several changes of water until moderately free from salt; dried hides are, after a preliminary soaking, some times "stocked" or "milled," in a large machine which pummels the hide and gradually breaks up the fibres, after which the hides are returned to the water. Revolving drums and other similar appliances are also used. The softening of flint dried hides is by no means an easy operation and considerable care must be exercised in bringing the hide back to its natural condition without loss of pelt substance through putrefaction, the germs of which are present in the hide. With some hides it is difficult to soften in less than six to eight days, and to aid in the softening process sulphide of sodium, or caustic soda is often added to the soak water. These materials have a swelling effect which accelerates the penetration of the water, and the subsequent softening of the fibres, but at the same time they slightly increase the solubility of the hide. It has been shown that the higher the temperature at which the hides are dried for preservation in foreign countries, the more difficult becomes the subsequent absorption of water, and consequent softening in the tan-yard. It is very essential that hides should not only be thoroughly softened but they should be in a clean state before passing to the next process. The English tanner has a great fear of losing pelt substance by using too much water at this stage; but it is undoubtedly wrong to leave hides in a foul dirty water, and the more clean water they have the less is the loss of pelt substance. I was very much struck some three years ago when visiting the large tanneries in the United States, to note the efficient way in which their process of soaking was carried out, no hides being allowed to pass on to the next process without at least three changes of water, to which sometimes a half hour's running in a revolving drum was added. The pelt looked much healthier, there was no loss of pelt substance, and the hide gave a better leather, owing to the fibres being more open, and better prepared for the subsequent process.

The hides are placed in a saturated solution of lime containing lime in excess for the purpose of loosening the hair and swelling the hide. This process lasts from 7 to 10 days. The hides are laid flat one upon another in a pit containing the necessary amount of water to which slaked lime is added in the proportion of 8 lb. per hide. Formerly it was believed that the lime swelled the fibres of the hide, dissolving the hair bulb or root and loosening the epidermis, thus rendering the removal of the hair easy; but the liming process is now known to be both chemical and physical, the loosening of the hair being largely due to the action of enzymes, and the products of bacteriological action. Hides cannot be unhaired by sterile lime, so that the process of Payne and Pullman by which the hides were first soaked in caustic soda and afterwards in calcium chloride, so as to form lime within the fibres, was unworkable unless preceded by the soaking of the hides in a foul soak to obtain the necessary bacteriological action. By the action of lime on hides other products are formed, salts of amino acids and compound amines which play a vital part in the loosening of the hair and in their turn act upon the hide and influence the quality of the resultant pelt. The longer a lime pit is used, the more alkaline it becomes, the quicker the loosening of the hair, the greater the loss of good hide substance by solution, and the more flaccid the resulting product. Hides in the lime are frequently hauled, the lime pit thoroughly plunged up in order to keep it up to strength of saturation, the hides returned, and the process repeated until they are ready for unhairing.

The scientific control of the liming process deserves far more attention than it has hitherto obtained, for in this process, to use an old tanner's expression—"the leather is made or marred." At a well known tannery some months ago I found that from one of the pits over 24 lb. of dissolved hide substance was going down the drain each time a "lime" was run off. Assuming that even only 50 per cent. of this loss could have been avoided, this would be equal to 12 lb. of dry hide substance (no unimportant matter with wet hides at 6½d. per lb.) which in the ordinary course of events would have produced 24 lb. of leather. If leather trades' chemists had given as much attention, time and thought, to this part of the process as they have to the vexed question of the method of analysis, it would have been more beneficial to our industry. Sodium and calcium sulphides are now becoming more largely used in conjunction with lime. These have an accelerating action on the process and are claimed to improve the results both in weight and firmness of texture. They have however, a destructive action on the hair, reduce the value of the flesh and require considerably more care and control, otherwise more serious losses may result than with lime alone.

After the hides have been properly limed the hair is removed; either by hand or by machines. The most satisfactory machines consist of a revolving spiral roller which travels over the hides as they rest upon a rubber bed, which yields to the pressure as it is increased and thus avoids damage. The reverse side of the hide is then freed from superfluous flesh, consisting of a thin network of coarse fibres heavily loaded with fat. This is removed on a similar shaped beam, the knife in this case being kept sharp. This by-product, together with the hide trimmings, including the nose, ears, shanks, tail, etc., form the raw material for the manufacture of glue and gelatine. The hide in this condition now becomes known as pelt, and on the pelt weight the tanner bases his calculations as to value and the probable yield in leather; he is also able to judge its quality, the fineness of the grain, etc. It is now customary to divide up the hide into "butt" or "back," shoulder and belly, a process known as "rounding." The back is the thickest and most valuable part, used altogether for the heavy soles of boots, belting and harness; the shoulder, being somewhat thinner, is used for light boots, and ladies' shoes; while the belly is of a porous nature and is used chiefly for stiffeners, heels, insoles, and sometimes even for the outer soles of the cheaper class of slippers and boots. This rounding process requires great skill and judgment to determine what size to cut the different parts, which is regulated by the growth and character of the hide. As a general rule hides should yield 50 per cent. of their pelt weight in butt, 24 per cent. of shoulder and head and 26 per cent. of belly. Some well-grown hides from the Scotch and Hereford cattle yield 51 to 52 per cent. of butt and from best Italian hides a higher percentage is sometimes obtained. The "pelt" or rounding table weights are important, for if the liming process has been regular the tanner can gauge at this stage whether his hides have been honestly weighed and well bought, which is difficult to judge in the salted or dry condition, and whether the grain is of good, smooth texture. From these weights the tanner calculates that he should obtain 72 per cent. of finished leather from the weight of butt pelt, 52 per cent. from that of the bellies and 54 per cent. from that of the shoulder, giving a total weight in leather from the green hide of some 56 to 60 per cent. These percentages vary with different classes of tannage.

The weighed and trimmed pelt is in a swollen condition; for the lime has not only swelled the hide and opened the fibres, but also made it firm and rubbery. As a general rule the pelt contains from 2½ to 3 per cent. of lime. Before entering the tan-yard proper a large proportion of the bulk of this lime must be removed and the swelling caused by the alkalinity of the lime must be reduced, otherwise a harsh, brittle, brown, blotchy colored leather would result. Thirty years ago, or even less, tanners used to rely upon the acid early tan-yard liquors to do the necessary deliming, but investigation has shown that if the liquors in the early process of tanning are too weak and contain an excess of acid, not only is the lime removed from the pelt, but pelt substance is dissolved in the form of soluble leather. It is now known to be not only safer and better, but also cheaper, to delime the pelt in a weak solution of boric or one or other of the organic acids, lactic or formic being in most common use. The pelts are suspended on poles by means of strings in a pit containing water to which the requisite amount of acid has been added. They are handled frequently to insure regularity of action or kept in continual movement by mechanical means. The deliming is for sole leather never quite complete, a trace of lime is always left in the interior of the hide, and it is usually sufficient if the hides, on leaving the deliming pit, show no pink color to phenolphthalein when a few drops are sprinkled on the surface. After a rinse through soft water, the butts, bellies and shoulders are ready for the tan-yard.

Formerly the hides for sole leather were tanned whole without rounding, and, after coloring from six to twelve weeks in weak sour liquors made from oak bark and water, were frequently handled and moved forward from time to time into liquors of gradually increasing strength. After this coloring process, the bottom of a deep pit or vat was covered with a layer of ground oak bark, and the first hide was spread out on it, grain upwards, the head and flanks turned in. This in its turn was covered with a layer of bark, another hide on top and a further layer of bark and so on, hide and bark alternating until the pit was full. Water was then pumped in to saturate the bark, and the hides were left for about two months; after which the liquor was pumped off and used to supply the coloring pits. The hides were then raised, freed from the adhering bark, and then laid in a fresh pit for a longer period with more bark and this process repeated four or five times, each time increasing the quantity of bark between each hide and the length of time of laying away, and as the hides got older, bark liquor was pumped on the dry bark instead of water and frequently a little ground valonia was mixed with the oak bark in the last layer. The hides, after from 18 months to two years, being considered tanned, were removed, rinsed through liquor or brushed to remove adhering bark, allowed to drip for a couple of days, oiled on the grain, hung up in the lofts to dry and when nearly dry laid on a wooden, rounded beam or a hollowed stone bed and hammered to flatten out the leather and render it firm. Finally they were completely dried and were ready for the bootmaker who in those days bought the hide in its whole state. The strongest liquor in the tan-yard probably never exceeded 1.030° specific gravity or 30° Bk. containing perhaps at most 2 per cent. to 3 per cent. of tan. How different are present conditions, where the strongest liquor in a modern tan-yard often contains from 14 to 16 per cent. of tannic acid, and has a density of from 130 to 150° Bk! Then an ox-hide of 80 lb. weight yielded about 30 lb. of finished leather; to-day from a similar hide a yield of close upon 50 lb. weight is obtained, which even the severest critics must still call honestly tanned leather.

With the introduction of new materials, and the gradual substitution of machinery for hand labor, the old process above described has been gradually altered.

Among the newer materials which have come into use during the past century, valonia, the acorn cup of the Turkish oak, must be the first mentioned. Although introduced into this country at an earlier period, it is only in the early forties that it began to be used in other than experimental lots to blend with oak bark; its more extended use was chiefly due to the enterprise of some West of England tanners, who having allowed a shipper to store a large quantity of this material in their bark barns until it could be sold, had permission to use what they required in their process. Using a little at a time in more or less homeopathic doses they found that not only did its use do no harm to their leather, but it actually improved it and made it firmer and more solid. With further experience came more confidence so that a larger proportion of this material was blended with the oak bark, and still the leather appeared to improve, until the whole of the shipment of over 200 tons were used and they became regular buyers. Other tanners in the district followed suit, until in the seventies, Bristol or West of England leather, chiefly tanned with valonia, had achieved a reputation for solid hard wear, especially suitable for heavy walking boots and for repairs. It was not long before tanners all over England commenced to blend with this material.

Myrobalans (often miscalled myrabolams), the fruit of the "*Terminalia chebula*," one of the Indian forest trees, which had been used by the native tanners of India for many years, soon found favor when introduced because of its power of rapid penetration, the light color which it imparted to the leather, and its somewhat rapid souring properties.

"Terra Japonica," or gambier, was early used for the purpose of modifying the sharpness or astringency of valonia, and in West of England tannage played an important role in the early tanning stages; its special characteristic was its swelling powers, thus keeping the texture of the hides open and nullifying the contracting action of the stronger tans.

Acacia bark (mimosa) from Australia and South Africa, dividivi from India, algarobilla from South America, all of them containing over three times as much tannin as does oak bark, had a considerable influence upon the changes that have taken place. Reference has been made above to the heavy layer of bark between each hide; this was afterwards burnt or thrown away half spent, but with stronger and better tanning materials in use, it became general to put this dusting material into large pits, called leaches, lecks and spenders, in which the tannin of the bark was extracted by means of water. These leaching pits were arranged in series and the liquor pumped from one pit to the other, until by passing through successive pits of partly spent material it gained sufficient strength for use in saturating the bark between the hides, producing liquors of much greater tanning strength.

The introduction of Tanning Extract in the early seventies, however, had more effect on the method of tanning than anything else. It was first introduced from France made from chestnut wood, and later from Hungary produced from oak wood. In the manufacture of this material, the wood is reduced to fine shreds by powerful machinery and the rasped wood is afterwards extracted in large wooden vats by the aid of hot water. The resulting liquor is decolorized by means of blood which is added to the cooled l'quor; the temperature is then raised and the coagulated albumen separating out carries with it the dark red coloring matter of the bark together with some of the tan. The clarified liquor is then concentrated in large copper vacuum pans at a comparatively low temperature, and shipped to England in concentrated form in casks containing upwards of 30 per cent. of soluble tannin ready for immediate use, for blending in with the tanner's leach liquors.

The effect of these stronger liquors was that the thin part of hide which had hitherto been tanned in one piece, became too much tanned before the thick part had had sufficient tan, with the result that "rounding" became more general. This brought about a great change; and square pits sunk in the ground became general. These were half filled with liquor of the required strength, a butt thrown in and before it had time to sink in the liquor was sprinkled with a layer of bark, a second butt quickly following to be likewise sprinkled, and so on until the pit was full. By this means a greater volume of liquor was used than bark, and as the butts became older and more tanned they passed to stronger liquors and were dusted more heavily with valonia, myrobalans and mimosa bark, instead of oak. With the use of liquors of increasing strengths came an increased yield of leather as the fibres became saturated with stronger tan. Machines began to supersede hand labor, and machines for rolling the leather instead of hammering came into general use, followed by others for scouring, stretching, and polishing the leather. Boot manufacturers began to demand an article of better finish and appearance, smooth grained and flat. For the modern boot manufacturer, the leather must be prepared flat and smooth so that it will pass with ease through his sole cutting machinery and it must be of such a quality that it can be stitched direct by machine without soaking and without the aid of the cobblers' awl.

To return now to the delimed properly prepared pelt. The butts enter the suspender pits. These are a series of deep vats containing old weak liquor graduated in strength. In these the butts are hung on poles, being frequently handled to insure regular coloring and to accelerate the tannage, moved forward to stronger liquors once or twice daily, while in some yards it is customary to have these pits connected by a pipe from the top of the strongest pits to the bottom of the vat next lower in strength; by this means the liquor may be caused gradually to flow from the strongest to the weakest to replace the tan absorbed by the "hungry" hide. Mechanical means are also employed to rock the goods. In this process, which lasts from one to two weeks, the butts absorb tannin with great rapidity, some 50 per cent. to 60 per cent. of the total tannage taking place at this stage. The butts are then taken off the poles, and laid flat in pits containing liquor, which are called "handler pits," as the butts are here handled daily from one pit to another, into a liquor of greater strength; they remain in these for about four weeks. This early stage is almost the most important in the tanning process proper, as it is here that the color, substance and to a large degree also, the quality of the leather is made. The liquors in the handlers and suspenders must also not only be graduated so as to contain the requisite amount of tan to keep the pelt constantly feeding, but there must be the necessary amount of organic or mineral acid to swell and keep the pelt open, and so counteract the natural astringency of the tannic acid. If the pelt is not kept open at this stage and becomes contracted, it can never be recovered, and does not take up the normal amount of tannin, producing a thin, poor leather. The blending of the materials is also of great importance; at this stage considerable amounts of myrobalans, gambier and other light colored plumping materials are used. When the butts leave the handler, they are usually "struck through," *i.e.*, penetrated to the center, and about 80 per cent. of the total tannage has been completed in the first six or seven weeks.

The butts are then taken to a series of pits known as "dusters" or "layers." These pits contain fresh, strong and more astringent liquors. The butts are laid flat in these pits and between each butt as it is thrown in is sprinkled a layer of tanning material, some 3 or 4 cwt. of the dry ground material being sprinkled in between say 100 butts, which generally forms a pack. The butts are allowed to lie in the first liquor for about a week, again lifted and placed in a still stronger liquor for a second week, once more lifted and the process repeated, each time increasing the strength of the liquor and increasing the time in the layer, with a corresponding increase of tanning material dusted between each butt. In early dusters or layers, myrobalans and bark are used, but as the goods get older, ground valonia is substituted, until in the last layer the goods are left from 4 to 5 weeks. Thus they receive a total tannage of about six months, which is an average time for modern better class sole leather and strikes a happy medium between the 12 to 14 months still taken by the oak bark tanner and the three months or less required when a large proportion of tanning extract is used and no oak bark. In these layers the actual tanning which takes place is comparatively small when one takes the long time into consideration, but the goods gain greatly in firmness and solidity; in these pits the leather comes directly in contact with the fresh tanning material and from the fresh tanning liquors is deposited bloom or ellagic acid which is an almost insoluble product produced by the splitting up of the pyrogallol tannin; from the catechol tans, difficultly soluble anhydrides, which are of a gummy and more or less sticky nature, also deposit. This deposition occurs on and in the fibres and in the interstices of the leather and it is to the deposition of these difficultly soluble products that the resulting sole leather to a large extent owes its water-resisting characteristics, and its firm and solid nature. Leather which has been largely tanned by suspension with continuous handling or even drumming never possesses this water-resisting, hard-wearing, characteristic, as no time is given in these tanning processes for the deposition of these more or less insoluble matters, nor for the subsequent complicated changes which normally occur in the interior of the butt.

The material which has been used for strewing between the butts in the layers is put on to the leaches to be thoroughly spent and plays a very important part in the production of the liquors. Many tanners, however, use this half-spent material to produce the liquors necessary for tanning bellies and shoulders, retaining the fresh material for making butt liquors, the butts being the most important part of the hide, having a value almost double that the shoulders and bellies. The tannage of shoulders and bellies follow on in a similar manner to the butts, the only difference being that as this pelt is much thinner; and in the case of the bellies more porous and open, the time for tanning the shoulders seldom exceeds three to four months, and for bellies nine to twelve weeks. The strengths of the liquors are nearly as high as those given to the butts but generally a blend of somewhat cheaper material is used; in other words, less valonia and a higher proportion of myrobalans and chestnut extract.

Among the points that specially require attention and chemical control is the ratio of tans to non-tans in the early liquors, *i.e.*, the ratio in which the tannic acid exists in proportion to the natural acids formed partly by hydrolysis of tannins and partly by fermentation of the glucoses ever present in all tanning materials. If the early liquors are allowed to become too weak, stale or putrid, the pelt, instead of feeding and plumping, begins to fall, the grain becomes loose, and a pipy, flabby leather is produced; but if the liquor is allowed to become too astringent with tannic acid with an insufficiency of the natural organic acids (produced by ferments), the leather will become harsh and brittle, and when finished is liable to be hard, to crack on the grain, and to be generally of bad color. The speed of tannage should be controlled regularly by taking small samples of the half-tanned leather as it leaves the head suspender, and again on leaving the top handler, determining the nitrogen in it by Kjeldahl's method. In this way the progress of the tanning may be accurately checked. New blends of material can thus be tried, additions of special materials at this stage can be accurately tested without waiting six or seven months before the result can be ascertained on the finished goods. The nature of the layer liquors, which are subsequently used to make the handler and suspender liquors, must be examined, as also the leaching and extracting of the material. Whereas samples of the so-called spent tanning material from 22 of the larger tanneries in Great Britain, taken some 17 years ago, jointly with Professor Procter of Leeds, showed that over one-third of the available tannin in the material was being wasted and thrown away, recent analyses show that this waste has been reduced in many cases to below 5 per cent. It has been proved that the tannin contained in most tanning materials is not all readily soluble in cold water, and that each material appears to possess a special leaching temperature, at which the best yield of tannin is obtained. In most of the tanning materials this temperature is at least 80° C.; hence most tanners use hot water for the extraction of their tanning material.

The question of the water is of vital importance to a sole leather tanner. In a large sole leather tannery 5000 gallons of water in 24 hours is not by any means excessive. The average "hardness" of the water in the chief tanning districts of England is about 20 parts per hundred thousand. This means on 5000 gallons of water, that each day the tanner is adding 10 lb. of lime in the form of chalk to his liquors, which unites with tannin and forms useless tannate of lime, which is lost in the leaches and in the liquors. By forming insoluble products in the fibre of the tanning material it retards the extraction and diffusion of the tannic acid through the cell walls in which the tannin is contained; it also darkens the color of the liquors and has a material effect upon the resulting leather, as it is well known that salts of tannic acid become oxidized and rapidly form dark compounds.

The drying and finishing of sole leatther, as I have already indicated, was formerly simply a process of drying and hammering; to-day the shedwork of sole leather is almost a separate art, and there has grown up a body of journeymen finishers specially skilled in this process, which requires from three to six weeks, depending upon the period of the year. The butts are taken from the last layer and after lying in pile for two to three days to drip (during this dripping process the strong tan tends to solidify, and the butts become firmer and more solid). they have scoured on the grain side by hand or machine with stone blades and brushes. The object of this scouring is to remove from this grain surface the insoluble "bloom," small particles of solid fibre, and other products which have settled on and in the grain. This process also removes a considerable quantity of the uncombined tan and presses out the strong tan liquor from the interior of the leather. It also softens and cleans the grain and renders it more supple. Up to a few years ago, the goods after scouring were simply rinsed through liquor, oiled and removed to the drying sheds, but to-day, in order to replace the weight that has been lost by scouring and if possible to add further weight, the butts are treated by a retanning process in its pits containing a strong solution of some bright coloured tanning agent. For this purpose a comparatively new extract made from the wood of the quebracho tree, which grows in large quantities in the Argentine Republic, has been introduced. The wood of this tree contains over 20 per cent. of a red, very difficult soluble tanning material. At first this material was little used, owing to the fact that it could not be made up into strong liquors. Lepetit, however, found some eight years ago that, by treating this material under pressure with sodium bisulphite, not only was it rendered easily soluble, but that the sulphite treatment bleached the objectionable red coloring matters and produced an extract which gave to the leather a warm yellow color. This process also increased the penetrating powers of the tan, and has almost revolutionized the older methods of shedwork. This material is, therefore, largely used in the vatting of butts after scouring. The liquor in the vats made up to great strength and then heated to a temperature of from 60° to 65° C. The butts are entered (sometimes suspended on poles, in other yards laid flat), and handled frequently; the process is continued for three to four days. This vatting or retanning not only replaces the tan which has been scoured out, but at the same time bleaches the leather to a regular even color, transforming the natural brown of the ordinary tannage to yellow fawn. The butts, on removal from these hot pits, are lightly rinsed through a weak sumac liquor to remove the extract from the surface, are allowed to drip for 48 hours and then go to the drying sheds. Here they are carefully wiped over on the grain with a damp cloth, and then well oiled with cod oil. The oiling process is extremely important. The oil used should be suitable; it should possess the necessary drying properties, it should be pure, and should not have too high an acid value. The object of the oiling is to soften the grain, and at the same time to prevent tthe leather drying through the grain side, the aim being as far as possible to make the leather dry from the flesh side so that the uncombined tan liquor be not drawn out upon the surface where it would become oxidized, darken, and make the leather "cracky." The leather is then hung up in dark sheds, and a cool draught of air allowed to pass through. The slower the drying at this stage the better is the product. If it is dried too rapidly the leather is dark, blotchy, brittle on the grain, and practically unsalable. When the butts get to a rubbery condition, *i. e.*, if the grain of the leather becomes slightly slimy so that one could write one's name with the finger on it, they are laid down in pile on one another to come to "proper condition." At this stage they are put through another machine similar to the scouring machine, but having steel or brass blades instead of stone, whereby the leather is stretched and the grain made beautifully smooth and level. The butts are again re-oiled, this time slightly, and further dried. In this condition they will stand a little more air until they begin to show signs of drying round the thinner parts, they are again laid in pile to come to "condition," and are rolled under a heavy roller to make them firm and solid; if rolled out of "condition" they "dry dark"; after the first rolling, known as "rolling on," the goods are redried. When they have taken their natural color but are still damp in the interior, the butts are usually split down the centre into two parts, which are then known as bends. They are now re-rolled, the second rolling being called "rolling off." The bends are now taken to a heated drying room, and dried at a temperature of from 85° to 100° F. The leather thereby becomes very firm, and when perfectly dry it is brushed and polished on the grain and is ready for the warehouse, where it is sorted according to weight, color, and quality.

This shedwork has been described in some detail, because this process in recent years has become one of the most important in connection with the manufacture of sole leather; needless to say, the time and trouble expended has also increased the manufacturing costs. Why should leather need take on an even yellow color without irregularities, highly polished and smooth? The boot manufacturer cuts it up into soles and soaks them in water which is seldom clean. The damp sole is then stitched on to the boot, and as it passes through the various processes becomes stained with iron and grease; when firmly stitched on the boot, and practically finished, it is put over an emery wheel, and the whole of the beautiful polish, colour, and finish, on which the tanner has spent so much time and money, is ground off. The boot manufacturer then paints the sole with a yellow or black varnish stain, which completely hides the colour and character of the leather, and finally polishes it. Even were it not for this custom of staining the leather, why should it be necessary to take all the care and trouble to produce leather of an even color and regular shade only afterwards to be dirtied in the boot factory? And even if that were not the case, what difference does it make to the wearer of boots on a muddy day whether the color of the soles be brown, black or green? This absurdity would not be serious, were it not for the fact that, as is generally acknowledged by the trade, this vatting and bleaching seriously reduces the wearing properties and the water resisting character of the leather. The process of bleaching in hot liquors containing bisulphite of soda does to the insoluble products in the leather which have been deposited in the layers exactly what Lepetit found it did to the difficultly soluble quebracho tans; it renders soluble and removes from the leather those products which are so valuable for the production of a sole leather which would not only wear well but would also resist water. This is surely a case of science misapplied, and this fad or fashion which demands that the sole leather shall be of a light yellow color is, in my opinion, having disastrous effects. The bleaching of sole leather is one of the most unnecessary processes that has ever been introduced, and must sooner or later destroy the reputation which British sole leather has long enjoyed all over the world, as a firm, hard wearing, water resisting material, and is certainly contrary to all the accepted principles of sole leather tanning.

The chemistry of the hide is not fully understood and the exact composition of many of the tannins is not yet established. Finally the newer science of colloidal chemistry urgently demands consideration and application.

In the discussion which followed the paper Professor H. R. Procter said he wished to emphasize the statement as to the great waste in the cost of production of the leather and the great injury done to the leather by the bleaching process. The substances that gave firmness and waterproofness to the leather were soluble in the bisulphite solutions used and probably were actually dissolved in combination with the base of the bisulphite. In any case they knew this solvent action took place. Occasionally this sort of thing happened to a chemist in an analysis; they used generally a Berkfeld candle for filtering the tannin extract solution. These cost money, and they could not afford to use a new candle every time, so they washed them out; but if they had been using a candle for one of these extracts containing difficultly soluble matters and washed it as well as they could and then used it for an extract solubilized with bisulphite, they might find more than 100 per cent. of the solid bodies in the extract. The extract not only went through itself, but actually dissolved out some of the previously deposited matters in the candle which all the washing had failed to get out. When people complained of the leather of the present day was not equal to that of the good old times, there was a certain amount of truth in it, but a large part of it was due, not to the fault of the tanner, but to the desire to obtain a particular color for which there was no real object, and to the use of bleaching extracts in order to get that color.

AN OUTLINE OF THE LEATHER INDUSTRY.

By Allen Rogers.[1]

For most leathers it is not only necessary that the lime be completely removed, but that the skin should be brought from its swollen state to a soft and open condition. To accomplish this result on the heavier classes of dressing leather, such as split hides, kips, colt, and calf skins, the stock is run in a weak fermenting infusion of pigeon or hen manure, the time depending upon the strength of the liquor and the nature of the goods under treatment, the process being known as "bating." "Puering" is a very similar process, applied to the lighter and finer skins, such as glove kid and moroccos, in which dog manure is substituted for that of birds. As the mixture is used warm and the skins are thin, the process is complete in a few hours. Neither bating nor puering is very effective in removing lime, but they seem to act by means of bacterial products upon the hide substance, thus causing the pelt to fall, that is, to become soft and flaccid.

Following the bating, or sometimes taking its place, comes the "drenching" operation, the purpose of which is to remove the last traces of lime and to slightly plump the skins. The drench liquor is prepared by allowing an infusion of bran in warm water to ferment under the action of special bacteria which develop lactic an acetic acids.

The method of deliming just mentioned, although it presents many difficulties and is uncertain in its action, is very largely used, notwithstanding the fact that many substances have been put on the market to replace it.

Having passed through all of the processes mentioned above, the hide or skin is now in the proper condition for the actual tanning operation, which may be conducted by any one of several different methods.

The oldest method in vogue is that known as "oil tannage," which consists in treating the skin or hide with a mixture of fish and other oil in a machine which works the skin by a sort

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[1] Parts of an address before the New York Section of the American Chemical Society, published in the *Journal of Industrial and Engineering Chemistry*, for August, 1910.

of kneading motion known as the "stocks." During this operation heat is developed, resulting in the formation of aldehyde and other oxidation products. The excess of oil is removed by scraping and pressing, the product obtained being known as "dégras." The skins are then washed with a fairly strong alkaline solution, and the alkaline solution neutralized with an acid, with the result that fatty acids are produced, known as "sod oil." This method of tannage is used especially for the so-called "chamois" leather.

For the manufacture of white and light colored leather it is customary to employ an "alum tannage." This method consists in treating the skins with a mixture of sulphate of aluminium, salt, flour, egg yolk and olive oil. This treatment produces a hard "crust" in which the skins are allowed to remain for quite a length of time, after which they are softened, sized and finished.

The most important method of tanning is that in which a vegetable material is employed, the results obtained being due to the presence of tannic acid. The operation consists in placing the skins in a dilute solution of the tanning material, such as quebracho extract, and gradually increasing the strength of the liquor until the treatment is completed. On removing from the tanning solution the skins are washed, dried, softened, colored, seasoned and finished as desired.

A recent process, and one which is meeting with increased application, is that known as "chrome tannage." The Schultz process was the first to meet with any commercial application and consists in saturating the skin with a solution of dichromate of sodium or potassium together with hydrochloric acid. The chromic acid thus produced is absorbed by the hide substance, and is finally reduced to the chromic hydroxide condition by means of sodium thiosulphate and hydrochloric acid. A second process, brought to perfection by Martin Dennis, consists in treating the skin with a basic sulphate of chromium. The latter method has the advantage over the former in that it is more easily controlled and less expensive in its operation.

Within the past few years formaldehyde has been introduced as a tanning material and bids fair to open up a new field for the production of leather by chemical means.

ABSTRACTS.

How to Distinguish Genuine Goat Leather.—Tanned goatskins can be distinguished from sheepskins by the harder and rougher feel of the grain, because they are thicker and consequently firmer. But if a single separate skin is taken this characteristic will not be so evident; and in finished leather the difference is often not sufficient to enable one to tell offhand which is which. Therefore some other means of distinguishing them is desirable.

One of these is to slice off with a very sharp knife about one-fourth of the thickness of the grain. If this piece of the grain surface is held up in the sunlight the hair pores can be seen through it; and as is well known in goatskins, the hair grows in little clusters, generally of three, but sometimes of two hairs together, with small empty spaces between. This is a sure proof of the genuineness of goatskin. Often when the leather has been blacked the color shows through the pores on the back, and the clusters of two or three points can be seen by the naked eye. The fine under wool between the larger hairs, that goats usually have in winter, have such small pores that they are not visible in this test, and therefore offer no hindrance to judging.

The large hair pores in goatskins slope in the skin the same way as the hairs, and go in about half the thickness of the skin. On sheepskins, on the other hand, the pores are much closer together and smaller, and they enter the skin perpendicularly, while no grouping is observable.—Allgem. Schuhmacher-Zeitung, translated for American Shoemaking.

Gelatine and Tannin. H. TRUNKEL. *Biochem. Zeits.*, 1910, [26], 458-492.—The author has made numerous experiments on the interaction of solutions of gelatine and tannin, using solutions of from 0.18 to 0.6 per cent. concentration in the case of the gelatine and 1—5 per cent. in that of the tannin. The gelatine before purification contained 2.34 per cent. of ash, and after purification, from 0.20 to 0.28 per cent. The tannin had the rotary power, $[a]^{21} = + 72.7°$, and after purification by Rosenheim and Schidrowitz's method (see preceding abstract), $[a]^{20} = + 72.5°$. It was found that under suitable conditions both the gelatine and the tannin are quantitatively precipitated, and the precipitate is then insoluble in and resistant to water. With an insufficient proportion of tannin the filtrate from the precipitate contains both gelatine and tannin, whilst with an excess of tannin, the filtrate contains tannin, but no gelatine. In all cases except where quantitative precipitation of both tannin and gelatine is obtained, small quantities of gallic acid can be detected in the solution. A given quantity of gelatine in a freshly prepared solution requires more tannin for complete precipitation than when the solution has been allowed to stand. In a freshly prepared solution 1 gram of gelatine requires about 0.7 gram. of tannin, but after 24 hours only about 0.4 gram; on more prolonged standing the effect gradually becomes less and less pronounced. If a gelatine solution which has stood for some time be warmed, it regains its original tannin-precipitating-power. With excess of tannin, the precipitate produced may contain up to 3 parts of tannin to 1 of gelatine, but it is no longer insoluble in and resistant to water, readily yielding tannin. Neither the stable nor the unstable precipitate can be completely resolved into its components. By repeated treatment with alcohol, 97 per cent. of the tannin can be extracted, but the remainder is obstinately retained, and from the residue only small quantities (up to 6 per cent.) of unaltered gelatine, capable of gelatinizing, can be recovered. Both the stable and the unstable prcipitate yield small quantities of gallic acid on prolonged treatment with water or alcohol. Although both the gelatine and tannin undergo chemical alteration to a slight extent, and the experimental data do not give very concordant results when calculated according to the exponential formula, on account of unavoidable experimental errors, the author states that the mutual precipitation of the gelatine and tannin is undoubtedly an absorption process, this being shown most clearly by the behavior of the gelatine-tannin precipitates towards alcohol.—Jour. Soc. Chem. Industry.

Analysis of Vegetable Tanned Leather. HANS SICHLING. *Collegium*, 1910, No. 423, pp. 327-336.—Von Schroeder and his assistants Bartel, Paessler and Schmitz-Dumont founded the methods which are now generally used. These are not uniform in details, hence the author here outlines the methods of analysis according to von Schroeder's principles, following chiefly Paessler's manuscript directions for instruction in the Freiberg Tanning School.

Sampling.—Great care is essential to get an average sample; several pieces should be cut if possible, from different hides, from the back, neck and belly. If material is scant, the neck is the most representative. The leather is coarsely cut and generally ground in a mill, but finely cut instead when greasy. Care should be taken to avoid over-heating of the leather during grinding. In a complete analysis, for uniformity of record and comparison of the results, the order of analysis given below should be adhered to.

Moisture.—10 grams leather are dried at 100-105° to constant weight. When exactness is required, cut samples are used as there is a loss of moisture during grinding. According to von Schroeder ungreased leather may vary during the year 2½ per cent. in moisture, and greased leather 2 per cent. Analyses are therefore reckoned upon an average water content of 18 per cent. for ungreased leather. For greased leather, the water content $W \frac{1800\,(100 - F)}{82 + 18\,(100 - F)}$,
where $F =$ the fat content.

Mineral Matter (Ash).—Five grams sample are taken, preferably cut to avoid the risk of iron particles from a mill, and slowly ashed in a platinum dish, finishing with ammonium nitrate if needed. If the ash somewhat exceeds 1½ per cent. of the dry leather, there has been faulty work in the beam house, leaving too much lime, or the leather may be over dressed or bleached. If 2 per cent. be exceeded, artificial loading may be suspected which is then a subject for mineral analysis.

Fats.—Twenty grams leather are placed in a No. 603 S and S capsule and extracted in a Soxhlet apparatus for 3 to 4 hours. The solvent is distilled off and the residue dried at 100-105° and weighed. In ungreased leather the normal fat is from 0.2 to 3 per cent.

Organic Solubles (Soluble Tans and Non-tans).—The degreased leather from above is left under water pressure over night in a Koch extractor without the sand layer, and then extracted 1½ to 2 hours to 1 liter. Practice varies in the method of extraction, there being a difference of opinion as to what is soluble and what is combined tannin. Of the extract, 100 cc. (2 grams leather) are evaporated in a platinum dish, the residue weighed and ashed. The ash deducted from the total solubles leaves the organic extract (mineral free), which eliminates any error from soluble salts which might have been used in weighting. For the non-tans, 800 cc. of extract are concentrated to 200 cc. and the determination made according to the official method. In computing, the ash is deducted from all evaporated residues. The amount of solubles in leather varies greatly and may amount to as much as 25 per cent. When glucose has been used in weighting, the non-tans are in excess.

Leather Substance (Hide Substance and Combined Tannin).—This makes up the remainder of the leather, after deducting all the preceding. The hide substance is determined directly by a nitrogen estimation according to Kjeldahl. One per cent. N = 5.62 per cent. hide substance in neat's horse and swine leather, 5.75 per cent. in goat and buckskins, and 5.85 per cent. in sheepskins. The determination is important and should be repeated until concordant results are obtained.

Rendement Number (R).—This is computed as the amount of air dried leather obtained from 100 parts of hide substance. Von Schroeder and Paessler have shown that this theoretical number derived from the analysis agrees satisfactorily with the results of practice.

Tannage Number (D).—This shows how much tannin is fixed by 100 parts of hide substance; the number is generally below 100. A high tannage number merely confirms that sufficient tannin has been fixed by the hide but does not necessarily indicate a good leather. Further judgment is derived from the behavior of a section on swelling in dilute acetic acid.

Glucose.—A preliminary test is first made to roughly show the relative amount. For the determination, 400 cc. of the extract from 20 grams leather are concentrated to 100 cc. and to this 10 cc. basic lead acetate solution added, shaken and filtered through a dry filter after 15 minutes. For the lead solution, 300 grams pure lead acetate are rubbed up with 100 grams PbO and warmed on the water-bath until white, then made up to a liter and finally filtered. If all the tannin has not been precipitated, 15 cc. lead solution are added to the concentrated liquor. To 50 cc. of the filtrate (3.637 grams leather) a solution of sodium sulphate equivalent to 5 cc. lead solution is added, the $PbSO_4$ let settle and the liquid filtered through a dry filter. Of the filtrate, 40 cc. (2.945 grams leather) are taken when the amount of glucose is moderate, and this determined according to Fehling's method. In case the leather has been loaded with molasses, it is also necessary to determine cane-sugar. A second glucose determination is made with 40 cc. of lead free filtrate after inverting the cane-sugar by heating with 10 cc. dilute H_2SO_4 (1 :5) for half hour on water-bath. The additional amount of reduced copper over that of the first determination × 0.95 = cane-sugar.

Lime.—Twenty grams leather are let stand with about 750 cc. 1 per cent. HCl 24 hours at 30 to 40° C., and then made up to 1 liter and filtered. 500 cc. are evaporated to dryness, ashed, redissolved and analyzed in the regular way.

Sulphuric Acid.—250 cc. of the HCl solution above are evaporated, moistened with soda, redissolved in a little HCl and precipitated with $BaCl_2$. Total sulphur is thus determined. Free sulphuric acid is determined by Balland and Maljean's method with modifications. Ten grams leather are moistened with 10 cc. 10 per cent. pure soda, dried and ashed at a moderate heat over an alcohol flame. Schopper's electric ashing furnace is well suited and cobalt oxide hastens the oxidation. (Abstr. this JOURNAL, (3) 364). The S is finally determined as $BaSO_4$. A parallel determination is made, ashing without soda addition, the difference representing free SO_3 after deducting the S in hide which amounts to 0.14 per cent. SO_3 for fat free leather of 18 per cent. H_2O. If Fe, Cl or Cr be present in the leather, the volatile SO_3 found must be correspondingly lowered since the sulphates of these metals evolve SO_3 on heating.

The Complete Analysis of Leather. J. PAESSLER. *Collegium*, 1910, No. 423, pp. 337-8.—Parker and Paul (reprint, ante p. 305) have pointed out a supposed mistake in the computation of the degree of tannage according to von Schroeder. The author declares the error does not lie with von Schroeder but with the English chemists. In the original papers published by von Schroeder and Paessler and by Bartel after von Schroeder's death, the expression "organic solubles" (durch Wasser auslaugbare organische Stoffe) is always used and it is explicitly directed that the ash of the solubles be determined and subtracted from the total solubles (see above abstract), hence the mineral matter is not reckoned twice. If the computation is made according to von Schroeder, as the author has always done in his published leather analyses, practically the same results would be obtained as by the English colleagues in their somewhat roundabout modified method.

The Estimation of Glucose. B. KOHNSTEIN, *Collegium*, 1910, No. 420, pp. 301-4.—Hoppe-Seyler's reagent for glucose in wine is employed, namely ortho-nitrophenylpropiolic acid. This reagent warmed with glucose and alkali is converted into indigo blue. Some other reducing agents, as H_2S and $FeSO_4$, but not Sn and HCl, give the reaction. Neither do albumin, starch or cane-sugar interfere, hence the method is adapted to detect glucose in tanning liquors and leather extracts. The reagent is not kept in solution but applied fresh for the test. The liquor to be tested is diluted if too dark, made alkaline with NaOH and warmed with about 0.05 grams *o*-nitrophenylpropiolic acid for one-fourth minute. In presence of grape sugar, the liquor becomes a weak blue and later an intense blue and after 2 to 3 hours standing, deposits a deep blue precipitate. From the amount of this, one may roughly judge the quantity of glucose originally present and the author is studying the quantitative estimation by gravimetric and volumetric methods. The precipitate may be washed with dilute acid and dilute alcohol, dissolved in chloroform, recovered and weighed. In the presence of colored liquors the indigo blue may be recognized as forming a violet metallic mirror or shimmer on the surface of the liquid and the walls of the tube, it being volatile with cautious heating. Indigo blue dissolves in chloroform with a purple red color, in paraffine with a blue violet. In the case of hemlock or pine liquors which give a green color with alkali alone, the test precipitate is washed above and redissolved in chloroform, giving a purple red if indigo blue is present. The reaction is still more distinct if before applying the test, the liquor be first shaken with MgO and filtered; this removes the tannin and dye-stuffs. In loading leather, partially altered starch product are sometimes used which would not be correctly judged by the test. In this case, the leather sample is first treated with dilute H_2SO_4 to convert the starch into glucose, the liquid treated with MgO, filtered and then tested as above.

Acetyltannin and Ammonia. M. NIERENSTEIN. *Ber. Deutsch. chem. Ges.* 1910, (43), p. 1688.—The author reports the results of unsatisfactory attempts to de-acetylize acetyltannin (abstr. this JOURNAL, 1908 (3) 148) with alcoholic ammonia. The purified original material, m.p. 202-4°, acetyl number 40.62 gave products of melting-points varying from 174 to 237° and acetyl numbers from 12 to 20. At higher temperatures, among other products of the reaction gallic acid and gallamide were obtained. Triacetyl gallic acid on treatment with 3 molecules of alcoholic NH_3 gave diacetylgallic acid as confirmed by combustion and determination of the acetyl number.

Algarobilla. U. J. THUAU, *LeCuir*, 1910, (3) No. 16, pp. 419-21.—This is the fruit of *Balsamo carpum brevifolium*, a tree of the carob family which flourishes in South America and the West Indies. The pods are about 3 cm. long and 1 cm. thick containing round, hard grains. The entire fruit is composed of:—cellular tissue 21.2, powder 50.3, seed 28.5 per cent; these contain 45.5, 62.8 and 5.6 per cent. tannin respectively.

The mean tannin content of the entire fruit is 42.8 per cent. An entire average analysis is

Soluble assimilable tannin	43.0
Soluble non-tans, organic	20.0
Total minerals	1.6
Insolubles	21.9
Water	13.5
	100.0

The 20 per cent. of non-tans include 8.2 per cent sugar, corresponding to 19 parts of sugar to 100 of tannin. Algarobilla sells in Europe at 40 fr. for 100 kg., but it is necessary to distinguish the different grades. One kg. tannin costs agout 1 franc.

Most of the tannin belongs to the pyrogallol class. The liquors are rich in gallic and ellagic acids arising from decomposition of the tannin; also fermentation acids are present produced from the glucose. The tannin is easily soluble and may be totally extracted below 50° C. The crude material is best ground in a mill similar to that used for divi-divi and the grains sifted out. Algarobilla is not suitable for layers as it gives a spotted leather; for such work it should only be used in mixture. It is valuable in tanning very rapidly, giving a soft, supple tannage of a clear yellow color. To avoid spots, it is best to lay the hides grain down or better grain to grain without tanning material next the grain. Algarobilla is a good substitute for sumac and penetrates more quickly. It is also employed for retanning harness and upper leather. For sole leather it may be used as divi-divi in North Germany, mixed with quebracho wood, myrobalans and valonia to tan in lay-aways. Mimosa bark, which alone gives a leather apt to be brittle, may be advantageously mixed with algarobilla, especially at the commencement of a sole with a single chrome bath. This valuable tanning material finishing with a single chrome bath. This valuable tanning material is much better known in the United States than in Europe.

PATENTS.

Art of Manufacturing Leather. U. S. Patents Nos. 967,986 and 969,570. JAMES T. SMITH, Newark, N. J.

These two patents relate to a process of "setting out" leather, and it is a misleading title to call the patent an art of manufacturing leather. The leather is stretched upon a board while wet, some adhesive being placed between the leather and the board. The leather is then dried, and is thus in a condition to be japanned or otherwise finished.

Method of Unhairing Skins and Apparates for Unhairing Skins. U. S. Patents Nos. 967,988 and 967,989. WILLIAM R. SMITH, Buffalo. N. Y., assignor to Buffalo Leather Co.

The method involves the use of a current of air drawn through a slot by some exhausting device. The skin is drawn over the slot and worked with mechanical fingers as it passes over. The current of air is said to blow the hair off without any mechanical pull.

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THE PARIS CONFERENCE OF THE I. A. L. T. C.

By R. W. Griffith.

In writing a brief account of the above conference for the benefit of Members of the A. L. C. A. it is not the present object to enlarge upon the programme which has already been published, nor to go into the details of the various subjects discussed, but rather to attempt at a general outline of the proceedings and the mode of conducting them.

The Meetings of the International Association of Leather Trades Chemists are not only the occasion for discussing technical matters of common interest but advantage is taken of the opportunity to develop the social side by hospitable entertainment. The same general lines are followed at all conferences.

The proceedings in Paris were opened with a reception to members of the Conference by the various Syndical Chambers connected with the Leather industry in Paris and the French Section of the I. A. L. T. C. This occasion gave the various members an opportunity of renewing acquaintances and of making new ones and strict formality is relieved by the supply of refreshments. Professor Meunier, president of the French Section, welcomed the delegates to Paris.

The business of the Conference commenced the following day at the Sorbonne with a short address by the President of the International Association, Professor H. R. Procter—who in the course of his remarks extended a hearty welcome to the delegates from the American Leather Chemists Association—Messrs. Alsop and Griffith. This was acknowledged and the greetings of the American Association duly conveyed by Mr. Griffith.

The President then announced the winner of the "Seymour-Jones Prize" which consists of a gold medal and fifty dollars in cash, and is awarded at every conference to the chemist who in the opinion of the prize committee accomplished the most original research work. This year the prize was awarded to Dr. Fahrion whose work has been chiefly directed towards establishing a theory for the tanning process.

The treasurer's report and the reports of the secretaries of the various National Sections were read and the place for the next conference was briefly discussed. Mr. J. T. Wood, president of the British Section formally invited the association to meet in London in 1912, and the invitation was accepted.

The election of officers here took place and Dr. J. Gordon Parker was elected president, Professor Meunier was re-elected Hon. Treasurer and Dr. Stiasny was elected Hon. secretary.

The executive authority of the I. A. L. T. C. is vested in the president, two vice-presidents, the honorary secretary, the honorary treasurer and the honorary editor. It was now proposed that the executive committee be enlarged and it was decided that not more than three members from each Country should be elected.

With regard to the conduct of the various sectional commissions which are elected for the purpose of testing and standardizing analytical methods, the danger arising from the premature publication of reports is to be eliminated by the sectional committee exercising supervision over the commission belonging to their section and that matters in dispute should be referred to a referee.

The I. A. L. T. C. conferences have to contend with difficulties which are happily unknown in our American conferences. The whole of the business of the conference is carried on in French, German and English and whatever is said in one language has to be translated into the other two. In this way a great deal of time is taken up and misunderstandings arise which have to be straightened out. When little progress is being made in a discussion, the rules are suspended for a few minutes and a "free for all" discussion ensues and upon the meeting again being called to order a resolution is framed which apparently reconciles all parties.

It is somewhat surprising to learn that the rules of the International Association and the official methods of analysis have not been published in book form since the first conference which was held some twelve years ago.

The present rules and methods, which bear little resemblance to the original ones, can only be ascertained by diligently searching the I. A. L. T. C. Journal—the Collegium—and it was now decided to publish the Amended Rules and Methods in pamphlet form in three languages.

Some criticism was offered by the British members on the general appearance of their official Journal and it was suggested that the example provided by the A. L. C. A. Journal might be emulated with advantage.

Before concluding the general business and commencing the technical programme of the conference, it was proposed by President H. R. Procter and carried unanimously that the thanks of the I. A. L. T. C. be conveyed to the A. L. C. A. for their kindness in sending delegates to that conference.

The first item on the technical programme dealt with the vexed question of Tannin Analysis and in addition to a report by the chairman of the International Commission two additional reports were submitted by the German Sectional Commission and the French Sectional Commission respectively. These reports had already been published so that the discussion upon them was commenced at once.

Professor Dr. Paessler on behalf of the German Section urged the adoption of Zeuthen's method, which provides for the use of dry lightly chromed hide powder washed free from salts. Altho' many figures were given which showed extremely close results the majority of the members were opposed to any change in the present method of detannization on the ground that the latter gave excellent results when manipulated according to the rules of the association, and furthermore the Zeuthen method had not been tried sufficiently long to warrant its official adoption. It was finally decided to refer the matter to the International Commission on Tannin Analysis to report definitely by the next conference.

Mr. Seymour Jones, the chairman of the commission on the Preservation of Hides and Skins gave a brief outline of the reports which he has received from various parts of the world relating to the methods employed for preserving hides and skins. It is expected that the full report will be ready for publication shortly.

The remainder of the technical programme was gone through quickly, the chairmen of the various commissions briefly presenting their reports, the only subject which gave rise to considerable discussion being the proposed official method for analysis of leather which was introduced by Messrs. Meunier, Paessler and Parker. Subsequently the matter was referred to a committee.

The business of the Conference was suspended at noon on the second day to permit members to enjoy the hospitality of the syndicate of the manufacturers of Tanning and Dyeing Extracts of France which consisted of an elaborate luncheon served at the Trianon-Palace Hotel at Versailles.

The members were driven to Versailles in automobiles provided by the French section of the I. A. L. T. C.

The conference concluded at noon on the fourth day, and in the evening all the foreign members were invited to attend a banquet offered by the Syndicate General des Cuirs et Peaux de France, under the Presidency of Mons. Haller—member of the Institute, Professor of the Sorbonne.

The conference was very well organized and the tact displayed by the executive committee in smoothing difficulties and reconciling opposing factions deserves the greatest credit.

The arrangements for the meetings and receptions were excellently carried out by Professor Meunier and Mons. Thuau, the secretary of the French section.

The delegates of the A. L. C. A. carried away the pleasantest impressions of their visit and would take this opportunity of thanking the members of the I. A. L. T. C. for this kind reception.

ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

The Seventh Annual Convention of the A. L. C. A. was held in Chicago at the Hotel La Salle, October 6, 7 and 8, 1910.

The first session was called to order by President H. T. Wilson, at about 10 o'clock on Thursday, October 6th, in the "red room" on the 19th floor of the hotel. The Convention was opened with an address by the President as follows:—

PRESIDENT WILSON'S ADDRESS.

Gentlemen:—In opening this meeting, I wish to state first that the remarks which follow are in no wise intended to constitute an address, such as has been customary to deliver before our Conventions. Our program is unusually lengthy, and we have one day less in which to hear the reading of papers and take part in the discussions of same. Therefore, it was not deemed wise nor proper by your presiding officer that he should consume much valuable time by going into a lengthy discourse.

This is the Seventh Annual Convention of the American Leather Chemists Association and each one of the preceding six has been attended by increasing interest and a broader understanding of the purposes and the necessities for such an organization. The number seven is considered to be a lucky one, and I trust that it may be true in this case. In any event, the seventh annual meeting makes a new and distinctive mark in the history of our association of which all should be keenly appreciative.

Ever since the birth of the organization it has been its endeavor to enlist the interest and support of the great tanning interests and bring them to the realization of the fact that technical science and practical experience can work together for the advancement in the perfection of both. This fact, as established by European countries has started the leaven of interest in our own to the extent that, this year we have the unique opportunity of holding joint sessions with an organization representing the greatest body of tanners in the world. (This was prepared with the idea that there would be some tanners here. I fail to see them.) It is only fair to state here that this result has not been brought about solely by the endeavors of the chemists, for a number of those engaged strictly in the practical end of the tanning business have added immense impetus to the movement, and without this interest this present occasion would be impossible. It is with gratification, therefore, that this convention is opened under such seemingly auspicious conditions.

It may be thought by some that a joint meeting of the organizations will not prove to be so satisfactory as expected, while others may have the contrary view. Speaking entirely from a personal point of view, I should say, that with conditions properly arranged both parties should be benefited by mutual association and the discussion of matters which are of vital interest to the work in which both are engaged. It is admitted that primarily, the American Leather Chemists Association is a scientific body, and the National Association of Tanners is a practical body, but we fail to see why this should preclude general conference any more than it should preclude the necessary conference of every day business. If the tannery chemist is to be strictly a man of science and not mix in with the practical end of the business, I fear that his work will be of limited value to his employer. The decision as to the advisability of holding joint sessions will rest largely upon the degree of success and interest taken in this meeting.

One of the prime objects of the A. L. C. A. as organized, was the investigation of methods of tannin analysis, and this was, beyond doubt, wise and proper, but to-day we will have to begin to reach out beyond this line of limitation. On a previous occasion the speaker has remarked that to him, the mere matter of standardizing methods of analysis was placing too narrow a scope upon the natural requirements of our association. There are many technical questions demanding the attention of tannery chemists which seem to be quite as important as the standardization of methods of analysis, and in this connection, I will quote a paragraph from a letter recently received from Prof. Henry

R. Procter as follows:—"On this side, we are settling down steadily to our present official method of tannin analysis which in most respects is identical with your own, and we are devoting ourselves more to other problems." This seems to be a pointer that we should fall into line and begin to study the real problems of tanning as well as the problems of tannin measurement.

I beg to quote again from the same eminent source referred to above. "Both Associations have, up to the present time, and I think rightly and wisely, devoted much time to the perfecting of analytical methods, for these are the tools with which we must work, but we must not forget that they are the tools and not the final object of our efforts, and that our ultimate aim is to understand and improve the manufacture." These statements come from a source which should demand the earnest consideration of all.

It is only proper to state in this connection, that it was with this thought in mind that the American Leather Chemists took such an active interest at the last meeting in regard to the movement for the establishment a school of tanning, or a research laboratory, where such problems as heretofore mentioned could be worked out in their proper channels by men of ability whose time should be devoted exclusively to the work in hand, and I trust that our hopes may find realization in the development of the school of tanning, the prospectus of which has recently been outlined by the committee in charge of this important work. Although the American Leather Chemists Association has had no voice in the conclusion of this matter, it is keenly alive to the crying need for such an institution in this country, and fully realized the great possibilities which lie before it. Any work which may be accomplished through the researches of this institution tending toward the advancement of tanning chemistry or modern practical tanning will be counted as so much gain by all who are engaged in the perfecting of the leather industry, whether they be men of technical or of practical training.

The principles of tanning in their technical application to that art, have not long been a matter of serious consideration in this country, and it might be said that we have only begun to formulate theories in regard to same. Theories mark the endeavor to attain to the principle, some may be false and others true, but they are all stepping stones to the principle for which the endeavor is made. The principles of tanning have been in existence ever since creation, but because of the limited comprehension of man it requires ages of theorizing, experimenting and labor before we may finally arrive at the ultimate result. It is only through the application of an exact science that we may hope to bring practical questions of the day in regard to manufacture to a satisfactory conclusion.

Simon, the tanner of biblical time, might have produced the same quality of leather that is being made to-day, if he had had the benefit of the experience of two thousand years more, but he was probably content with the work of his hand and happy in his ignorance. Thousands like him may or may not have produced a very acceptable piece of merchandise, but they did not know why. This is the age of wanting to know *why*, and the task of removing the accumulated dust and cobwebs of ignorance and spent theories from the signboards to success will, of necessity, rest largely upon those men of keen perception and profound scientific knowledge, who may be chosen to devote their researches to the end that, the manufacture of leather may be conducted not by rule of thumb, but through the exact knowledge of science.

That the success which we all desire may be the more promptly realized, it would seem that there should be a constant and intimate association of the three factors which have been laboring more or less singly for the cause which is common to all. I would admonish, therefore, that you give your sincere efforts to the support of the National Association of tanners, the Tanning School and the American Leather Chemists Association.

The report of the Secretary-Treasurer was next read, including the following statistics of membership:—

Oct. 6, 1910, number of active members	101
number of associate members	121
Total	222
New members received during the year, active	13
associate	16
Total	29
Members resigned during the year, active	4
associate	5
Total	9

The gain in membership during the year has thus been about 20.

The chair appointed Messrs. J. H. Russell, C. W. Norris and C. C. Smoot, 3d, as Auditing Committee.

The President said that early in the summer he had asked Professor Procter to come over and attend this Convention. He could not come, but sent a letter to the Association, which the President now read.

LETTER FROM PROFESSOR H. R. PROCTER.

To the President, Council and Members of the American Leather Chemists Association.

GENTLEMEN:—It is with the greatest regret, and owing to the pressure of University duties, that I am compelled to decline the invitation to take part in your meeting which has been so kindly extended to me, but I trust you will accept in written form my most hearty wishes for the success not only of your coming gathering, but for the continued advance of your Association, (of which I am also a member), and I feel sure that I may do this not merely personally, but as President of the International Association, which you must not regard as in any sense a rival but rather as a territory to be federated with a common aim, an independent internal government, but if possible with mutual citizen-rights.

The two associations have always followed the single and identical aim of adopting and standardizing the best analytical methods without national or personal consideration, and the result has been that in all cases, and especially in tannin analysis, almost identical methods have been adopted, and these will necessarily tend to become still more so, since each Association keeps a vigilant eye on the work of the other, and is ready to adopt any change so soon as it is satisfied of its real advantage. We all, I think, recognize that National feeling, whatever its place in politics, should have none in technical science.

Both Associations have, up to the present, and as I think rightly and wisely, devoted much time to the perfecting of analytical methods, for these are the tools with which we must work, but we must not forget that they are the tools and not the final objects of our efforts, and that our ultimate aim is to understand

and improve the manufacture. While in detail most of this work must be done in the tannery, and by private effort for a financial end, it is yet dependent like all technical science, for its continued advance, on a knowledge of the general scientific principles which underlie it, and which should be the common property of all leather chemists. Thus we have before us, in addition to our private and personal interests, a public and unselfish aim and duty, and those who can contribute even a trifle to this fund of common knowledge, may be greater benefactors of the human race than the man who spends his doubtfully gotten millions on questionable philanthropies. It must, however, be remembered that many of the questions we have to solve are problems of great complexity, which cannot possibly yield a direct profit to the investigator, but demand for their investigation, much time, labor, and expense, and which can only be undertaken by men provided with means and leisure, and of the widest general scientific knowledge, and I trust that in the foundation of a great American school of Leather Chemistry, the need for such men will not be forgotten, I am,

Very sincerely yours,
HENRY R. PROCTER.

The Secretary was directed to answer this letter on behalf of the Association.

Mr. Veitch was now called on for the report of the Committee on Analysis of Leather. He gave a summary of the report, which had been published in the JOURNAL for October. An extended discussion followed which will be published in a later issue of the JOURNAL.

The President then called for discussion of the report of the Acid Committee, Mr. Alsop, chairman, published in the October JOURNAL. Parts of this discussion will be given in a later issue.

Mr. C. R. Oberfell then gave a review of the report of the Committee on Chroming of Hide Powder, of which he was chairman. This report also called forth some discussion, which will be outlined in a future number of the JOURNAL, the report having been published in the October issue.

The President then announced the program for the afternoon, and the Association adjourned until 2 P. M.

The afternoon session, Thursday, October 6th, was conducted by Mr. Joseph H. Russell, Vice-President. The first announcement was a notice that a meeting of the Council would be held at the close of the session. Dr. Allen Rogers then read his paper on "A Trade School for the Leather Industry," describing the provisions which are being made at Pratt Institute, Brooklyn, N. Y., for the tanning school to be established there under the auspices of the National Association of Tanners, and giving the courses, as outlined in this JOURNAL for August, 1910. Dr. Rogers' paper was published in full in "Hide and Leather" for October 8th. At the conclusion of this paper Mr. T. J. Mosser asked whether any provision had been made for the carrying on of scientific research in connection with the tanning school. Dr. Rogers replied that while no arrangements have yet been made for research work, the plan is such that a department of that kind may be added later, the Institute being prepared to furnish the facilities whenever called upon.

The next paper was by Mr. George A. Kerr on "The Manufacture of Chestnut Extract in the United States." It is printed in full elsewhere in this issue.

Mr. F. C. Rose then read his paper on "Leather Oils," which we also print in this number.

Mr. J. H. Yocum's paper on "The Disinfection of Hides," also printed in this issue of the JOURNAL, followed. In the discussion of Mr. Yocum's paper, allusion was made to Mr. Alfred Seymour-Jones' method of disinfection of hides, which he recently placed at the disposal of the British Government. It is proposed to apply this process to the disinfection of hides from India and other countries, before they are shipped. No definite information in regard to the method has been published, so far as we are aware.

Mr. M. F. Nichols mentioned that ozone is now being successfully used to disinfect water for town supply in some places, and asked whether this agent had been tried in disinfecting hides. No one answered this question, and Mr. Nichols expressed the hope that some work would be done along this line.

At the close of the session Mr. Cudworth Beye, Executive Secretary of the National Association of Tanners, requested members to register, and on behalf of the National Association of Tanners invited the active members of the A. L. C. A. to be present as their guests at the banquet on Friday evening.

On Friday, October 7th, most of the members of the A. L. C A., attended the meeting of the National Association of Tanners in the morning, and in the afternoon went to the stockyards or to Gary, Ind.

In the evening a fine banquet was served at the Hotel La Salle, attended by nearly 200 members of the two associations and their friends. The toastmaster on this occasion was Mr. John E. Wilder, and his opening remarks were in a particularly happy vein. He introduced first Mr. Wm. George Bruce who gave a very interesting and informing address on "Employers' Liability Legislation and Industrial Insurance." Mr. Bruce is Secretary of the Milwaukee Merchants' and Manufacturers' Association. He has spent much time abroad studying German and English legislation on the protection of employes.

The second speaker was Dr. Allen Rogers, who gave a talk on the "Department of Industrial Chemistry," over which he presides at Pratt Institute, Brooklyn. This address was illustrated with a large number of lantern slides.

President H. T. Wilson, then responded to the toast, "A. L. C. A." in a few well-chosen words.

The last session of the Convention was called to order at about 10 o'clock on Saturday morning, October 8th, by President Wilson.

Papers were read as follows:—

Extraction of Leather by Various Solvents, Mr. Geo. A. Riker.

The Tannage of Heavy Leather in California. Mr. Jos. H. Russell.

The Detection of Menhaden Oil in Cod Liver Oil, Mr. A W. Hoppenstedt.

Conservation in the Leather Industry, Mr. F. P. Veitch.

The Necessity of Proper Sampling, Mr. T. A. Faust.

These papers will be published in the JOURNAL later.

The next item was the report of the Committee on Rapid Cooling of Tan Solutions and the Asbestos Kaolin Filtration Method, of which Mr. W. P. Maxwell was chairman. A summary of the report was given by Mr. F. H. Small. The entire report and some of the discussion which followed Mr. Small's presentation of it are printed elsewhere in this number.

The Association then proceeded to the election of officers Mr. Joseph H. Russell was elected President, Mr. F. P. Veitch Vice-President, and Mr. Herbert C. Reed Secretary-Treasurer. Messrs. W. H Teas and A. W. Hoppenstedt were elected members of the Council for a term of two years to succeed Messrs. F. H. Small and G. A. Kerr.

The Secretary then announced the result of the vote on the proposed change in the method of sampling, the proposed acid methods, the proposed method of analyzing crude materials such as sumac and the change of lead sub-acetate to normal acetate in the determination of glucose in leather. All of these changes were adopted by large majorities. The proposed changes in the By-Laws, Sections 6, 22 and 23 were all adopted. The result of a test vote on the proposition to report analyses to one decimal place instead of two, was then read. On this suggestion, the vote on which was merely an expression of opinion, 28 voted "yes" and 23 "no." The Secretary remarked that the question had been made too broad and expressed the opinion that if it had been restricted to the proposal to report extract analyses to one decimal place, there would have been a much larger vote in favor of doing it. Mr. Reed also expressed the wish that the whole question should be taken up during the year and worked out, to decide what analyses should be reported to two decimal places and which should be carried to only one place.

Mr. Veitch called attention to the fact that the Eighth International Congress of Applied Chemistry meets in Washington and New York in 1912. He has already suggested to the committee of arrangements that a subsection on leather chemistry be inaugurated at that time. Mr. Veitch now suggested that the International Association of Leather Trades Chemists might be induced to hold a meeting in this country at that time as a subsection of the Congress of Applied Chemistry. On motion, Mr. F. H. Small, Hon. Local Secretary of the I. A. L. T. C. was directed to communicate with the officers of the International Association, and if they were willing to consider holding a meeting in this country to refer the matter to the Council for further action.

Mr. Veitch remarked that even if the I. A. L. T. C. did not assent to holding a meeting in America that would not prevent American leather chemists from meeting as a sub-section of the Congress of Applied Chemistry.

On motion of Mr. Small a vote of thanks and appreciation was extended to the retiring President for his efficient work on behalf of the Association. A vote of thanks was also extended to the National Association of Tanners for their entertainment of our Association. The Convention then adjourned.

Active members of the Association present included the following:—

Lloyd Balderston, Walter H. Byron, Oma Carr, Harrison L. Clough, Walter H. Dickerson, Thomas A. Faust, E. J. Haley, H. H. Hurt, A. W. Hoppenstedt, Geo. H. Kerr, Aug. W. Kilp, C. B. Kinney, Louis E. Levi, D. McCandlish, M. E. Mason, H. F. Moench, Thos. J. Mosser, M. F. Nichols, C. W. Norris, Chas. R. Oberfell, H. C. Reed, C. A. Reisig, G. A. Riker, Allen Rogers, J. H. Russell, B. Shields, F. H. Small, C. C. Smoot, W. H. Teas, F. P. Veitch, B. D. Westenfelder, H. T. Wilson, John H. Yocum.

THE MANUFACTURE OF CHESTNUT EXTRACT IN THE UNITED STATES.

By G. A. Kerr.

It is not my intention that the history of the manufacture of tanning extract in North America shall come within the scope of these notes, as I wish to confine them chiefly to the present methods of manufacturing chestnut wood extract, but, in passing, I will say that, while it is only during the past decade the industry has seriously engaged the attention of leather manufacturers, the idea of producing a concentrated tanning extract is a very old one, dating back at least one hundred years. The feasibility of using concentrated extracts has long been demonstrated, but the high cost of production offered little inducement for its use by tanners, who, until a few years ago, had an adequate supply of bark at a lower tannin unit cost, especially those using hemlock.

In 1900 the annual production of tanning extract made from native materials was only about 125,000 barrels. (A barrel by the way is 500 pounds.) At the present time the rate of output is about 500,000 barrels, and, when the factories now under construction are completed, this will be increased to 600,000.

In this connection those familiar with the rapid exhaustion of the bark supply naturally think first of the supply of chestnut wood, its volume, duration and permanency being of first importance. To manufacture 600,000 barrels of extract annually 400,000 cords of wood of 160 cubic feet each are required. These figures are based upon using mature timber, that is, timber from forty to eighty years or more growth. At fifteen cords per acre, which is, if anything, a high yield, it is necessary to cut over approximately 27,000 acres per year or 90 acres every working day. This area appears somewhat extensive, but it is really such a small proportion of the whole chestnut timber area that there need be no anxiety at this time as to the future supply of chestnut wood. A very conservative estimate puts the present available area at 250 00 square miles or16,000,000 acres, which, at a yield of only five cords per acre, would at the present rate of consumption, furnish wood for two hundred years, so there is every indication that chestnut extract will be a staple tannage when the use of hemlock bark and other tanning agents has long become extinct.

However, all this timber is not likely to be manufactured into extract, as the decreasing supply of lumber is creating a market for chestnut wood that, a few years ago, would not pay for logging, and a large quantity of material heretofore rejected will doubtless find its way to the saw mill. But even then it is very doubtful if more than 25 per cent. of the whole can be manufactured into lumber profitably. Trees more than fifty years old, are, as a rule, practically worthless for this purpose, and such lumber as is manufactured from chestnut will be cut from trees of from twenty-five to fifty years' growth. In the virgin forest the vast majority of chestnut trees are badly wind shaken, worm eaten or rotten at the heart. Granting, however, that lumbering will materially decrease the quantity available for extract, chestnut timber possesses two most valuable characteristics, which will preserve it to the use of man indefinitely. The most important of these is that of reproduction, which is rapid and profuse. The eminent Forester, Dr. Schenck, states that he is now cutting chestnut on the Biltmore estate on a thirty year footing, and that he finds young chestnut forest of the average growth will produce at the rate of one cord per acre per annum. The other feature is that most of the chestnut timber grows on land, that is virtually worthless for other purposes—certainly for no purpose at this time that yields greater revenue than chestnut wood. Unfortunately, in a sense, for the extract manufacturer, the great bulk of this raw material stands upon the most rugged and inaccessible land, which makes the problem of getting it to the mill a difficult and costly one.

Recently attention has been called in a magazine article to the destruction of the chestnut tree by a species of parasitic fungus, which, working on the inner bark, virtually girdles the tree and kills it. How serious a menace this is to a growth is problematical. So far as the present stand of timber is concerned, it will not matter from the extract manufacturers' standpoint, provided the damage does not proceed faster than the timber is cut. With one exception, I know of no considerable area of chestnut which has died entirely, but well to the East of the Blue Ridge in Virginia there is a strip stretching from South to North on which the chestnut has almost entirely died out. I do not know that this is due to the fungus referred to, if it is, it would seem to have taken a course parallel to the mountain range, as there has been no evidence of it in the mountains proper. During the past two years I have noticed in Amherst County, Virginia, some dying chestnut timber of young and thrifty growth, which, so far as my knowledge goes, is the furthest West this condition exists, and as soon as the leaves are down, I hope to make an investigation with the view of determining the cause. That is to say that the line of the Southern Railroad from Danville to Washington is practically the boundary line of that dying timber. Whether it is confined to that area because of the latitude and different climatic conditions I do not know. The prevailing winds in that section are from the southwest and that has some effect in keeping the spores from blowing toward the mountain. They are blown rather toward the seaboard.

Next to the preservation of the mature timber now standing, re-forestation claims attention. It is true chestnut reproduces profusely, but, unless this young timber is protected from the ravages of fire and parasitic enemies, it is not to be depended upon as a source of future supply. With the immense quantity now in sight, this may not appeal to the present day manufacturer, but, as the reproduction of this timber progresses most rapidly upon the most accessible land, I venture the opinion that the time will come when it is more profitable to cut young timber from localities easily accessible than to go further afield for virgin or mature timber, and, when it is remembered that 50,000 acres of rugged mountain land, worth to-day not over $1.00 per acre, will, under intelligent re-forestation, maintain indefinitely an extract plant turning out two hundred barrels per day, the importance of guarding the young forest against damage requires no emphasis. I question if any extract manufacturer can imagine a happier solution of his raw material problem than the possession of a sufficient tract of chestnut plantation, made accessible with wagon roads and railroads of permanent construction and having it equipped with all the necessary appliances for getting wood to the mill at the lowest cost. The question of raw material would no longer keep him awake of nights, nor would he be subject to the thousand and one uncertainties he has to contend with under existing conditions.

Coming to the establishment of a factory, the first consideration is one of location. It is requisite for an extract plant to have, (naming them in the order of importance as nearly as possible) :—

Twenty-five years' supply of wood visible at full rate of consumption.

An abundant supply of soft water.

Plenty of labor.

Good coal at reasonable price.

First-class railroad facilities, both for incoming and outgoing freight.

Convenient machine shop and foundry facilities.

A great many other things are desirable, but, as they are rarely all found in one spot, the foregoing list may be said to include the cardinal necessities.

Assuming these conditions to have been met, the next question is that of determining the most economical unit of output, proceeding, of course, on the basis that the product is to be made for sale in the open market. Experiment has shown there are two points at which the greatest economy may be obtained, the one in a plant of limited production—say seventy barrels per day—and the other not less than two hundred and fifty barrels. In the first instance a sufficient supply of raw material can usually be purchased from the farmers and small lumber men, thereby obviating the necessity of a large investment in timber lands and equipment. A further saving is effected in the smaller fixed charges. A good manager, with a bookkeeper and foreman, can easily conduct the entire business. Such a factory is also easily kept in repair, as it can be safely constructed and operated on a very condensed plan, the installation calling for the minimum investment. A single unit of grinding and other machinery will produce comfortably the output mentioned.

When the capacity of a plant is increased above this point, the cost of operation increases until it again reaches the diminishing point at an output of about one hundred and seventy-five barrels per day. Under such conditions the investment for raw material becomes a factor to be reckoned with. Fixed charges increase, and the plant itself requires an investment in buildings and equipment which is out of proportion to the output, and, if a large plant must be built, it is better to figure upon an output of 250 to 300 barrels daily.

Referring again to the small plant, unless it is kept in full operation, it does not have sufficient elasticity of output to successfully meet the competition of larger plants under adverse business conditions. By that I mean any decreased output affects the earning capacity to a much greater extent than in a larger plant, which can stand a greater reduction without actual loss. This is a point which seems to be fully recognized at this time. A few years ago there was only one plant with a rated capacity of two hundred barrels per day, whereas there will soon be nine, the actual output of which exceeds this capacity, and one or two of the nine are now turning out nearly three hundred barrels per day.

The next requisite in the erection of an extract plant is a suitable site, and by suitable I mean one which is nearly level and not less than ten acres in area; twenty is better. Ample trackage is necessary for handling the deliveries of wood, as they are usually beyond control. One day may see fifty cars on the yard and the next none. In fact, I have seen as many as one hundred and ten cars of wood placed on our yard within twenty-four hours, and, without several miles of trackage and unloading room, we should have been compelled to pay a large bill for demurrage.

The factory proper will not occupy more than an area of 150,000 square feet, if it is a 200 or 300 barrel plant, but sufficient use for the balance will be found to justify its possession. The site should also have good drainage, to a stream preferably, and be within reasonable distance of its water supply. If a gravity supply can be made available even by a reasonably long pipe line, the manufacturer may consider himself fortunate.

As to the factory buildings, to be permanent and easy to maintain, and also a first class fire risk, they should be of brick or concrete throughout. Such construction means a greater outlay of capital, but it is a profitable investment. If, however, it is necessary to save money in this direction, and construct the buildings of frame or frame and iron, they should be protected with fire walls and automatic fire doors, built in accordance with the Underwriters' specifications. In any event the power plant and mill room should be of brick or concrete. The existing plants are chiefly of wooden construction, a few wooden frame and iron sheeting, and only one or two of brick or brick and concrete. As a matter of fact there are but few extract plants in operation in which a fire, once under good headway, would not mean the total destruction of the plant. Here, I would remark, is a danger much dreaded by tanners who are dependent upon the extract manufacturers for their tanning material, and, if the extract maker wishes to encourage the use of his product, he cannot do too much to give his customers the same assurance of supply as they had when they could stack bark enough at their tanneries for more than a year's run.

In discussing the equipment of an extract plant with the necessary machinery and apparatus, I wish to emphasize the fact that successful operation depends almost first and last upon mechanical efficiency. In every department, from the grinding of wood to the shipping of the finished product, results are wholly dependent upon the continuous operation of machinery and apparatus, which is liable to fail at any moment, and the failure of a single machine in most instances reduces the volume of output. And here I would remark no extract plant is complete without well equipped machine and carpenter shops and a stock of the more important duplicate parts.

Beginning with the steam plant, which is the heart of the factory, I find the present installation varies from seven to ten horse-power per barrel of output, a good deal depending, of course, upon local conditions. However, it is always best to provide sufficient power to avoid forced steaming, and, in fact, the plant should be sufficiently large to permit of laying off more than one or two boilers, so that, in case of repairs being necessary, the capacity of the plant will not be affected. To be safe in this respect, I think the latter figure is probably the better ratio.

In every instance, except one, the return tubular type of boiler is employed, for which I think custom and low initial cost are largely responsible. It is no economy, however, to save a few thousand dollars initial outlay by installing a steam plant which, at best, will not evaporate more than 8½ pounds of water per pound of coal, when other types can be obtained which will give an efficiency of 11 pounds or more of water per pound of coal. Next to raw material and labor, the fuel account is the largest one on the books, and a standard type of water tube boiler is much to be preferred. In addition to a greater evaporative efficiency, they require much less room and less labor to fire per horse-power than the old fashioned type. This in turn means smaller buildings, shorter conveying machinery and the delivery of steam at a higher temperature, in itself an important advantage.

Steam in an extract plant is generated under unusual conditions, and the problem of reducing the coal bill has in late years been given a great deal of attention. In a large factory there are from three to four hundred tons of exhausted or spent chips to be disposed of daily. The general way of doing this at present is to use it as fuel. At first glance, it seems a comparatively simple matter, but, when it is considered this spent wood contains from 65 to 75 per cent. of water, the problem assumes a different aspect. In order to get rid of this waste material in the cheapest way and at the same time realize upon some of its heating value, it has been and is the custom to employ one or another of the many variations of the Dutch oven. They, however, fall so far short of the ideal that manufacturers are constantly working to improve the combustion of spent wood and quite a good deal has been accomplished in this direction in the past few years, although there still seems much room for improvement.

It is only a few years since the manager of an extract works told me, with a suggestion of pride in his tone, that he could make a ton of extract with a ton of coal. To-day, however, two tons of extract per ton of coal is not unusual, and several plants are doing even better. Time does not permit of going into the details of furnace construction or practice, but in brief I will say that present methods of consuming spent wood are not, as in the past, in the direction of making it burn as a live fire and thereby impart its heat directly to the boiler, but rather in converting it into gas, which in turn is ignited and burned by passing over a live coal fire. The present degree of efficiency is due to the employment of this principle, and, when well carried out, furnishes a clear and smokeless fire of very high temperature.

Mechanical stokers of various types have been thoroughly tried, but a study of the conditions necessary for the most effective combustion of spent wood indicates they are not adapted to this class of fuel.

The next step in the conversion of steam into power, the largest unit of which is the engine for driving the high speed grinding machinery, with the necessary conveyer system. The prevalent practice is to employ a plain slide valve type of engine for this purpose, set in pairs or as a twin engine.

Custom is also the basis of this feature, although there exists an idea that engines of a more delicately adjusted type are not suitable for such rough work. Of regard for steam consumption there has been little, the average manufacturer apparently assuming that, as he could use all the exhaust steam he could make, the quantity of live steam used for power did not matter much. Experience has demonstrated that this is a great mistake, and the less exhaust steam there is to consume the better, for there is no profit in converting live steam into exhaust merely because it can be used elsewhere. The simple twin engine doubtless has some points in its favor, especially where they are overworked and subject to violent changes of load, as they often are in single unit factories, when the load frequently jumps from zero to overload in less time than it takes to tell it. A well run large plant, however, is not subject to these conditions to the same extent, and there is no reason why economy should be sacrificed to expediency, and the most highly developed type of steam engine is none too good for the present day factory. The minimum consumption of live steam is worth striving for in every department, and the selection of engines and pumping machinery should be given the utmost consideration.

Before dismissing the discussion of power, I will say the advantage of high-class slow speed engines has been well demonstrated in the reduction of wood, and is by no means an experiment.

Electric power is being employed in one of the largest plants, and, with regard to continuous operation and low cost for maintenance, is claimed to be very successful. In the absence of any data bearing upon the cost of delivered power, I am unable to express any opinion, however, as to whether it has any advantage over direct steam.

Following the course of manufacture in chronological sequence, we come to the comminution or grinding of the wood. The machinery by which this is accomplished is usually set in a shed roofed building, with the front entirely open, and situated so as to permit of the most convenient conveyance of ground wood to the extraction or leach house. The chief reason for leaving the front open is to permit of placing loaded cars directly in front of the machines and provide the greatest freedom and ample light for handling the wood. The machines for chipping or grinding are most commonly what is known as a "Hog," those manufactured by Mitts & Merrill being used as a rule. These machines, which are too well known to require detailed description, are very efficient as to capacity, that of the open throat type apparently being only limited by the power furnished to drive them and the rate at which wood can be thrown into the hopper. Five cords of five foot wood can be ground hourly under normal conditions, but their extravagant consumption of power, when a cutting capacity anything like that cited is required, is an objection, as the action of the machine becomes one of breaking and splintering the wood rather than cutting it, owing to the extreme set which must be given the knives. Under such circumstances it is necessary to further reduce the chips and splinters, and for this purpose a shredding machine of one of the several types now on the market is employed, notably those known as the Williams and the Jeffreys. These machines are of the swinging hammer type, but you are doubtless familiar with them, as they have been used quite extensively by tanners for shredding bark. They are also great consumers of power, and so expensive to maintain that it is still an open question with me whether or not it is better to shorten the cut of the hog and install more of them and so do away with the shredder altogether. Much depends upon the system of extraction employed and other minor conditions peculiar to each individual plant.

For some years two factories have been using the disc type of chipper, similar to those used in cutting pulp wood. The machines of this type found best adapted to cutting chestnut wood are those with a cone shaped face and knives. On green wood they have been very successful, showing a great saving in power and improvement in the preparation of the wood. On old, seasoned or knotty wood, however, their capacity is reduced to such an extent that it greatly offsets the saving in power. I should say here that, in both plants where these machines are in operation, a large proportion of the residual chips are, after extraction, utilized for the manufacture of paper pulp, and, as the chips produced by the hog and shredder are not adapted for this purpose, the use of the disc chipper in these factories is compulsory. There have been numerous machines for the economical and satisfactory preparation of wood designed and experimented with, but so far the ideal machine has yet to be developed.

With regard to setting the machinery in a grinding room, there seem to be as many ways as there are factories. Some are set with the chipper or hog and shredder superimposed, some tandem, others side by side, the method being adopted to suit the general plan of the plant. However, there are one or two points in setting these machines, which should be observed in all cases. Heavy brick or re-inforced concrete foundations should invariably be built, and, when the machines are set tandem, or side by side, ample space must be left between them, so that every part is easily accessible in the case of a break-down, and also to give sufficient distance between centres to reduce the angle of the conveyor carrying the chips from one machine to the other as much as possible. It is also advisable to keep the height of the hopper low enough for the men feeding the machines to toss the wood downward rather than upward. This is apparently a small matter, but it makes a very material difference to a man handling some forty tons of wood in the course of ten hours. With regard to driving these machines, the most approved practice suggests arranging the drive below the floor, as this keeps the belts and driving equipment cleaner and freer from dust, thereby lessening the danger of fire.

Last, but not least, the wall or partition between the grinding room and other departments, especially, if that department be the engine room should always be of heavy brick or re-inforced concrete construction, the latter preferably; this for the purpose of protecting adjacent machinery in case of accident. As most extract manufacturers know, shredders and chippers occasionally come to grief, and, when they do, there is great danger of injury to the plant from the flying pieces of metal. Accidents have occurred which resulted not only in completely closing a plant down for weeks, but which cost many times the value of the machine in damage to other portions of the equipment.

From the grinding room the wood is conveyed to the extraction or leach house, and in this department construction follows so closely that which obtains in modern tanneries that a lengthy discussion of it would only be a *resume* of a subject most of you are familiar with. The newest features perhaps in the equipment of a leach house are the concrete leaches and the automatic leach emptying machines. The concrete leach has scarcely been in use long enough to pass final judgment upon it. From all the data at my disposal, concrete seems to possess no great advantage over cypress until large dimensions are reached. Up to 16 ft. in diameter, the latter is as cheap to install, and will last a good fifteen years under hard service. Just how the concrete will stand the attacks of heat and acetic acid for a like period remains to be determined. In building leaches over 16 ft. in diameter and up to 20 ft., the cost of concrete is less than that of cypress, as the increased thickness of staves and additional hoops make a greater difference in ratio to the size than with concrete. The chief thing, however, in a leach house is the method of extraction and its final results.

The principal requirements are rapidity and completeness of extraction, with the least volume of water and expenditure of heat. There are in vogue at least three methods of extraction, all of which leave much to be desired in accomplishing the foregoing. In the order of their popularity, they are open diffusion, decoction and percolation.

The diffusion system is that of continuously pumping forward the liquor from one extractor to the next, the wood being immersed during the entire time of extraction. The means employed for transferring the liquor forward is either compressed air or a steam jet, the mechanical lift or pump having been discarded long ago. When air is employed, the liquor is heated by means of a steam coil or an arrangement of perforated steam pipes under the false bottom of each extractor, direct steam being the most efficient and economical, as every heat unit is utilized, and dilution by water of condensation is balanced by reducing the quantity necessary on the weakest or tail leach. The steam coil method of keeping the liquor hot requires more heating surface than is usually applied, and there is always considerable loss from the cooling of the water of condensation before it is returned to the boiler.

The greatest objection to open diffusion, compared with the other systems, is the extended time it requires to complete the extraction, it usually being from two and a half to four days from the time an extractor is filled until it is emptied. This entails the use of a much greater number of extractors and the continuous heating of a tremendous volume of water. At the same time the liquor is so much exposed to the air that it is claimed to be deleterious by many authorities.

Decoction is a much older method than diffusion, and, as it has been discarded to a great extent by tanners, it will seem strange to those who have employed it that, when applied to the extraction of wood, it is more efficient than the diffusion method. Extraction by decoction means immersing the raw material to be extracted in the solvent (which in this instance is water), and then boiling it. This is exactly what is done in leaching wood by this method. Of course more than one application of water is necessary to complete the process. Instead of keeping the wood continuously immersed, the water or liquor is drawn off as soon as the wood becomes saturated with the strongest solution possible of the solvent matter, and the drained extractor refilled with the weaker solution from the preceding one. Next to extracting under pressure, this, in my opinion, is the most rapid and consequently most satisfactory method employed. It takes only from fifteen to twenty minutes to saturate the solvent and the wood with extractive matter, and, with proper pumping capacity, not over fifteen minutes more to discharge the liquor to the leach ahead and refill from the one behind. With a properly equipped system, a battery of ten leaches can be turned over in less than twenty-four hours; that is to say, instead of two and a half to four days, the time is reduced to less than one, and the number of leaches and volume of water in service per cord of wood is reduced in like proportion. In addition to these advantages the method is extremely simple, and there is little liability of interrupted operation.

There is still another advantage in extracting by decoction, and that is with reference to the preparation of the wood. In diffusion and percolation not only the completeness of the extraction but the time and volume of water necessary to effect it are largely governed by the fineness of the preparation. With decoction the preparation must come within well defined limits to get the best results, but it is not necessary to carry it to the same degree as is required by the methods just mentioned. In common with the other methods, however, the volume of water necessary per cord of wood is greater than desirable.

The third and last method I shall speak of is that of percolation, which consists of sprinkling water over the surface of the leach with a mechanical sprinkler and drawing it off under the false bottom as fast as it collects, never allowing the wood to become immersed. To properly carry out this system, the wood must be steamed by means of perforated steam pipe in the bottom of the leach until it has settled as uniformly and compactly as possible. The water, which must be heated to the boiling point, should then be started on and the sprinkling continued at a rate not exceeding 2.5 gallons per hour per square foot of area, with a 12 foot column of wood; thus a leach 16 ft. in diameter and with 12 ft. of wood will take 500 gallons of water per hour and a like ratio for leaches of other dimensions, until extraction is complete, which will be in about twenty-four hours. When properly carried out this method is very thorough in its results and possesses the advantage of making every leach a separate unit, if desired. As to the volume of water, less is required than with the others. However, it requires constant and intelligent attention.

Under the present practice it is necessary to evaporate about 1,400 gallons of water for every cord of wood leached, and, as the average liquor obtained from the leaches is about 14 degrees Barko. (1.014 S. G.), it will be observed that each degree requires the evaporation of 100 gallons of water. In a 250 barrel plant, the quantity of water evaporated daily to make 25 per cent. tannin extract is approximately 225,000 gallons on the above basis, therefore the importance of improving the methods of extraction will be appreciated when it is seen that for each Barkometer degree increase in gravity the evaporation of about 15,000 gallons of water is saved.

In the matter of extraction, it will be remarked the extract manufacturer has to a great extent followed in the wake of the tanner, without doing much to improve his methods, whereas the practice of dye-stuff manufacturers offers many valuable suggestions that possibly could be turned to advantage. Here I might refer to the methods of European extract makers and also those of quebracho extract manufacturers but, as I am confining my remarks to American chestnut extract I will pass them over at this time.

In making what is known as ordinary or standard extract, in contradistinction to that which is refined and decolorized, the liquors from the leach house are conveyed directly to the tanks, which supply the evaporators. Before evaporating, it suffices to merely run the liquor through a strainer to remove the particles of wood which may have escaped through the false bottoms of the leaches. This brings us to the final stage in the process of manufacture—that of concentration.

Volumes have been written upon the subject of evaporation during the last fifty years, but the subject is so broad that a very respectable treatise might be written on the single subject of evaporating tanning extract liquors, and the searcher of Patent Office literature gets the impression that patents for improvements on evaporators, numerically at least, run those on the ubiquitous car coupler a close second. In fact, genuinely original ideas on this subject are not often met with.

Until twelve years ago the concentration of extract liquors was accomplished altogether by means of the old coil type single effect vacuum pan, which subjected the material to very extended boiling and consequent damage to both tannin and color, besides being very wasteful of steam. In 1899 a multiple effect was installed at the Lynchburg plant, the first in an American tanning extract works. It was a standard triple effect, with vertical tubes, and built on the same line as the sugar evaporators which had been in use for many years previously. This installation proved such a great improvement over the old method that it was quickly adopted by all the factories then in operation, and those erected between 1900 and the present time have followed suit, most of them still further promoting economy by installing quadruple effects.

While the standard vertical tube evaporator is the type most generally used, several plants have installed what are known as film evaporators, for which greater efficiency is claimed, but the difference does not seem sufficiently great to afford any great advantage in the cost of production.

The vertical tube evaporators installed consist of two styles, one in which the steam drum is of sufficient depth to give a tube length of about 42 inches in an apparatus of 8½ feet in diameter, and with one vapor inlet. The other is constructed with a comparatively short tube, those in an apparatus of the foregoing dimensions not exceeding 24 inches in length, and the vapor is delivered at four equidistant points on the drum by an external arrangement of pipes. In other respects the apparatus is much alike. For a given diameter the first described style has the greater capacity, because of the greater heating surface afforded by the long tubes, but against this is the uneven boiling due to the vapor being delivered at one point and the somewhat sluggish circulation in the low temperature effects, where the liquor becomes more viscous. It may be said in favor of the short tube apparatus that it gives considerably greater efficiency per square foot of heating surface, which is explained by the more even distribution of vapor to the tubes, producing uniformity of boiling and therefore better and more rapid circulation. In vertical type evaporators good circulation is of great importance, as it is only by exposing a greater liquor surface that vapor is liberated rapidly.

The film evaporator now in use, briefly described, consists of a bank of tubes suspended horizontally in a header placed in one end of a horizontal drum or belt, arranged so that the vapor fills the interior of the tubes, while the liquor, distributed more or less uniformly over the outside of the top row, runs over each succeeding row downward to the liquor chamber, from which it is pumped to the next effect. In passing over the tubes, the liquor forms a very thin film, from which the vapor escapes with great facility. A notable feature of this apparatus is that the liquor passes only once over the tubes in each effect, whereas in the standard it makes many passages through the tubes before being syphoned to the next effect. On account of this feature it is usually desirable, if not necessary, to pass the liquor through the apparatus twice before getting it to the proper density, while for heavy extract, such as is now commonly made, it is not adapted unless supplemented by either a standard apparatus or a strike pan.

There is another type of evaporator being introduced to the extract manufacturer at the present time, which, it is claimed, will effect a revolution in this department, but I am informed that, while an installation has been completed, the apparatus has not been fully tested. A study of the principle, however, indicates that it will be well worth while for extract makers to watch the performance of this latest development.

The greatest advantage of the multiple effect evaporator is the saving of fuel. The old single pan, under best conditions, could not evaporate more than 8½ pounds of water per pound of coal, while each effect of a multiple will do almost this much when clean and in good working order. On the basis of evaporating 8½ pounds of water per pound of coal at the boiler, a double effect of the best type will evaporate 16 pounds, a triple effect 22 pounds and a quadruple effect 28 to 30 pounds.

In practice, however, such efficiency is rarely, if ever attained, on account of the various losses of steam or heat between the boiler and the last effect of the apparatus. This is especially true where exhaust steam is used. The greatest obstacle to efficiency, however, is the scale which deposits on the tubes. This incrustation takes place from the second to the last effect, and forms so rapidly that the efficiency of a triple or quadruple effect will fall 25 per cent. or more in a week. A reasonable efficiency can only be attained by frequent and regular cleansing of the tubes. The heating of the liquor depends altogether upon the conductivity of the metal, and, when the tubes become coated, the passage of heat becomes very much impeded. An incrustation of 1/16 inch will decrease the efficiency over 25 per cent. and ⅛ inch will cut it about 50 per cent. So far no suitable means for removing this scale with a solvent has been discovered, and cleaning is performed with scrapers, operated either manually or by compressed air, steam or water.

The first effect seldom scales, and the tubes often remain bright after years of use as when they are put in. This is due to the liquor still being sufficiently thin to keep most of the scale forming salts in solution, and also the presence of acetic and other organic acids in the liquor. Also the great rapidity of the circulation through the tubes has a scouring effect and prevents the deposit of such precipitation as may exist.

The above conditions have been taken advantage of by Mr. G. W. Childs, who has designed and patented an arrangement of the vapor pipes for multiple effect evaporators which permits of each effect becoming in succession 1, 2, 3 and so on. It is claimed that, when the change of liquor from one effect to the other is made daily, no incrustation ensues. However, as this arrangement is not being sold on the open market, extract manufacturers in general have not been able to avail themselves of the improvement.

Proceeding with the concentration of the liquors, they usually enter the first effect at a gravity of 2½ to 3 degrees twaddle, and are passed through as quickly as extract of a density of 38 degrees twaddle can be pumped out of the last effect, the inflow and outflow being continuous under the most approved practice. This, however, is a difficult matter to regulate, owing to the irregularity of the evaporation caused by the various changes in the temperature of the liquor and the steam available, unless a preheater is used to raise the liquor to boiling point before it enters the first effect. In fact, the liquor should be invariably brought to as near the boiling-point as possible before entering the pan to obtain the best results,for without it the first effect has to act as a heater and much of the evaporating capacity is lost.

To obtain the most uniform boiling and delivery of finished extract, it will be found advantageous to first pass the liquor through the evaporator with sufficient rapidity to yield a gravity of about 20 degrees twaddle when making 25 per cent. tannin extract and 30 degrees when making 35 per cent., then, after accumulating a sufficient volume, finish the extract by passing it through the evaporator a second time.

In case of 35 per cent. extract, it is impossible to get satisfactory results, trying to finish the extract in one passage, as the viscosity and low temperature of the liquor in the last effect reduced the circulation to such an extent that evaporation is greatly impaired, and the capacity of the whole apparatus seriously interfered with. The best evaporation is obtained only when a maximum difference between the temperature of the steam or vapor and liquor is maintained, and with heavy extract in the last effect the desired fall cannot be secured.

Steam should never be admitted to the first effect at a temperature exceeding 227 degrees Fahr. which is equivalent to five pounds pressure at the boiler. Temperatures above this have a damaging effect upon the color of the product. In practice the best results are obtained about as follows:

Steam to the first effect 227 degrees Fahr., vacuum none.
Vapor to the second effect 199 degrees Fahr., vacuum 7 in.
Vapor to the third effect 172 degrees Fahr., vacuum 17 in.
Vapor to the fourth effect 144 degrees Fahr., vacuum 24 in.
Vapor from fourth effect to condenser 116 degrees Fahr., vacuum 28 in.

It will be noted the total difference is 111 degrees Fahr. with a drop of 28 degrees in each effect. I would here observe that all of the heat lost during the progress of the liquor through the apparatus is not available for evaporation, as much of it is lost by radiation, friction in the drum and pipes, and also from causes previously discussed, the total effective heat probably not exceeding 60 per cent. of the original volume.

Concentration practically completes the process of extract making. From the evaporators the extract is pumped to the storage tanks, and, after cooling and settling, it is ready for shipment.

There are many other important, though minor, details relative to extract manufacturing, and much could be said about supplementary machinery, also the making of refined and decolorized extracts, etc., but the exigencies of time do not permit of their treatment now.

Before concluding, however, I wish to refer to an article by Mr. Bailey Millard, "The Passing of the Chestnut Tree," published in Munsey's Magazine for September, and which some of you have doubtless read. He says:—

"Now is the time to ge into the tannic acid business. Chestnut trees are full of this valuable acid, and they can be had for little or nothing. Both the bark and the wood supply it in large quantities. The machinery required for its extraction is not expensive. All that is necessary is to break up the bark and reduce the wood to shavings or splinters, which are heated in boilers and then evaporated in vacuum pans."

This opinion is one commonly held by those who have never been in the extract business, but the men who have struggled through the last seven or eight years in extract manufacturing hardly sympathize with it. This industry has developed sufficiently to share the common hazards of all competitive industries, and fair returns upon the capital invested are only acquired by constant vigilance and a generous disregard for the size of the scrap heap, for, if there is any inexpensive machinery and apparatus employed in the business, I have yet to learn it. In response to an inquiry as to the cost of an extract plant from the United States Bureau of Chemistry, I submitted an estimate about as follows:

"For the erection of a plant with a capacity of 200 to 250 barrels per day, if on a permanent basis, $2,000 per barrel of minimum daily output; if the buildings are of temporary character, $1,500 per barrel.

For raw material $500 per barrel. As extract is now sold mostly on long term contracts, this is, covering a year or more, it is necessary to have at least 100 days' supply of wood constantly available. A factory of any size endeavoring to operate otherwise cannot guarantee fulfillment of contracts and prompt deliveries, and of course, will soon lose out.

Tank cars $25 per barrel.

Book accounts $25 per barrel."

This estimate may be questioned by some more favorably located than the average plant; that is, there are one or two plants which have their wood delivered to them by large lumber companies, and the lumber company carries the raw material account instead of the extract plant. This method of doing business will work for a while, but, as the wood supply depends largely upon the facility with which it can be obtained and the profit to the contractor, the manufacturer usually in the end has to depend upon his own efforts and money for raw material.

It has also been a popular idea that there is a large margin between the cost of extract and selling price, figures being often quoted in support of such argument. This is also misleading, as such costs have usually been based upon the operation of new plants, before the heavy repairs began, and without due charges for depreciation, interest, insurance, selling of product, etc. Doubtless there will be great improvements and consequent reductions in the cost of operation, but so far it has taken all the efforts of the manufacturer to reduce the cost fast enough to meet the constantly increasing costs of raw material and supplies of all kinds, and, when it is remembered that few, if any, plants are able to turn out annually extract equal in value to the money invested, the prospect of large profits appears somewhat remote.

LEATHER OILS.

By F. C. Rose.

Three classes of oils are necessary and of equal importance in the manufacture of leather. All of these are indispensable for the following reasons.

Animal and fish oils because of their properties of assimilation and emulsification.

Vegetable Oils because of their drying and adhesive properties.

Mineral Oils because of their antiseptic and penetrating properties.

These three classes of fats appear commercially as crystalline, amorphous and fluid.

After rendering the animal, fish and vegetable fats are submitted to a process of fractional refrigeration whereby the crystalline bodies are separated from the more fluid constituents, thereby producing products having a better cold test, and thus leaving the amorphous and poor cold test bodies. These resulting products are then separated by the further refrigeration and pressing, and bleached in the usual way.

Petroleum crude oils are first distilled at such temperatures as will eliminate the volatile portions, which are then condensed and bleached, becoming naphtha, benzine, gasoline and kindred volatile hydrocarbons. The remaining stock is then further distilled for the production of heavier hydrocarbons and waxes.

The Mineral Oils best adapted for leather making are those grades which are thus separated, are homogeneous in character, and are not treated or decolorized by sulphuric acid treatment, but are made light in color by filtration through beds of either animal charcoal or specially prepared filtrating clay. These oils vary in body or density in accordance with the particular work desired, it naturally following that a lighter oil is better when the oil is actually used as a filler. All the oils, however, should be non-volatile, even when subject to a temperature of approximately 200° F. from 12 to 15 hours.

the purpose is simply light oiling off than when

The wax contained in the crude oil is carried over in one of the distillates mentioned above, and is separated by a process of refrigeration and pressing, as indicated. The wax obtained is bleached by washing and filtration, and from the crude wax the various grades are separated out ranging from plastic to very hard crystalline-structured refined wax.

Certain heavy oils carry a percentage of amorphous wax which cannot be separated by pressing. It is, therefore, necessary to resort to refrigeration to accomplish this purpose, which results in improving the fluidity of the oil and produces a very soft type of wax.

As a rule no single distillate will serve the requirements of the leather manufacturer. It has, therefore, been found necessary to select special stocks made within narrow range and blend them so as to secure the definite results desired.

Oils have three distinct missions in the manufacture of leather: giving to it the desired pliability, the essential tensile strength, and the necessary water-resisting properties.

The animal and vegetable fats in their natural state contain more or less free fatty acids—particularly so if they are allowed to deteriorate or become rancid; this is not uncommon with tallows and fish oils which contain moisture, and for this reason, following the rendering process, the admixture of petroleum, which does not contain fatty acids, is essential to prevent deterioration of other fats. As most fish and vegetable oils, except castor and olive, are drying, it is important, therefore, that some non-drying or hydrocarbon oil should be used to prevent excessive oxidation.

For the production of harness, belting and lace leather and splits, the crystalline and plastic or amorphous fats of the different grades are necessary.

In the production of enamel leather, the vegetable and animal oils are essential because of their drying and adhesive properties, and with these mineral oils are blended in such proportions as are necessary to give the desired results.

By the use of a large percentage of petroleum, oxidation of animal and vegetable oils is prevented, and the difficulty of spue and gumming is eliminated, which conditions are brought about because of the action of fatty acids, whereas, no action whatever takes place with the non-drying petroleum or hydrocarbon oils.

USES.

The scientific research work on the above subjects is one that the leather trade chemists and their organization are taking up in a very able manner, and in many respects is beyond the writer's personal knowledge.

The excellent results secured by the leather manufacturers with oils produced according to the above standards, have been very gratifying to them, because of the more uniform and desirable production in the finished leathers.

The essential point most seriously considered by chemists and which is most appreciated by the practical leather manufacturer, is the determination as to the percentages in which the animal, vegetable and mineral or hydrocarbon oils or fats from different sources should be blended to produce the most desirable results in the many grades and various finishes covering the field of harness, belting, sole, shoe, upper and fancy leathers.

DISINFECTION OF HIDES.

By. J. H. Yocum.

In 1908 there appeared an epidemic of the foot and mouth disease in various parts of the United States, which necessitated local quarantine of hides and skins. This brought about from the Government methods for such disinfection as would satisfy the officials and in their judgment prevent the spread of the disease.

The Treasury Department has had various methods of disinfection of imported hides, both dry and salted. During the period when Rinderpest was prevalent in South Africa, a quarantine was placed against hides from this locality unless such hides had been immersed in a 1 to 1,000 bichloride of mercury solution.

Dry hides have been considered disinfected if cured with the so-called hide poison, which is arsenite of soda, but no general rules have been laid down and published until this year. I might interject there that the arsenite of soda is not regarded as a satisfactory germicide. The Government this year presents three different methods, which if followed will be considered satisfactory methods of disinfection, and hides so treated will be considered satisfactory for transportation or entry.

1. By immersion in a 1 to 1,000 solution of bichloride of mercury.

2. By immersion in a 5 per cent. solution of carbolic acid.

3. By exposure to the fumes of sulphur dioxide in a room tightly closed........hides suspended separately......at least four pounds of sulphur burned per thousand cubic feet of air space......hides to be subject to the fumes at least six hours.

Mr. Beye, in a letter sent to the members of the National Association of Tanners, May 16, 1910, states—"This office has reason to believe that any system of disinfection now existent is absolutely without effect with respect to anthrax, and that therefore all measures adopted by the Government, the primary purpose of which is to kill the anthrax germ are unnecessary burdens to the tanning industry."

It appears that this is literally true, but by a modification of the first method the destruction of anthrax as well as all other germs and spores can be effected without injury to the hides or skins so treated.

The trouble with the 5 per cent. solution of carbolic acid is that it is difficultly soluble in water and will not act on fats, and in the presence of fats has no antiseptic properties, and being acid in its character and having tendencies to injure animal matter, a solution of this strength will cause burned spots in the hides, as well as in the case of green salted hides, draw the salt or pickle from the hide, which leaves it in an uncured condition, and even then does not produce a satisfactory destruction of the anthrax spore.

Exposure to the fumes of sulphur dioxide or burned sulphur as under Rule 3, is not only inefficient as a disinfectant, but may occasion all sorts of trouble to the hides and is not feasible on account of the apparatus necessary for its use.

In the case of Rule 1, like most of the salts of mercury, sublimate forms insoluble compounds with albuminoids, (as the albumin of the blood) and has then no longer any effect on bacteria. This reaction is prevented by the addition of five parts of salt per 1,000 of solution. Salt forms with mercuric chloride a double salt soluble in water, even though the water be hard and contains lime and magnesia in solution.

Dr. R. Koch, who made very exhaustive researches on the efficacy of various antiseptics, used the anthrax spore as a control test for the strength of antisepsis. He found that this spore was the most difficult of all to kill, and the cusfom among bacteriologists since has been to use this spore for the purpose of determining the strength of germicides, as well as the relative measure of germ resistance,

Comparing phenol (carbolic acid) with mercuric bichloride he states that in a 1 per cent. solution of phenol, the anthrax spore was not killed in 24 hours, but in a 5 per cent. solution it was killed in 20 hours. The anthrax bacillus was killed by a 1 per cent. solution of phenol in one hour. Phenol has no antiseptic properties when acting on fats.

Mercuric bichloride in a 1 to 24,000 solution kills the anthrax spores in 20 hours. The anthrax spore was killed in a 1 to 1,000 solution in 15 minutes, and germination of spore was prevented in solutions of 1 to 70,000.

Evans found that the anthrax spore was killed in a 1 to 1,000 solution of bichloride in 15 minutes. The bacilli themselves were killed in one minute by a 1 to 15,000 solution.

Koch, White, Evans and Wilcox all agree on the fact that mercuric bichloride destroys the anthrax bacillus and its spore in a very short time in a 1 to 1,000 solution, provided the action of the albuminoids in precipitating the mercuric bichloride be prevented.

In the fall of 1908, foot and mouth disease being prevalent the Government insisted on treatment with carbolic acid. A meeting of the hide dealers in New York was called, and on my suggestion a request was made to change this requirement so that a saturated salt solution could be used as an alternative method for the immersion of wet salted hides, which was agreed to by the Government and which was used by those interested. I have not heard of a single instance where this treatment injured the hide, or where there was any contagion resulting from hides so treated. By making a saturated solution of common salt and adding thereto the necessary quantity of bichloride of mercury, in which the hides are immersed for a short period, the action of the fats, albuminoids and hard water on the bichloride of mercury is prevented and an effective destruction of the germs and the bacilli is made at once. This brine solution of bichloride remains on the hides after bundling for various periods of time, ranging from two days upwards, during which period, it is acknowledged that even the anthrax spore would be effectually destroyed.

By the use of the brine, the hides come out after immersion in practically the same condition as when coming out of pack or pickle.

It is suggested that when hides are under quarantine a solution of 1 pound of $HgCl_2$ to each 2,500 lbs. of hide be made and the solution sprinkled over the hides as they go into the pack; this will effectually destroy any germ or spore existing therein.

Since disinfection is necessary at times, it seems to me that this method should be brought to the attention of the Government as being the most effective method, and that action by the Government should be taken along these lines applicable to our native hides and skins. The Government's idea of immersion in a 1 to 1,000 solution of bichloride of mercury alone without the brine, occasions a drawing of the salt and cure from the hide, leaving it in an unsatisfactory commercial condition, and in the presence of the albuminoids of the blood and the fats of the hide does not satisfactorily destroy such germs as the anthrax spore.

With reference to imported hides where anthrax, Rinderpest, foot and mouth disease or other reasons for quarantining hides either in the salted or dry condition exist, the same methods should be pursued, the determination of the fact of such treatment being necessarily the duty of our Consul.

With dry hides, the immersion in a saturated salt bichloride solution for 5 minutes would effectually destroy the germs without injury to the hides.

REPORT OF THE COMMITTEE ON RAPID COOLING OF TAN SOLUTIONS AND ON FILTRATION (ASBESTOS-KAOLIN METHOD).

W. P. Maxwell, Chairman.

Samples of Ordinary Solid Quebracho Extract, Clarified

Solid Quebracho Extract and Liquid Chestnut Wood Extract and a supply of acid washed asbestos were sent to the members of the committee with the following instructions:

Rapid Cooling of Tan Solutions.

Use the following amounts to make up solutions:

Ordinary Quebracho	**6 grams to 1000 c.c.**
Clarified Quebracho	**6 grams to 1000 c.c.**
Chestnut Wood Extract	**15 grams to 1000 c.c.**

Use on the basis of 12½ grams dry hide powder to 200 c.c. liquid.

Make all determinations in duplicate, that is, make up two separate solutions of each sample and two pipettings and weighings of each separate solution.

Methods:

1. Make up solutions and make complete analysis according to the Official Method.

2. Make up solutions with hot water at 80° C. to 900 c.c., cool under hydrant to 20° C. Make up immediately to 1,000 c.c. and, after pipetting the total solids, proceed with filtration and non-tannin determination at once.

3. Make up solutions with hot water at 80° C. to 900 c.c., place the flask in a pan of water kept at 15° C., remove when the temperature of the solution reaches 20° C., make up to 1,000 c.c., pipette total solids and proceed at once with filtration and non-tannin determination.

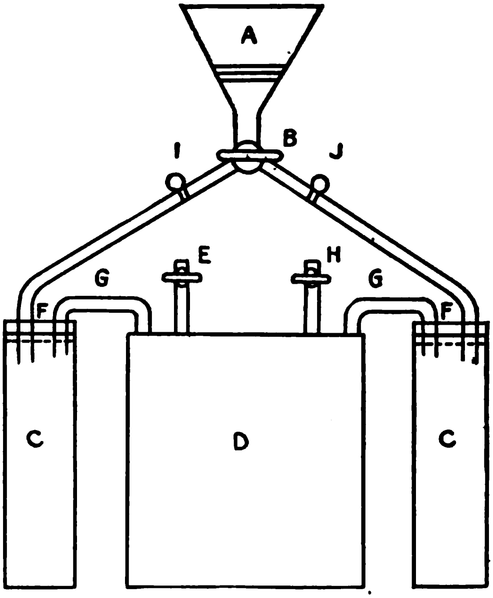
4. Make up solutions with hot water at 80° C. to 900 c.c., cool slowly, possibly by placing in an open window, to 20°—25° C. make up to 1,000 c.c. and proceed at once with complete analysis.

In cooling solutions, the temperature should not be allowed to go below 20° C.

FILTRATION, (ASBESTOS-KAOLIN METHOD).

Description of Apparatus.

A, glass funnel of sufficient size to hold enough solution to complete the operation. In this is placed a porcelain filter plate provided with a rubber ring. B, is a two-way cock, if not at hand, compression cocks on rubber tubing may be used at I and J, the latter, possibly, being preferable. C and C_2, wide necked bottles. D, vacuum tank, which may be a large necked bottle with cork having four perforations. E, cork to break vacuum. H connection with cock to vacuum gauge and pump. G, glass tube connections. F, perforated rubber stoppers. All connections should be air tight.



DIRECTIONS.

Do all work in duplicate.

Use the following amounts in making up solutions:

Ordinary Quebracho	6 grams to 1000 c. c.
Clarified Quebracho	6 grams to 1000 c. c.
Chestnut Wood Extract	15 grams to 1000 c. c.

Follow official instructions for making up solutions for analysis of extracts.

Methods:

1. Determine total solids by Official Method.
2. Determine soluble solids by Official Method.
3. Determine soluble solids as follows:

Digest 3 grams of asbestos with 100 c.c. of analysis solution in a small beaker.

Digest 2 grams of kaolin with 50 c.c. of analysis solution in a small beaker.

Using an apparatus like that shown in the accompanying drawing, start the suction pump going, and throw the solution containing the asbestos on the filter plate A, with the cocks I and H open, E and J closed. Pull the asbestos down to a firm mat by suction, then throw on the solution containing the kaolin and allow the vacuum to run up to 16 in. Hg. Close the cock H. Fill funnel with solution, at least 150 c.c. should be allowed to run through before beginning to collect. When filtrate passing through is brilliantly clear, close I, open J, and collect the 100 c.c. to be evaporated, in C_2. The mat should be kept covered and if it becomes necessary to add more solution during the filtration, do so carefully so as not to disturb the mat.

Separate determinations under Method 3, using asbestos prepared by yourself are requested.

In this connection it is suggested that the report of last year's committee in the *Journal* for Mar. 1910, page 179, be read.

The results submitted by those who took part in the work are as follows: (In each case the percentage given is the average of several different determinations made.)

RAPID COOLING OF TAN SOLUTIONS.

Ordinary Quebracho Extract.

	Methods	I	II	III	IV
1. R. H. Wisdom	T. S..........	93.77	93.81	93.94	93.79
	S. S..........	85.61	86.47	86.85	87.15
	Ins...........	8.16	7.34	7.09	6.64
	N. T....	7.28	7.22	7.22	7.56
	Tan..........	78.33	79.25	79.63	79.59
2. W. A. Fox	T. S..........	93.77	93.44	93.44	93.50
	S. S..........	86.31	86.06	86.13	86.52
	Ins...........	7.46	7.38	7.31	6.79
	N. T....	7.47	7.42	7.44	7.39
	Tan..........	78.84	78.64	78.69	79.13
3. W. P. Maxwell	T. S..........	93.43	93.41	93.18	92.70
	S. S..........	86.30	86.10	86.33	86.64
	Ins...........	7.13	7.31	6.85	6.06
	N. T....	7.25	7.20	7.32	7.60
	Tan..........	79.05	79.01	79.01	79.04

	Methods	I	II	III	IV
4. J. M. Seltzer	T. S.	92.77	92.73	92.91	92.89
	S. S.	85.06	85.08	85.70	86.80
	Ins	7.72	7.65	7.21	6.09
	N. T.	6.38	6.41	6.54	6.75
	Tan	78.68	78.67	79.16	80.05
5. F. B. Shields	T. S.	94.67	94.67	94.67	94.67
	S. S.	88.34	88.28	87.69	88.21
	Ins	6.33	6.39	6.98	6.46
	N. T.	7.45	7.26	7.32	7.57
	Tan	80.89	81.02	80.37	80.67
6. C. R. Oberfell	T. S.	93.53	93.40	93.89	93.82
	S. S.	87.72	87.45	87.27	88.02
	Ins	5.81	5.95	6.62	5.80
	N. T.	6.65	6.72	6.69	6.60
	Tan	81.07	80.73	80.58	81.42
7. T. J. Mosser	T. S.	93.89	93.05	92.77	93.48
	S. S.	85.65	85.72	85.93	86.53
	Ins	8.24	7.33	6.84	6.95
	N. T.	8.27	7.65	7.61	8.22
	Tan	77.38	78.07	78.32	78.31

Clarified Solid Quebracho Extract.

	Methods	I	II	III	IV
1. R. H. Wisdom	T. S.	88.38	88.33	88.44	88.40
	S. S.	87.77	87.64	87.79	87.83
	Ins	0.61	0.69	0.65	0.57
	N. T.	13.78	13.78	13.78	13.83
	Tan	73.99	73.86	74.01	74.00
2. W. A. Fox	T. S.	No report.			
	S. S.				
	Ins				
	N. T.				
	Tan				
3. W. P. Maxwell	T. S	87.70	87.97	87.80	87.24
	S. S.	87.20	87.56	87.43	87.02
	Ins	0.50	0.41	0.37	0.22
	N. T.	13.62	13.67	13.75	13.32
	Tan	73.58	73.89	73.68	73.70
4. J. M. Seltzer	T. S.	87.18	87.06	87.43	87.26
	S. S.	86.87	86.81	87.02	86.83
	Ins	0.31	0.25	0.41	0.43
	N. T.	12.94	12.99	13.04	13.31
	Tan	73.93	73.82	73.98	73.52

	Methods	I	II	III	IV
5. F. B. Shields	T. S.	88.61	88.61	88.61	88.61
	S. S.	78.60	88.47	88.46	88.38
	Ins	0.01	0.14	0.15	0.23
	N. T.	14.60	14.50	13.99	14.07
	Tan	74.00	73.97	74.47	74.31
6. C. R. Oberfell	T. S.	87.96	88.02	88.11	88.02
	S. S.	87.72	87.44	87.69	87.69
	Ins	0.24	0.58	0.42	0.33
	N. T.	13.35	13.45	13.53	13.44
	Tan	74.37	73.99	74.16	74.25
7. T. J. Mosser.	T. S.	88.19	87.19	87.09	87.76
	S. S.	87.15	86.22	86.86	87.15
	Ins	1.04	0.97	0.23	0.61
	N. T.	15.35	13.41	14.43	14.36
	Tan	71.80	72.81	72.43	72.79

Liquid Chestnut Wood Extract.

	Methods	I	II	III	IV
1. R. H. Wisdom	T. S.	40.68	40.61	40.64	40.64
	S. S.	40.46	40.19	40.30	40.33
	Ins	0.22	0.42	0.34	0.31
	N. T.	15.05	14.89	14.94	14.95
	Tan	25.41	25.30	25.36	25.38
2. W. A. Fox	T. S.	40.37	40.43	40.36	40.41
	S. S.	40.06	40.06	40.04	40.01
	Ins	0.31	0.37	0.32	0.40
	N. T.	14.69	14.75	14.50	14.67
	Tan	25.37	25.31	25.54	25.34
3. W. P. Maxwell	T. S.	40.47	40.64	40.50	40.38
	S. S.	40.14	40.19	40.11	40.02
	Ins	0.33	0.45	0.39	0.36
	N. T.	14.94	14.83	14.94	14.84
	Tan	25.20	25.36	25.17	25.18
4. J. M. Seltzer	T. S.	40.55	40.41	40.46	40.45
	S. S.	40.10	39.98	40.00	40.07
	Ins	0.45	0.43	0.46	0.38
	N. T.	14.70	14.80	14.71	14.85
	Tan	25.40	25.18	25.23	25.22
5. F. B. Shields	T. S.	40.71	40.71	40.71	40.71
	S. S.	40.52	40.39	40.48	40.43
	Ins	0.19	0.32	0.23	0.28
	N. T.	14.91	14.90	15.14	15.72
	Tan	25.61	25.49	25.34	24.71

	Methods	I	II	III	IV
6. C. R. Oberfell	T. S.	40.63	40.58	40.51	40.64
	S. S.	40.39	40.33	40.30	40.15
	Ins	0.24	0.25	0.21	0.49
	N. T.	15.08	14.79	14.84	14.90
	Tan	25.31	25.54	25.46	25.25
7. T. J. Mosser	T. S.	40.27	39.82	39.99	40.26
	S. S.	39.84	39.62	39.60	40.02
	Ins	0.43	0.20	0.39	0.24
	N. T.	15.35	14.58	14.78	15.21
	Tan	24.49	25.04	24.82	24.81

FILTRATION, (ASBESTOS-KAOLIN METHOD).

Ordinary Solid Quebracho Extract.

	Methods	I T. S. official	II S. S. official	III S. S. (A-K)
W. A. Fox	Per cent	93.77	86.31	84.66
	Time		100 min.	58 min.
	Appearance		Opalescent	Clear
C. R. Oberfell	Per cent	93.82	87.26	88.65
	Time		55 min.	20 min.
	Appearance		Opalescent	Clear
W. P. Maxwell	Per cent	93.35	86.25	85.66
	Time		180 min.	45 min.
	Appearance		Clear	Clear
T. J. Mosser	Per cent	93.32	86.44	86.92
	Time		115 min.	30 min.
	Appearance		Clear	Clear

Clarified Solid Quebracho Extract.

W. A. Fox	Per cent	87.84	87.08	86.80
	Time		45 min.	5 min.
	Appearance		Clear	Clear
C. R. Oberfell	Per cent	88.14	87.88	87.85
	Time		12 min.	1 min.
	Appearance		Clear	Clear
W. P. Maxwell	Per cent	87.80	87.25	87.15
	Time		60 min.	5 min.
	Appearance		Clear	Clear
T. J. Mosser	Per cent	88.19	87.29	88.67
	Time		30 min.	10 min.
	Appearance		Brilliant	Clear

Liquid Chestnut Wood Extract.

	Methods	I	II	III
W. A. Fox	Per cent	40.37	40.06	39.61
	Time		50 min.	5 min.
	Appearance		Clear	Clear
C. R. Oberfell	Per cent	40.75	40.22	40.28
	Time		15 min.	8 min.
	Appearance		Clear	Clear
W. P. Maxwell	Per cent	40.52	40.10	39.85
	Time		35 min.	10 min.
	Appearance		Clear	Clear
T. J. Mosser	Per cent	40.47	40.00	40.14
	Time		35 min.	15 min.
	Appearance		Clear	Clear

Mr. Wisdom sends report of Rapid Cooling of Tan Solutions on a Hemlock and Chestnut Oak Bark Extract, as follows:

Hemlock Bark Extract.

Methods	I	II	III	IV
T. S.	43.59	43.53	43.52	43.50
S. S.	38.93	38.90	38.90	39.52
Ins	4.66	4.63	4.62	3.98
N. T.	14.73	14.29	14.47	14.56
Tan	24.20	24.61	24.43	24.96

Chestnut Oak Bark Extract.

Methods	I	II	III	IV
T. S.	44.78	44.76	44.83	44.77
S. S.	43.38	43.57	43.74	43.41
Ins	1.40	1.19	1.09	1.36
N. T.	18.36	18.24	18.20	18.14
Tan	25.02	25.33	25.54	25.27

COMMENTS.

R. H. WISDOM:—I enclose also results on a Hemlock and Chestnut Oak Bark Extract which I think you will find interesting. In regard to the figures given, would say that the room temperature during these experiments was about 23° C. The hydrant water used to cool in Method 2 was 27° C., thus necessitating an after cooling in water at 15° C. In Method 4, the solutions were cooled slowly to room temperature (23°) and then brought to 20° in water at 15°. All soluble solids filtrations were perfectly clear with the exception of those from Ordinary Quebracho on Method 2, 3, and 4, which were slightly opalescent.

Remarks, (R. H. Wisdom)

Ordinary Quebracho.—The rapid cooling shows an apparent decrease in the insolubles, explained by the slightly opalescent filtrates, and no effect on the non-tannins with the exception of Method 4, which shows an increase, and at the same time, the lowest insolubles.

Clarified Quebracho.—The different methods of cooling here have practically no effect on either non-tannins or insolubles.

Chestnut Wood Extract.—In this case, the Rapid Cooling Methods as against the Official Method, shows merely an interchange of non-tannins to insolubles, resulting in practically no difference in the ultimate tannin figure.

Hemlock Bark Extract.—Here the rapid cooling has no effect on the insolubles with the exception of Method 4, which, in the case of the Ordinary Quebracho, gave the lowest insoluble figure. Rapid Cooling has evidently decreased the non-tannins.

Chestnut Oak Bark Extract.—In this case the Rapid Cooling shows a decrease in the insolubles with the exception of Method 4, which shows no change. All filtrates perfectly clear. The non-tannins also show a decrease.

In conclusion, I would state that the figures seem to show that with extracts containing low insolubles, such as Chestnut and Clarified Quebracho, the Rapid Cooling does not effect the ultimate tannin figure to any great extent. In extracts containing considerable insolubles, such as Ordinary Quebracho and Hemlock, the Rapid Cooling has a marked effect, and in the case of Ordinary Quebracho at least, seems to show error, in that by the Official Method a clear filtrate was obtainable, whereas in the filtrates from the Rapid Cooling Methods it was impossible to remove the slight opalescence, as reflected in the lower amount of insolubles shown.

C. R. Oberfell:—One point appeals to me which is as follows:—Most tan extracts, etc., do contain insolubles and in order to test these methods properly, I do not think we should limit ourselves to the three classes of samples set out. I suggest continuing the work of your committee into next year when additional work can be done which will cover a more varied class of tanning materials. I also would eliminate the Rapid Cooling Method 2, for here lies a great chance for variation. The hydrant water in every laboratory differs in temperature, as well as the same water in every laboratory differs with the seasons, *e. g.*, the hydrant water in my laboratory varies from 12° in winter to 22° in summer.

This is the third year I have been on the Asbestos-Kaolin Committee, and your apparatus is the first with which I have had any success. I also find that a two-way stop-cock is a distinct advantage, both in point of accuracy and time, over the screw pinch-cocks.

My results show that the method gives the same results as the Official Method on tolerably clear infusions, but on the Ordinary Quebracho they are poor. Perhaps this is my fault, but without any special investigation to prove my assumption, I am inclined to the belief that when the solution in the collecting flask is allowed to remain any length of time there is a rapid evaporation and hence concentration due to the rarified condition of the air over the solution in the flask. Thus, in the case of the Ordinary Quebracho, which took both 25 and 15 minutes to filter, the residue weighs more than that from the soluble solids as per the Official Method. The filtered solution was clear, showing no opalescence by reflected light, so is it not reasonable to ascribe the cause to evaporation.

THOMAS A. FAUST:—(Mr. Faust made no determinations on the samples sent out but sends results of his former experiments and writes as follows:)

I regret very much that I did not consent to serve on the committee, as I do not think one can come to a very definite conclusion without investigating it thoroughly.

The Asbestos-Kaolin Filtration Method certainly would be a great nuisance in a large laboratory, and as I said in my opinion on the subject, I would not be in favor of making it Official.

In regard to the Rapid Cooling of Tan Solutions, I have done some work on this during the past year, and have never been able to notice any appreciable difference in the results.

Remarks: (Thomas A. Faust.)

Rapid Cooling of Tan Solutions.—I have worked on this subject considerably during the past year, and as a result believe that by using certain precautions, there is no great difference between tan solutions that have been cooled rapidly and solutions cooled according to the Official Method.

After dissolving the extract, I allow it to stand for about one-half hour, then cool under the tap to room temperature, shaking frequently before and after placing under the tap.

I have compared the two methods on Chestnut, Sumac, Myrabolam, Clarified Quebracho and Ordinary Quebracho, and with the possible exception of Ordinary Quebracho, find all results within the limit of error. Ordinary Quebracho, however, on rapid cooling, will show a slight decrease in non-tannins with a corresponding increase in tannins, but this does not appear to average over 0.2 per cent.

In view of this, I am much in favor of adopting the rapid cooling of tan solutions as an alternative method.

Asbestos-Kaolin Filtration Method.—I cannot see that any great advantage is obtained by the use of the Asbestos-Kaolin Filtration Method. It must be admitted that Ordinary Quebracho, Hemlock and Oak Extract and Spent Tans are filtered more rapidly by this method, but in a large laboratory where a considerable number of determinations are run daily, the time saved is more than offset by the difficult manipulation and cumbersome apparatus.

The only advantage gained by rapidity in filtration would be due to preventing loss by evaporation, but is the loss by evaporation in the Official Method, using ordinary precautions, as great as in the proposed method by the vacuum?

With Ordinary Quebracho, the Official Method does not always give brilliant filtrates, while the Asbestos-Kaolin Method does, but more concordant results are obtained by the former than by the latter method. However, this may not be the case when one becomes more familiar with the apparatus and manipulation.

It does not appear that there is any loss of Tannin through absorption by the filter-paper or the asbestos when the methods are followed. I had some difficulty in securing a good mat, but I believe this would be overcome by practice.

I am not in favor of making this Asbestos-Kaolin Filtration Method Official, although it might be well to make it an alternative method.

W. A. Fox:—As I have not done the work I would have liked to, it would be hardly fair for me to make any criticisms.

T. J. Mosser:—*Rapid Cooling of Tan Solutions.*—Method 2, (Cooling under the hydrant) is not very desirable as the temperature of the tap water varies considerably. On the day that this experiment was run the water in our laboratory had a temperature of 21°, so you can see that it was impossible to get the solution down to 20°.

Method 3, (cooling in water-bath kept at 15°), seems to be the most desirable of the proposed methods in that the conditions of cooling would be constant the year around, but on the other hand it is very inconvenient in that ice had to be used in order to get water at that temperature.

Method 4, (cooling in an open window), is entirely out of the question as I had to wait several days in order to get a day in which the solution would cool enough in time to complete the analysis the same day.

In all cases the rapid cooling did not effect the amount of insolubles to any marked degree.

Asbestos-Kaolin Method.—This was my first attempt at using the Asbestos-Kaolin Method and I must say that I was very favorably impressed with the method. There was no difficulty in getting brilliantly clear filtrates in much shorter time than by the Official Method. An apparatus similar to the one you figured in your instructions was used and it seems to me that the fault of cumbersomeness could not be placed on this apparatus as several could be put in a very small space. The item of time is much shorter in comparison with the Official Method than the figures would indicate as the time required to get a clear filtrate is very short, in most cases 5 to 10 minutes, compared with the hour in the Official.

SUMMARY.

In examining the reports submitted by the different members of this committee, one is impressed at once by the lack of concordance in the values obtained and the non-conformity of results under the suggested methods of cooling. This is very striking in the case of the Ordinary Quebracho and only slightly less so with the Clarified. At first thought, this might seem to reflect discredit not only on the suggested modifications but on either the individual manipulations or on the Official Method as a whole.

It is unnecessary to state that Quebracho Extract, and especially the Ordinary, is extremely difficult to analyze accurately; and to obtain closely agreeing results by different analysts, exact uniformity of the minutest details of manipulation must be observed. When it is borne in mind that in these experiments a variation of one milligram (0.0010 grm.) in the average weights of the soluble solids residues makes a difference of nearly two tenths of one per cent., (0.20 per cent.) in the results it is evident, in order to obtain closely agreeing results, the residues must not only be dried to the same state but must be weighed accurately and under the same conditions.

Before any trustworthy results can be obtained on which to determine which is the better of suggested methods or if this or that modification of the Official Method effects the ultimate results, it would seem advisable to adopt uniform methods in even the minutest details of manipulation in order that individual analysts may work under the same conditions and thus obtain closer values. The Official Method requires that a uniform style of evaporating and drying oven shall be used and it would seem advisable to go a step further and require that a uniform method of heating the oven should be employed—if with live steam, state what pressure, in order that residues may be dried under the same conditions. In weighing doubtless better results would be obtained if the dish containing the residue were covered before removing from the desiccator and kept covered during the weighing, in this way avoiding contact of the room atmosphere with the residue. Quebracho residues pick up moisture from the ordinary room atmosphere very quickly and but a little is necessary to so influence the weight as to make close concordance of results impossible. Doubtless these minor details and possibly a difference in the temperature of the room and solutions during filtration are responsible for much of the discrepancy in the results given on the Quebracho Extract reports.

In attempting to obtain any information from the results submitted on which to base an opinion it is impossible to consider them as a whole and averages of the results would show little. Considering them individually and beginning with the analysis of Ordinary Quebracho Extract under the diffierent methods of cooling, analyst No. 1 finds that the rapid cooling gives higher solubles, lower insolubles practically the same nón-tannins and higher tannins. Analyst No. 2 finds little difference in any of the values by the different methods except 4, (cooling in current of air) which gives about the same non-tannins as the other methods but higher solubles and tannins. Analyst No. 3, little difference in the values, the rapid cooling seemingly by giving slightly higher solubles and non-tannins but practically no difference in tannins. Analyst No. 4 higher solubles and tannins by the rapid cooling. No. 5, slightly higher solubles and tannins cooled under hydrant but slightly lower values for both by the other rapid cooling method than by the Official. Analyst No. 6 Method 2 and 3 lower Soluble Solids and tannins, Method 4 higher for both than by official.

Analyst No. 7 slightly higher soluble solids and Tannins by rapid cooling than by Official. In the case of the Clarified Quebracho and the Chestnut Wood Extract, but very little difference is found in the values obtained by the Analysts under the different methods.

In summing up, possibly no better statement can be made than to quote one of the analysts when he says: "The figures seem to show that with Extracts containing low insolubles, such as Chestnut and Clarified Quebracho, the rapid cooling does not effect the ultimate tannin figures to any great extent. In extracts containing considerable insolubles, such as the Ordinary Quebracho and Hemlock, the rapid cooling has a marked effect, and in the case of the Ordinary Quebracho at least, seems to show error, in that by the Official Method a clear filtrate was obtainable, whereas in the filtrate from the rapid cooling method it was impossible to remove the slight opalescence, as reflected in the lower amount of insolubles shown."

While the results of the work of this Committee are not conclusive, still taken in conjunction with the reports of previous committees on the same subject, it would seem that some method of rapid cooling might be adopted, at least, as an alternative method. It is therefore, suggested that further experiments be made with a greater variety of tanning material, making up the solutions according to the Official Method, allowing them to stand half an hour, then cooling to 20° by placing in a water-bath kept at 15° C., the evaporating and drying to be under uniform conditions and weighing with dishes covered.

The results of the small amount of work on the Asbestos-Kaolin Filtration done by this year's committee, prove little and leave the matter practically where it was before. It seems to be generally admitted that it is possible with a proper apparatus, proper mat and proper precautions, to obtain a clearer filtrate and lower solubles in less time than by the Official Method, but it is quite evident that the results obtained by different analysts with the Asbestos-Kaolin Filtration Method show greater variation than by the Official Method. It may be possible to so perfect this method that concordant results can be obtained, but at present its adoption would tend to produce greater difference in the values than those obtained by the Official Method. The opinion of the Committee seems to be that it would not be advisable to recommend its adoption.

DISCUSSION.

Mr. Hoppenstedt:—I have found that when extracts are rapidly cooled that they should be kept in constant motion because in using water at 15° the outside portions of the solution are cooled down far lower than the inner portions, and in that way incorrect results are obtained. I would suggest that the committee next year working on the rapid cooling of extracts should keep these solutions in constant motion during cooling, and I think that they would find better results.

Mr. Veitch:—It seems to me that any method of rapid cooling would be objectionable, and certainly would not give comparative results with our present method if we cool below analysis temperature. Now if we are going to analyze at 20° the solution in cooling should not be cooled below 20° at any point, because if it is there will be more insoluble material thrown out and part of that insoluble material at that temperature will certainly not go in solution, and we may expect from that cause lower results. I think that is the explanation of the lower results in those cases where lower results are gotten.

Mr. Faust:—I would state that I followed the same procedure of keeping the flask in motion as it is being cooled. I let it stand at least half an hour before starting to cool it. During that time I shake it every two or three minutes vigorously, and that was the reason I made the statement that in my opinion the difference is not very great except in the case of quebracho. With the exception of quebracho I find that following that procedure there is very little difference,—within the limits of error.

Mr. Hurt:—I want to make a statement in connection with the error. There is always considerable error in the weight on account of the small amount used in analysis,—that is, one milligram makes a difference of two-tenths of one per cent. Now why couldn't the method be so changed that the amount of extract used where the tannin content is very high should be say sufficient to give a total solid weight or soluble weight of 0.7 of a gram on the soluble solids and total solids, the solution for non-tannins to be diluted as per the official method? I think most of the cause of the trouble with the official method is due to the error in the weight of the soluble solids, which could be eliminated by using a larger proportion for that work.

Mr. Veitch:—In that connection I might say that while I agree perfectly with Mr. Hurt on the fact that the error is increased, the working error is multiplied, where we run less than a gram, figuring back to percentage; yet we used to have the 0.7 of a gram and abandoned it for some cause or other, and undoubtedly we got smaller error due to the multiplication of that working error, but we introduced probably other errors due to imperfect drying, or long-continued drying.

ABSTRACTS.

Meeting of the Belgian Section. J. WAUTERS. *Collegium*, 1910, pp. 343-4.—M. Godfrind reported that leather loses 30 per cent. in resistance when scarred by warbles. Anatomists have shown that the healing is never perfect.

Dr. Nihoul found that an alternating electric current promoted plumping in HCl or water. With vegetable tans the current causes loss of tannin in bath up to 50 per cent. according to the amperage. At the anode insoluble flocks separate, either polymeric or oxidation products. If the electrodes be connected by hide, the tannage is improved with increased rendement. These researches are to be continued.

Rules for Sampling Liquid Extracts. R. LEPETIT. *Collegium*, 1910, pp. 382-4.—The writer dwells upon the importance of representative sampling and doubts whether the method prescribed by the I. A. L. T. C. is well suited. He proposes the following procedure. The cask is rolled over a course of about 20 meters then stood one minute first on one end, then the other. Two buckets of extract are then drawn off of about 18 liters each. The cask is again agitated vigorously, the portion drawn off replaced and all again agitated a little before sampling. The operation is carried out 6 or 7 times as rapidly as according to the official method, and leaves the ware in good condition. Instead of sampling a uniform 5 per cent. of the total number of casks, the writer prefers a sliding scale, the ratio decreasing as the number increases. For 20, 50, 100, 200, 300, 400 and 500 casks he would sample 3, 6, 9, 13, 16, 19 and 22 casks each, these numbers being derived by extracting the square root and subtracting one.

Apparatus for Tannin Extraction. GEORGE GRASSER. *Collegium*, 1910, pp. 345-7.—The ordinary extraction apparatus has the disadvantage of frequent blocking of the sand filter and requires at times over 1,000 cc. of water. If an ordinary Soxhlet extractor be used, the protracted boiling decomposes some of the easily soluble tans, besides the apparatus is fragile. The writer gives a drawing of a modified Soxhlet extractor. An adapter tube of 2 mm. sheet copper, 50 mm. × 20 cm. is connected by a cork with a liter flask. Inside the adapter tube rests loosely a similar tube 38 mm. × 16 cm. loosely plugged at the bottom by cotton and charged with the material for extraction. Small amounts of water, rising from 25° to 60° C. are gradually added until about 400 cc. extract are obtained. The liter flask is then substituted by an Erlenmeyer flask containing 250 cc. water which is kept boiling one hour, using an inverted condenser. No decomposition need be feared. In some cases another hours' treatment with a fresh portion of water may be needed. For the analysis of spent bark the preliminary leaching with hot water is omitted.

New Method for the Determination of Nitrogen in Leather. U. J. THUAU. AND P. DE KORSAK. *LeCuir,* [3], 1910, pp. 506-9.—This determination requires accuracy since in computing the dermal substance any variation is multiplied by 5. In the usual determination by Kjeldahl, it is difficult to judge when the last traces of ammonia are expelled. The method here described is an adaptation of the well known process of decomposing ammonia, urea and other amines by alkaline hypobromite into gaseous nitrogen which is measured. The leather sample is decomposed with H_2SO_4 as in the usual Kjeldahl process, the oxidation being completed by addition of MnO_2. The acid ammoniacal solution is then transferred to a special burette which cannot well be described without the author's illustration, but resembles the Bunte burette and permits the introduction of the reagents within the burette before mixing. The burette is immersed in water in a cylinder to secure uniform temperature. Analyses of about 0.3 grams leather yielding about 17 cc. N gave 6.85, 6.87, 6.86, and 6.85 per cent. N while 0.5 grams Kjeldahl gave 6.90, 6.95 and 6.81 per cent. The instrument may be obtained at the Maison Fontaine, 20 rue Monsieur-le-Prince, Paris, and is called the Desmonlières ureometer or the Thuau and de Korsak nitrometer.

Experiments upon the Determination of Tannin Without Hide Powder. ROBERTO LEPETIT. *Collegium,* 1910, pp. 375-9.—Insolubles, total solubles and water were determined as usual. The tannin was precipitated by ammoniacal zinc acetate. Twenty grams pure zinc acetate (Merck) were dissolved in 80 cc. water, and 12 cc. of ammonia acetate added which had been prepared by saturating glacial acetic acid with concentrated ammonia until blue litmus paper turned violet and red paper bluish. To the mixture were then gradually added with stirring 8 cc. concentrated ammonia. The cooled liquid deposited a slight crystalline precipitate; the filtered solution was used as reagent.

To 100 cc. of liquor containing 4 to 5 grams tannin per liter, 6 cc. of the zinc acetate solution were added in portions of 2 cc. with vigorous agitation, let stand 5 minutes and filtered. The filtrate gave no reaction with gelatine or cinchonine sulphate. The excess of zinc in 65 cc. of the filtrate was precipitated by NH_4HS. The filtrate was evaporated at 102-5° in vacuo to constant weight. A blank test gave non-volatile residues in the reagents of 0.0139 grams to be deducted, giving corrected nontans.

Comparative analyses gave per cent. non-tans in extracts of 14 grams per liter:

	Chestnut, decol.	Chestnut, crude	Mimosa, D.
Zinc method ...	8.46 8.43	6.56 7.00	11.81 11.95
Filter method	7.62	5.33	10.52 10.81

	Sumac	Quebracho	Mangrove, purif.
Zinc method	14.3 1.44	1.87 1.91	7.67
Filter method ...	13.8	2.06	

Estimation of Free Acid in Chrome Leather. GEORGE GRASSER. *Collegium,* 1910, pp. 381-2.—This determination is important not only in the green leather coming from the bath, in order to control the alkaline treatment, but also in the examination of the de-acidified leather, especially when it is to be dyed. The author warms 20-30 grams finely cut sample, waste from the splitting machine for instance, with 30-40 cc. normal HCl or H_2SO_4 in an Erlenmeyer flask with invert condenser to clear solution, requiring one-half to one hour. After cooling, a few drops of methyl orange are added and normal alkali equivalent to acid used. The titration is then continued to neutrality. If the green color of the Cr salt masks the end-point, spotting on litmus paper is employed. All the chromic acid originally present is reduced and if desired the Cr may be determined by a volumetric method (to be described later), since the organic matter would hinder precipitation.

Tanning Materials; Birch Bark, Canaigre. U. J. THUAU. *Le Cuir,* [3], 1910, p. 479.—Birch bark is used chiefly in northern Europe, the tree growing in Russia, Finland, Norway and certain parts of Germany. In North America the varieties differ from those of Europe. The average tannin content is 10 per cent., but varies from 6 to 18 per cent., being greatest in the trunk. The sugar is from 2 to 3 per cent., and the water 13. The inner portion of the bark is richest in tannin. A Bohemian bark analyzed 17.6 tans, 10.7 non-tans, 58.7 insoluble, 13 per cent. water. This material is used chiefly for upper and harness leather. To the volatile oil of birch is due the peculiar odor of Russia leather. The tannage is very clear, especially adapted for leather to be dyed. The tannin penetrates rapidly and gives a soft, supple leather. In Norwegian ports the bark sells for 9 to 10 francs per 100 kilos.

Canaigre, the root of a herbaceous plant, Rumex Nymenosepalus Torr. comes from Mexico and neighboring countries. It comes in commerce as the dried root or the extract which is made direct from the fresh root. The tannin content varies from 20 to 35 per cent., being almost completely soluble in fresh water. The root since it contains starch should not be extracted above 50° C. Sugar is high, the ratio to 100 parts of tannin being between those of oak and pine, or 26 to 31. It colors leather much like oak; used alone, it serves for upper and saddler's leather, giving a soft ware. In mixture it is a good adjunct to valonia and mimosa. It is too dear to be much used, costing from 20 to 25 francs per 100 kilos.

D. D. G. Extract and its Employment in Tanning. M. CORRIDI, from Report of Experiment Station at Naples, through *Ledertechn. Rundschau,* 1910, p. 293.—This product has been in the market some time and is claimed to be a good substitute for puer in glove leather tanning and to effect a considerable saving in egg yolk and meal. The author's experiments were made to test these points. The extract consists essentially of an aqueous solution of malt made by a special process, being a thick, syrupy liquid, not entirely soluble in water of an acid odor and sweet taste. It analyzes:

Water and volatile matter	28.50
Solids, dried at 110°	71.50
Ash	0.27
Fixed acid (as tartaric)	1.27
Volatile acids	traces
Reducing sugars	32.0

The practical experiments were made with small goat skins, using in place of the puer and bran baths both D. D. G. Extract alone, 8 to 10 grams to each hide and 2 grams extract with sufficient lactic acid to neutralize the lime. The hides were tanned in the usual way with egg yolk, meal and alum, and were remarkably white, soft and elastic. The softness was indeed excessive and it was found that better results were obtained on reducing the amount of egg yolk. The proportions vary according to the hide but in general one-third sometimes one-half the usual amount may be saved. The leather obtained was dyed in light shades very satisfactorily.

Artificially Colored Extracts. GEORGE GRASSER. *Collegium*, 1910, pp. 379-80.—A sample of extract had a suspicious yellow color in dilute solution and a drop on filter-paper gave a peculiar yellow zone. To test for auramine, the author first made a trial test as follows: to a pure chestnut extract one-half per cent. auramine was added and to 5 cc. of this mixture, 2 cc. dilute NaOH (1.10). This was extracted with 5 cc. benzol by shaking, the benzol solution separated and filtered through a dry filter on which it left a yellow zone. From the benzol solution, a yellow color could be extracted with dilute H_2SO_4 and concentrated acetic acid. The same tests applied to the suspected extract gave similar but more marked results while the pure chestnut extract alone and several samples of other manufacture gave no reaction. Nine other yellow dyes were tested but gave little or no color. Picric acid is fixed by alkali and is then insoluble in benzol and can be thus distinguished from auramine.

Russia Leather Manufacture. *Les Laines et Cuirs* through *Le Cuir*, [3], 1910, p. 458.—The hides are softened 4 days, then removed from the horses for 3 days soaking; if they do not soften readily, 150 to 160 grams sulphate of soda are added to each 100 liters water. They are then placed flesh upward in the limes which are prepared with 24 l. hot water, 10 k. sulphate soda, 10 k. slaked lime. In 2 to 3 days they may be unhaired and then replaced 8 days in a lime bath. They are then thoroughly rinsed, the flesh side aired and placed in a bath of 300 l. warm water, 20 k. wheat bran, 5 k. sour starch paste (yeast). The bath is maintained at a constant temperature, the bating lasting 24 hours; then both sides of the hides are rinsed. The tanning is carried out in a liquor containing 10 k. sumac 2½ k. birch tar (sic. *goudron*), which last is first dissolved in boiling water. Willow bark is best suited to fix it, the leather the characteristic odor to Russia leather. When the hides are well swollen, they are placed in vat, well spread out and separated by layers of willow bark, this being renewed several times during some weeks until the tannage is complete. The hides are then plunged in a bath bran, yeast and salt which gives a marvelously velvety touch to the leather and great suppleness. For red colors aniline dyes are used. For dull black, the inferior skins are chosen, a treatment with logwood preceding the application of the black itself.

Process for Liquefying Organic Colloids. Friedrich Supf. *Zeit. Chem. u. Ind. d. Kolloide,* [5], No. 5.—It was found that the salts of organic sulpho acids and their derivatives, especially the salts of the cheap naphthalene sulpho-acids, exert a liquefying action upon a number of organic colloids such as agar, gelatine, casein, starch and dextrin. This property may be applied in the preparation of a number of useful technical products, especially from animal glue which gives an almost colorless permanent solution at ordinary temperature. Commercial dextrin, particularly the thick white solutions, treated with naphthalene sulphonates, become more transparent, liquid and adhesive.

PATENTS.

Treatment of Leather with India Rubber. U. S. Patent No. 970,734. Alexander McLennan, London, England.

Tanned leather is treated with a solution of sulphur in carbon disulphide, then with a solution of rubber, and then heated, the apparent purpose being to produce vulcanized rubber among the fibers of the leather.

Method of Making Formates and Formic Acid. U. S. Patent No. 970,825. Henry Howard, Brookline, Mass.

The method consists in mixing sodium hydroxide and sodium sulphate and subjecting the mixture to the action of carbon monoxide, producing sodium formate.

Tanning Compound. U. S. Patent No. 972,518. John M. Dill, Artesia, N. Mex.

A tanning compound consisting of the following named ingredients in substantially the proportions specified: water, 15 gallons, borax 1 ounce, garden sage, 3 ounces, fluid extract of wild cherry bark 1½ ounces, catechu 1½ pounds, carcuma 1 ounce and gasoline 4 ounces.

Fleshing, Unhairing, Working-out and Setting Machine. U. S. Patent No. 972,792. Henry Alefs, Milwaukee, Wis.

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CORRECTION.

In Mr. Kerr's article in the November number, p. 485, his name is given as G. H. Kerr instead of G. A. Kerr. On p. 486, line 21, 250,000 should be 25,000, and 6,000,000 should be 16,000,000. P. 496, line 3, 168 should be 16.

NEW METHOD OF COLOR MEASUREMENT.

By H. C. Procter.

The following has been received from Professor Procter:

It has been decided by the Conference of Paris, 1910, that in addition to the ordinary tintometer measurement, color measurement by the new method should be given, in order to familiarize the trade with it with a view to its official adoption in place of the tintometer.

The standard color represents the proportion of red to yellow (with, if necessary, a small correction of ±blue). +Blue represents that the color is somewhat less brilliant; — Blue that is more brilliant than the standard, but not necessarily that it is darker or lighter.

The standard strength represents the quantity of extract (or of tannin) required per thousand parts of solution to give the standard color in a cell of 1 cm. thickness. It is obvious that the larger the standard strength required, the paler the extract, and the larger the quantity which can be used without darkening the liquor. For fuller information see this JOURNAL, August, 1910, p. 352.

The following is the form adopted by English chemists for reporting the new method of Color Measurement.

COLORIMETER MEASUREMENT.

The following are the results of the color-measurement, by the above method, of your sample of marked

STANDARD COLOR:

Yellow
Red = Blue.

STANDARD STRENGTH in 1 cm. cell:

Extract grms. per liter.
Tannin grms. per liter.

ANALYSIS OF LEATHER.

Discussion at the Chicago Convention.

MR. WILSON:—We will now take up the various committee reports. The first one which I will call for will be Mr. Veitch, on "Analysis of Leather."

MR. VEITCH:—All of the report I have to make is contained in the October JOURNAL. Most of you have doubtless read it and I will not take the time to read it now.

The methods are not entirely satisfactory, particularly the method of determining water solubles and possibly also the determining of moisture and grease in greased leather. The detection of loading materials such as glucose, barium, sulphate and magnesium sulphate of course are simple, and it does not seem to me that any great amount of time need be spent in working out methods for their determination.

Water solubles have given us a great deal of trouble, and I do not think we have a method yet that we can rely on to give satisfactory duplicate results. Whether this is due to the large amount of material used or whether because of the short time of extraction, I am not prepared to say; conditions are not much worse in regard to leather than in regard to tanning materials, and I think in time a satisfactory procedure can be devised. If, in the determination of moisture and grease, moisture is made first it is higher than if made after grease; if grease is made first it is higher than if made after moisture. There is undoubtedly a slight error here; not very great, but one which should be avoided if possible.

I don't know as there is anything much more to be said about the matter. The results are not entirely harmonious, as we would expect.

The samples sent out were not entirely satisfactory. After grinding they were not allowed to come to ordinary atmospheric moisture conditions. We were rather late in getting them out, and they were bottled rather hastily. This may partly account for the differences in moisture. For instance, take the work in my own laboratory, where the work was done on samples which had been kept in glass stoppered bottles; you will notice our results are very much lower than those of the other workers. When we exposed the samples and allowed them to get to atmospheric conditions our results were practically the same as those of the other workers. All analytical methods should be, of course, as easily and quickly operated as possible. The tannery chemist is a pretty busy man and he wants his methods to be rapid, and for this reason I have made the recommendation that more work be done with the view of shortening the time for fat extraction. I think this would be very desirable. The standard methods for fat extraction usually run fifteen to sixteen hours. If we could shorten this so that the determination can be made within the working day it would be very desirable.

I have recommended further work on extraction of water soluble material, with particular reference to the effect of previous heating or treatment with fat solvents on extraction.

Work on determination of nitrogen in original and fat-free leather is also recommended.

Then I have recommended to substitute normal lead acetate for subacetate. I suppose that will be done by the recent mail vote.

MR. WILSON:—You have heard Mr. Veitch's report. We will now call for discussion, and especially along the lines of extracting water solubles before and after the removal of the fat. We would like to hear from Mr. Small on this line.

MR. SMALL:—With regard to what Mr. Veitch says about the sample not having been allowed to reach normal atmospheric conditions before it was bottled; the weight of any sample of leather varies with the moisture content of the air, this variation being often as much as five per cent., so that the only way in which moisture determinations on a sample of leather can be made which will be comparative will be to have the samples sealed in a bottle before they are sent and then have them weighed immediately from the bottle with the least possible exposure to the air. The moisture determination seems the least important of the determinations in the analysis of leather, and on that account if we must accept the alternative of an error in the moisture determination or an error in the grease determination, the error should be thrown onto the moisture determination. The procedure which I am following in my own laboratory is to divide the sample as prepared for analysis into two parts making a moisture determination on one portion of the sample of 5-10 grams, and using the second portion of 30-40 grams for the remaining determinations. This second portion is extracted to remove the grease,—then after the extractive solvent has been evaporated from the leather it is used for the water soluble determination. Some of this same leather from which the grease and the water soluble have been extracted is used for my Kjeldahl determination, thereby avoiding any error due to nitrogen in the material in the leather which is soluble either in water or in the grease solvent.

MR. YOCUM:—With reference to the extraction of water solubles in leathers containing large quantities of grease, the great difficulty is that in drying the grease it runs from the leather and carries more or less water with it and it is almost impossible to remove this water from the grease. For that reason on harness leathers and leathers containing large quantities of grease it is almost necessary, to obtain the proper moisture content, to first remove the grease.

MR. WILSON:—Mr. Veitch, are any of the members of the committee here?

MR. VEITCH:—Mr. Riker, I believe.

MR. WILSON:—We would like to hear from those members who have done the work, if possible.

MR. RIKER:—I favor the determination of grease first in preference to the moisture first. I also favor the A. L. C. A. method of water extraction. If moisture is determined before grease, on leather containing considerable quantities of fats and oils, such as belting, upper, chrome and harness leather, great difficulty is experienced in determining accurately the moisture and fats because of the fats melting out of the leather and retaining considerable of the moisture in the fatty matter at the bottom of the dish. Also a great deal of it sticks to the sides and bottom of the dish used in drying the leather. The method I have been pursuing has been to weigh out 15 grams, extract in a Soxhlet with petroleum ether at 50-80° C. to free from grease. Evaporate ether and weigh. Dry the fat free leather at 100° C for 10 hours, desiccate, cool and weigh. The difference between this weight and the original is the amount of moisture and grease. The difference between the loss of weight after drying and the grease is the moisture. This is the only method I have found to give concordant duplicate results.

MR. WILSON:—Is there any further discussion on this point?

MR. OBERFELL:—I would like to ask Mr. Veitch if he gets more or less water soluble after the grease is extracted.

MR. VEITCH:—In one of these samples we got more. As a rule we get less water soluble after the grease is extracted than we do before.

MR. OBERFELL:—If it were more it would seem to me that the grease surrounding the fibers of the leathers might have a tendency to hold some of the soluble matter. If it runs lower I would not have any explanation to offer.

MR. VEITCH:—I think the explanation may be that the leather is so thoroughly dried out, that the water does not penetrate it as quickly and as thoroughly when undried leather is used.

MR. YOCUM:—The great difficulty about the water soluble determination is the physical condition which the leather gets into after the first or second extraction through the soxhlet. It runs .together into a sticky mass and you cannot expect any consistent results from that sort of mass material to extract.

MR. VEITCH:—A temperature high enough to run leather together should not be employed.

MR. HOPPENSTEDT:—I would like to say a few words about some experiments I made in order to find a better way to determine the water soluble in leather. The course which I pursued was to take the ground air dry leather, weigh out 10 grams, place it in a shaker bottle, and 500 cc. of water at 20° C. and shake for one, two and three hours on the shaker. After shaking the requisite length of time, the contents were thrown on linen whereby a clear filtrate resulted, and of that filtrate I pipetted a certain amount for evaporation. I didn't do very much work on it as I did not have the time, but the results I obtained were very satisfactory and ran one or two per cent. lower than working according to the official method. By shaking one, two, and three hours, practically no difference was obtained. It seems to me that working in this way, by not using a high temperature, even 50° such as the official method calls for wherein the leather undoubtedly is broken up especially at prolonged extraction, but by working at a uniform temperature of 20° C., very concordant results would be obtained. At least I found it so in my experimental tests. I should like to recommend further work on that line.

MR. SMALL:—I would inquire if Mr. Hoppenstedt tried different amounts of leather and water, that is, if he tried small amounts of leather and large amounts of water and large amounts of leather and small amounts of water. It would seem as though different proportions would yield different results by such a method as he describes.

MR. HOPPENSTEDT:—The only proportion I tried was ten grams of leather and 500 cc. of water.

MR. REED:—I would like to ask Mr. Hoppenstedt how he kept it at the uniform temperature of 20° during the shaking.

MR. HOPPENSTEDT:—The temperature raised one or two degrees possibly, but very little.

MR. REED:—If you had a laboratory at around twenty-eight or thirty degrees?

MR. HOPPENSTEDT:—Naturally that would make some difference. At the time I made the experiments the laboratory was about twenty degrees.

MR. REED:--You made no experiment to prove what difference ten degrees would make?

MR. HOPPENSTEDT:—No.

MR. RIKER:—The paper I am going to read Saturday deals with this subject, and I have pursued all the methods I have heard of. This method I have now is altogether different. It is using alcohol to extract the uncombined tanning material and I do not know whether to bring the subject up now or wait until Saturday when I read the paper.

MR. WILSON:—You would better wait till Saturday, I should think. Has any one else anything to say on this subject? It seems to me that the line suggested by Mr. Hoppenstedt might be a very interesting one for future work.

MR. HOPPENSTEDT:—In regard to substituting normal lead acetate for the subacetate, I would ask Mr. Veitch if he has done any work on that to see what difference is obtained by using those two different salts. I know from experience in sugar work that the subacetate of lead makes a considerable difference when using that salt instead of the normal lead acetate but in tannin solutions we have entirely different conditions; we have different substances there which are liable to form soluble lead salts with the normal lead acetate, which possibly might not with the basic lead acetate, and I would like to hear if work has been done to show that correct results are obtained by using the normal lead acetate. The basic lead acetate precipitates some of the glucose, but possibly we might be introducing a far greater error by using the normal lead acetate, on account of bringing into the filtrate other substances which would not be present if the basic lead acetate had been used and which would precipitate the Fehling solution. I would like to hear something about that.

MR. VEITCH:—I can only say in response to that that the question has been very thoroughly studied, in sugar solutions, and it has been definitely shown that the basic lead acetate gives erroneous results, being decidedly low. Last year I gave results of our work on a number of samples. We used a leather to which we had added eight per cent. of glucose; with basic lead acetate we got six per cent; with normal we got eight per cent. That is as far as we went. I did not study the nature of that precipitate or its composition, but I do not think there is a material error as suggested by Mr. Hoppenstedt.

MR. HOPPENSTEDT:—That eight per cent. that it contained originally; was that placed in the leather—actual amount put in?

MR. VEITCH:—Yes, sir; that was put in there.

MR. WESTENFELDER:—I would like to ask Mr. Veitch if that same argument holds good relative to grape sugar.

MR. VEITCH:—I don't know. We worked with the ordinary commercial glucose.

MR. WESTENFELDER:—I carried on some work a few years ago relative to this matter and I found that the basic acetate does not remove any of the sugar. I weighed the leather carefully and weighed the sugar and put it under normal conditions. I had quite a large piece of it, extracted it and we determined the sugar, and I found that I got a little more sugar than I put in. By using 15 grams of sugar I obtained in the leather 15.4.

MR. HOPPENSTEDT:—I would like to corroborate those results. I carried out a number of experiments along that line by determining the sugar fundamentally present in the leather, then weighing with a known amount of commercial grape sugar then extracting and determining the sugar again, using basic lead acetate, and I received the amount of sugar that I put in. Now naturally the grape sugar is the sugar which is used for loading leather. Of course in unweighted leather there is only a comparatively small amount of glucose present and it makes very little difference which salt we use.

MR. VEITCH:—What do you mean by grape sugar,—the ordinary sugar made from corn?

MR. HOPPENSTEDT:—Yes.

MR. VEITCH:—That is what we use.

MR. HOPPENSTEDT:—There is liquid and solid. I mean the solid.

MR. VEITCH:—Your results differ from those obtained by many chemists working in a different field.

MR. HOPPENSTEDT:—I formerly was in the sugar business and made a specialty of sugar work and I know that the basic lead acetate gives wrong results in sugar work, but in tannin work I would like to see it worked out more thoroughly to see if there are not other substances present which give soluble salts with the normal lead acetate which will later on act on the Fehling solution, but which the basic lead acetate will remove. I have found with some tannin solutions that if you add normal lead acetate, even a big excess, the filtrate will still be considerably colored. Now if you take the same solution and precipitate with basic lead acetate you will get it practically colorless. That shows that there are some substances not precipitated by the normal which the basic does precipitate, and I would like to know if those substances do not have an effect on the Fehling's solution. I know in *sugar work* the normal lead acetate is the correct one to use.

EXTRACTION OF LEATHER BY VARIOUS SOLVENTS.[1]

G. A. Riker.

There has been a great deal of work done on the analysis of leather, and on this subject I have made many experiments.

One of the weaknesses of our present methods is the water extraction for uncombined tannins and non-tannins, which I have

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[1] Paper read at the A. L. C. A. Convention, Chicago, Oct. 8, 1910.

had much to do with and which has occasioned me to try other than the prescribed methods for its improvement.

I have used various solvents to extract leather in my endeavor to find one which would remove only the uncombined tanning material. To obtain the correct degree of tannage, a very accurate analysis of the uncombined tannin is required. This factor is of great value as a means of ascertaining the quality of the leather, whether it is likely to be capable of good yield in finishing, the possibility of retannage, and also whether the process of tanning has been more or less rational.

A section of leather may show an apparently complete penetration of tannin and at the same time give a low tanning factor. This generally indicates that the tanning has been hastened by some mechanical means, such as drumming or some similar accelerating process, proving that the leather has simply been colored and the tannin has not completely penetrated and united with the fibres of the hide. The great importance of this tanning factor is admitted and its accurate determination is needed.

With the water extraction there is no decisive end point. At the temperature of 55° C to 60° C, after the first or second extraction, the leather coagulates to a tenacious sticky mass, and repeated extractions with water at that temperature causes the decomposition of the combined tannin and leathers of different tannages disassociate at various intervals during the extraction.

Extracting with water removes the sugars, Epsom salts and other soluble salts of organic and inorganic acids, and these are calculated as water soluble material, thus part of what was reckoned in the mineral ash is reckoned in the water soluble. A greater error occurs when analyzing the water extract, for some of the sugar and Epsom salts combine with the hide powder, making the uncombined tannin determination misleading.

I have used a number of solvents of tannin and find that 95 per cent. alcohol gives the best results. Sugars and Epsom salts are insoluble, and after experimenting with compounds of tannin and gelatine, I find that the tannin in the compound of tannin and gelatine is insoluble in alcohol. Also the tannin which is not combined with the hide is soluble.

All portions of water used in extracting bring over some soluble material and there is always a residue on evaporation. But when extracting with alcohol a decisive end point is reached when all the uncombined tanning material is removed and after extracting eight hours with alcohol, the last few portions that pass over show no residue at all on evaporation.

Thus an extraction with alcohol leads me to believe it to be more accurate than one with water to remove only the uncombined tanning material. This method obviates the necessity of determining the ash in the water soluble matter and the use of the expensive percolator as recommended by Dr. J. Gordon Parker in his article on the "Complete Analysis of Leather" in the Journal of the Society of Chemical Industry, March 31, 1910. (This Journal, June 1910, p. 305.)

My method of procedure is as follows: Place 15 grams of ground fat free leather in an S. & S. thimble and extract with 95 per cent. alcohol for eight hours in a Soxhlet extractor. 250 cc. of water is added to this solution and placed on a steam-bath to evaporate the alcohol. After this the solution is made up to 1,000 cc. and analyzed according to the official method of the A. L. C. A.

DISCUSSION.

MR. WILSON:—This paper is one which should incite considerable discussion from those who have had experience in the extraction of leather. I would especially call on Mr. Veitch, as he has done considerable work this year on that subject.

MR. VEITCH:—It is a very interesting paper to me, Mr. President, and there may be some advantages in the method proposed. I am under the impression that sugars would dissolve on long extraction with hot alcohol.

Other constituents such as, magnesium sulphate can be determined in the water extract, and such salts would lead to no error except the small error that is introduced on a non-tannin determination. As Mr. Riker says, it is undoubtedly true that a certain amount of these salts are taken up and calculated as tannin, and it would be a decided advantage to get rid of this objection to our present solvent, water.

MR. WILSON:—I would ask Mr. Riker if he has determined to what degree the sugars and salts are soluble in this alcoholic extract?

MR. RIKER:—I have made a number of experiments in order to find out the percentage of glucose in the alcoholic extract, and obtained 0.01 and 0.02 as an average of 10 samples. I am pretty sure that Epsom salts are insoluble in 95 per cent. alcohol. It might be slightly soluble, but there is only a trace of magnesia on precipitation.

MR. MOSSER:—I would like to inquire of Mr. Riker, if at the temperature of boiling alcohol, wouldn't there be the same trouble of the leather becoming a sticky mass as is the case with water at that temperature?

MR. RIKER:—After extracting with alcohol, the leather is almost in the same condition as it was before it was extracted. When the alcohol is evaporated off you can separate the leather just as you could before extraction; this you cannot do after the water extraction.

MR. WILSON:—Mr. Small, have you anything to offer on this subject?

MR. SMALL:—Sometimes it is of advantage to make an analysis of the extraction liquor. Was it Mr. Riker's idea with regard to obtaining an analysis of his extraction liquor where he makes an alcoholic extraction?

MR. RIKER:—In the alcoholic extraction I have been trying to find out something that would remove only the uncombined tannins and non-tannins in the material used to tan the leather, and trying to get rid of the epsom salts and glucose, so that in making a non-tannin determination of this substance so extracted, the soluble extracted material will contain nothing but what was in the tanning material used to tan the leather.

MR. SMALL:—How would you proceed to get out glucose and epsom salts?

MR. RIKER:—I would take another sample for glucose and extract it with water, and take another sample to determine the epsom salts.

MR. SMALL:—In extracting with water, you will get glucose and also tanning material, etc. Your idea then is to simply make a glucose determination.

MR. RIKER:—Simply to make a glucose determination on the water extraction solution.

MR. SMALL:—But if you did want to get at the composition of the tanning material, how are you going to do that, on either one of the extractions, with the water or the alcoholic extraction?

MR. RIKER:—In this alcoholic extraction, 250 cc. of water is added, the solution is put on a steam-bath and the alcohol evaporated off. The solution remaining is made up to 1,000 cc. and analyzed according to the official method. I claim this contains all the tanning material that is not combined.

MR. VEITCH:—There is one point on which it seemed to me that Mr. Riker's method might possess advantages. I would like to know if he has attempted to determine free sulphuric-acid in the alcoholic extract. The free sulphuric acid will dissolve in the alcohol while the sulphates are insoluble. Has Mr. Riker done anything with this?

MR. RIKER:—I did considerable work on determining free sulphuric acid in leather, and found that by taking a piece of leather before any grease is added to it and immersing it in a sulphuric acid solution of known strength, and then extracting this leather with absolute alcohol, that this method gave a slightly lower amount than was actually in the leather. Also by the ignition method, I got slightly lower amounts than were actually in the leather.

MR. VEITCH:—Lower than by alcohol?

MR. RIKER:—Just about the same. I think there needs to be a little work done on the determination of free sulphuric acid to devise a method whereby we will be able to get uniform and concordant results.

MR. YOCUM:—The present method of extraction with water is a nearly impossible proposition, and the variations analysts will make, even trying to duplicate their own results, are such as to prove that the method is erroneous. Some methods of extraction for the so-called water solubles, which of themselves are misleading—that term—some method of the determination of the uncombined tannins, must be devised, because with the improvements in the tanning methods we find that it is necessary to determine the extent of tannage, or the tanning factor. The alcohol method appeals to me in that it does not include in its determination sulphates or straight sugars. Mostly weighted leather has some sort of sulphate, like magnesium sulphate for instance, and some sort of sugar, and your determination of the water solubles, so-called, by the alcohol method would give what was soluble in the leather as it was originally tanned—or I shan't say that exactly, but rather it would give what the solubles were from the action of the hide in connection with the tannage and with the extract afterwards used, and would not include the sugars or the sulphates. It seems to me that by the adoption of such a method certainly some of the difficulties of making a hundred per cent. in our leather analysis would be overcome.

MR. MOSSER:—I would like to ask Mr. Riker how close his duplicates agree by using this method, and also how the figures compare with the water extraction?

MR. RIKER:—You get very good duplicate alcoholic extractions, better than with water, and comparing the non-tannins in alcohol extract with the non-tannins in the water extract, there is a big difference. That is due to the insolubility of the sugars and the epsom salts.

MR. OBERFELL:—I would like to ask Mr. Riker how he arrives at his combined tannin by using the alcoholic method.

MR. RIKER:—The regular method now is to sum up the uncombined non-tannin, uncombined tannin, grease, ash, H_2O and hide substance, and the difference between that and 100 per cent. is combined tannin.

MR. OBERFELL:—How do you get uncombined tannins with your alcoholic extraction?

MR. RIKER:—By analyzing the alcoholic extract.

MR. OBERFELL:—If your method does not extract all the non-tannins, how are you going to get at it?

MR. YOCUM:—This method simply extracts the tannin and non-tannin of the tanning material used to tan the leather, and you have got to make a separate determination of the sugars, salts,—the sulphates.

MR. OBERFELL:—You say it does not make an extraction of the non-tannins?

MR. YOCUM:—It does not make an extraction of *added* non-tannins.

MR. OBERFELL:—Will it give the non-tannins extracted from different tanning materials?

MR. YOCUM:—Yes.

MR. OBERFELL:—It differentiates between the added and natural non-tannin materials?

MR. YOCUM:—Yes. 95 per cent. alcohol does not dissolve sulphates to any considerable extent; neither does it dissolve sugars. Now what its solvent action might be on the natural glucosides found in an extract or in tanning materials, we do not know; but we are sure of at least one thing, that it will not dissolve the sulphates and will not dissolve the sugars as ordinarily used. It is selective to that extent.

THE TANNAGE OF HEAVY LEATHER IN CALIFORNIA.[1]

By Joseph H. Russell.

A description of tanning heavy leather in California is likely to be of about as much benefit to tanners in other parts of the country as are those advertisement column prescriptions for rheumatism cures of benefit to sufferers from that complaint. These prescriptions, after mentioning salt, pepper, vinegar, whisky, and a number of things which any one can obtain, wind up with a large proportion of Siberian Sage or Pomeranian pomegranate seeds or some other strange substance which can be obtained only from Doctor So and so. Thus it is with the tannage in California. We find the same familiar hides, the same salt, the same water, the same lime, the same extracts and even the same old grape sugar and epsom salts used in the same old way in very minute quantities for improving the finish and quality of the leather. But back of all these they have their Siberian sage which in this case is the California oak bark. Although the bark is different from any other and is not found in any other locality, the problems of tanning are much the same as elsewhere, thus it may be of interest to follow the tannage through, especially, as

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[1] Read at the A. L. C. A. Convention, Chicago, Oct. 8, 1910.

one can be a little franker in the description of it than one could be if other tanning materials formed its basis. Concerning the bark itself, Prof. Jepson has written as to the supply (J. A. L. C. A. I, 197) and Mr. Sprague and myself have given some notes on its composition (J. A. L. C. A. IV, 92). Suffice it to say here that the bark contains about seventeen per cent. of tannin and costs from twenty-two to twenty-three dollars per weighed cord of 2,400 lbs. at the tannery. I have a little piece of this bark. It might be said that this is a sort of sensational piece, but they do get a good deal like it. I will pass that around. (Mr. Russell passes around for inspection a piece of bark over three inches thick.)

Owing to trade conditions and the nature of the hide supply, the tanners on the Pacific Coast have in most cases adopted the policy of tanning harness, skirting and sole leather in the same yard. This is a pretty difficult proposition and it is much to the credit of the tanners that they have been able to carry it through so successfully. In no one yard, however, are all three produced up to the highest standard of each. If the tannage is carried on from the standpoint of economy in leaching and high yield in sole leather, it is done, to a certain extent, at the sacrifice of color or weight in skirting and of the best qualities in harness leather. While if the tannage is adjusted to produce fair skirting and high quality harness, it is done at the expense of efficiency in leaching and of yield in sole leather.

The tanning process in general is similar in the different tanneries although naturally not quite the same in any two of them. Such outlines as I give do not represent the complete process at any one tannery, but are rather what I consider typical of each stage in the California process.

The hides, which are mainly Western packer green salted, are soaked for two or three days in two or three changes of water. They do not receive any washing in a slush wheel before or after soaking. The liming takes six days, the hides being hauled each day. Some of the tanners use one pit for a pack simply handling the stock and strengthening the lime each day. Others have a series of six limes, the stock being handled forward. No reels are used in either soaks or limes. In the six lime system an attempt is usually made to keep the head lime fairly new and clean. The other limes are cleaned out once in two or four weeks. Sometimes the dissolved hide runs up pretty high in these old limes. In one tannery on the four week cleaning system the dissolved hide in the old limes ran up to thirty three pounds per vat. If this could all have been converted into leather, in that tannery it would have made eighty-seven pounds of sole leather. About a barrel (200 lbs.) of lime is used to a pack. The hides are split into sides about the third day in the limes. On coming from the limes the hides are washed in cold water in a still pit and unhaired by machine. They are then fleshed and washed sometimes in a paddle vat with cold water and sometimes in still pit with a mild bate. They are then grained and washed again. All these washings are made as short as possible. There is no hanging of stock overnight in water before going into the yard. The water is never cold and the tanners believe that the softness it gives stock hung in it any length of time is carried through to the finished leather. The stock is now ready for the yard. At this stage the white weights are taken. This is usually done on several packs from each lot of hides. These packs are then followed through the whole tannage and all the hides are tanned into rough leather or the same kind of stock that yields can be computed. On the best hides of summer take off they usually get a white weight around 120 per cent. During the winter and spring this falls below 100 per cent. On Frigorificos they get about 140 per cent. based on South American weights. Practically no attempt is made to delime the hides except in the few cases where the light surface bate mentioned above is used. Except what is worked out mechanically and washed out by the water, all the lime is carried over into the liquors. As no tail liquors are run away, the lime salts pile up in the yard considerably and cause troubles to which reference will be made later.

The sides from the beam house are hung lengthwise by head and tail in what are termed on the coast "stringers." In some cases these are ordinary mechanical rockers with the liquor run on the press system. In others the hides are not moved but the liquors are gently agitated from beneath. In the typical system the hides are hung on rocker frames which are moved by hand several times a day. In this system each stringer change, as it is called, is made up separately and a pack gets from three to six of these changes in the twelve to fifteen days it remains in the stringer. The tail stringer varies in strength in the different tanneries according to the amount of mineral salts in the liquor. When these are high it takes a twenty degree liquor containing 1½ per cent. tannin and 2½ per cent. non-tannins to make any impression on the hides, while in a yard with liquors of higher purity ten degrees barkometer is found strong enough to begin the tannage. The head stringer runs from 25 to 30 degrees barkometer and contains from 2½ to 3½ per cent. tannin. Owing to the manner in which the stringer liquors are made up, the acid is almost uniformly low, running from 0.25 to 0.3 per cent. in the tail stringer up to 0.4 to 0.45 in the head and reaching as high as 0.6 only where myrobalans are intelligently used.

The layers are three in number and ground bark is used as a dusting material. The amount of bark used varies, but the present tendency is to use only enough to keep the sides apart. The barkometer strength of the first layer is about 35 degrees and the tannin about 4 per cent. of the second layer 45 degrees and the tannin about 6 per cent. and of the third layer 50 degrees and the tannin about 7 per cent. The stock is in the first layer about two weeks and is then pretty well struck through. It is in the second layer two weeks more. In some of the tanneries the harness and skirting are sorted from the sole at the end of the second layer. This is good practice as the stock then contains all the tannin that leather for currying can hold. By sorting at this stage they are able to give the stock a stronger and more energetic third layer and use valonia as a dusting material to give greater weight and firmness. The time in the third layer is from one to two months. The second layer in some cases and the third in others finishes the tannage of the harness and skirting.

The sole leather, on coming from the third layer, is dried as expeditiously and economically as possible, which owing to the climatic conditions, can be accomplished most of the year by hanging in sheds with open sides or even directly in the open air. Naturally it dries hard and very dark in color. Then commences the arduous process of making firm stock from what is naturally a mild tannage. In the old days before gambier became a luxury, the dried sole leather was laid away in a strong hot gambier liquor. The amount which the stock took up overcame the mild nature of the material. Now the hot section liquor, as it is called, is made up from strong bark liquor brought up to seventy degrees and ten per cent. tannin with quebracho, cutch or myrobalans extract. This liquor is heated up to 120 degrees and the stock laid away in it for ten days or so. Some times the pack is raised and the liquor re-heated at the end of a week. When the stock comes from the hot section it is either dried and finished or else dried and given another hot section, or, if exceptionally firm stock is desired, dried and rolled and then given another hot section. The hot section liquor gains in strength during the process, thus one which showed 10 per cent. tannin when the stock went in showed 12.94 per cent. when the stock came out. This is due to the fact that the dry leather takes up water faster than it does extractives. There is a gain in weight from the hot section process, however, varying from 2½ to 5 per cent. over the rough weight. The finishing of the sole leather is simple owing to the light color of the tanning materials used. On coming from the hot section it is given a pretty thorough soaking, is brushed, given a fairly mild bleach, oiled and in some cases, sugared; then carefully dried for rolling.

The liquors are made chiefly from the oak bark which has been supplemented for some time with Mexican bark and more recently with myrobalans and the solid extracts. Some of the tannages now consist of as much as a third of materials other than oak bark, although the leather keeps the characteristics of the oak tannage. Two of the tanneries have vacuum apparatus for concentrating their liquors while a third has an extract plant in the bark country and uses the extract for making up the liquors and bark only as a dusting material. On account of the red coloring matter extracted at high temperatures which gives the skirting an objectionable color, and also owing to the fact that in most of the tanneries there is no place to use weak sweet liquors, the leaching is by no means close and spent tans often show from 4 to 5 per cent. tannin and rarely go below 3 per cent. There is no such thing as working the liquors down through the yard. Each sapped liquor is pumped up over the leaches and becomes a new liquor, while the stringer liquors are pumped over the nearly extracted leaches and over the layer bark which is extracted in separate leaches. As a result of this procedure, the layer liquors contain a considerable quantity of acid which is not utilized, while the stringer liquors get their acid only incidentally and usually not enough for adequate plumping considering the large amounts of lime salts which pile up in them.

The barkometer sappage from start to finish is about 20 degrees, the tannin sappage about four and one half, per cent., the acid sappage in the stringers 0.35 per cent. and the acidity development in the layers about 0.25 per cent. The liquors tend to become stringy and viscous and require frequent pumping over the leaches to keep them clean.

The yields in leather are not quite comparable with Eastern yields on account of cows and steers being almost invariably tanned together. Eighty per cent. on the green weight is considered good in sole leather, seventy-five per cent. in harness and from fifty-eight to sixty-five per cent. in skirting according to its quality. In tabular form I am giving results on analyses of representative samples of California sole, harness, skirting and rough leathers.

ANALYSES OF CALIFORNIA LEATHERS.

Samples taken from near Butt.

	Sole		Harness		Skirting		Rough	
	Air dry %	Dry %	Air dry %	Dry %	Air dry %	Dry %	Air dry %	Dry %
Moisture	16.80	..	12.52	..	14.98	..	10.01	..
Ash	0.60	0.72	0.39	0.44	1.82	2.14	1.06	1.23
Oil or grease	0.80	0.96	22.23	25.41	5.73	6.74	0.66	0.77
Hide substance	33.44	42.60	33.97	38.83	38.91	45.77	40.62	47.24
Combined tannin	31.33	37.66	18.49	21.14	22.50	26.46	28.52	33.17
Uncombined tannin	6.16	7.40	7.17	8.20	6.86	8.07	7.61	8.35
Uncombined non-tannins	8.87	10.66	5.28	5.98	9.20	10.82	7.52	8.74
Sugars as glucose	1.40	1.69	Trace	..	2.47	2.91	Trace	..
Barium sulphate	..	..	..	..	0.73	0.86	..	..

Before closing one ought to say something about the influence of the California climate on tanning. It is undoubtedly quite a favorable factor as the variations between different seasons of the year are small. The water in the beam house and the liquors in the yard do not vary much in temperature during the year, which favors uniformity in stock from beam house and in acidity development in yard. As there are few days of high humidity, the drying proceeds regularly and there is little tendency for the stock to mould. During the summer the north wind dries the stock too rapidly and care has to be taken in regulating the air supply of the lofts or the color of skirting and sole is injured. During the rainy season the open sheds are not very efficient for drying.

The days of three tannages in the same yard are nearly over. A description of how it is done is, I hope, more interesting than I feel sure, it can be helpful. But these tanners have shown that they are skilled in their art in so well adjusting their processes to their conditions, and I feel it is well worth while recording how they make a fair light colored skirting, a tough fibred harness, and a firm heavy sole leather from the same stock in the same yard in the tanneries of California.

I have no intention of holding a California Leather Fair here, but when I left the State I brought some samples of their tannages with me, harness, sole and skirting, and these I will pass around. You may be interested in seeing them.

DISCUSSION.

MR. WALLIN:—I would like to ask Mr. Russell, is this supply of bark rapidly approaching exhaustion?

MR. RUSSELL:—Mr. Wallin's question is one which is often asked on the Coast, and is answered "Yes" or "No." Some answer "Yes" and some answer "No." As a matter of fact the bark supply is entirely different from our eastern supply, because it is the whole useful part of the tree. The oak wood has no commercial value at present and is not used. When the bark is taken off the wood is just burned, and so far the bark has been obtained mainly in the process of getting at the redwood timber. They clear off the land to get at the valuable redwood, and they strip the bark as they go along. Now they are getting further and further back into the country, of course, just as we have in the past in Pennsylvania and Michigan, but there are undoubtedly great tracts of land which are still covered with the bark, and the supply is all right, but the cost of getting it out becomes more and more every year; so I think Mr. Kullman will agree with me that the price is likely to go up as time goes on, although the supply will last for some time to come.

MR. WALLIN:—I would like to ask also, is there considerable tannin in this wood?

MR. RUSSELL:—No sir; it was hoped that the bark being so high in tannin the oak wood would also show up high, but on a number of analyses I never found it to run over ½ per cent., on the dry basis. So that there is no possibility of working the wood and bark into extract together.

MR. NICHOLS:—I have noticed that the California liquors are different from our eastern liquors. There is one peculiar constituent in California oak bark liquors and I would like to ask Mr. Russell if he has ever ascertained what it is. They are sticky like sugary substance, and it seems to me they ferment and mold easily.

MR. RUSSELL:—I never have, Mr. Nichols. I have tried to find the origin of the thing and where it comes from, because it causes considerable trouble in the tannery. If the liquors get viscous the tan does not penetrate. At one time I thought it was due largely to the Mexican bark which is used in most of the tanneries, and in yards using that it seems to have a greater tendency to form that viscous condition in the liquors; but whether it is due to something peculiar in the tanning materials or is some peculiar bacterial condition of viscous fermentation I cannot say. I do not believe the stuff ferments particularly because in testing the acidity development with this bark and Mexican bark, which I found was very low, as time went on I found these liquors turning viscous, but an extremely low development of acidity in those liquors.

MR. NICHOLS:—Don't the tanneries there use any Washington or Oregon hemlock bark?

MR. RUSSELL:—That is pretty scarce. The tanners up there hardly have enough for themselves. They have to buy some of the California oak to supplement it. That is, in Oregon they do. At the tannery in Everett, Washington, they can hardly get enough to run their tannery.

MR. YOCUM:—I would like to say that the conditions of curing bark in Washington where the hemlock is are almost impossible owing to the rains there.

MR. WILSON:—Mr. Russell, I wish to ask if you think that the addition of myrobalans to those liquors might not modify this viscous condition?

MR. RUSSELL:—I would not like to say that, because one of the complaints I have heard from tanners in the east was that in trying to build up the acidity in their handler liquors with myrobalans they came up against a viscous condition they had never encountered before, but so far as my experience has been out there where myrobalans have been used and the liquors treated as carefully as they were before, there has been no trouble from that viscous condition. In fact, in a well-managed yard they don't get up against that condition much, but in some of the smaller yards where they haven't the pumping facilities and don't circulate their liquors and clean them out, then they get up against that, and they could very nearly sell their liquors as lemon jelly.

MR. YOCUM:—If continually returned to the leach house and not properly heated, and the bacterial action destroyed, you will get the same condition of ropy liquors with the Southern oak bark. In fact I think you will get it in any kind of bark liquor under these conditions.

MR. NICHOLS:—I wish to say that my experience in that viscousness in California oak liquors is entirely different from what I have seen in the east. I have never seen it in eastern oak liquors, and I have had some pretty old samples. I would like to know what causes it.

THE DETECTION OF MENHADEN OIL IN COD LIVER OIL.[1]

By A. W. Hoppenstedt.

I would like to say a few words to you about the detection of Menhaden Oil in Cod Liver Oil, as I feel that this subject

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[1] Read at the A. L. C. A. Convention, Chicago, Oct. 8, 1910.

is of interest to all, especially so as the methods at the present time do not afford ready means of detecting this common adulterant. I want to lay before you a reaction and test which are the result of considerable private research work which I carried out several years ago in order to find some particular substance or distinguishing reaction of Menhaden Oil whereby it could be detected in mixtures of God Liver or other oils. The work was never fully completed nor the test brought to that state of perfection as I desired it and therefore it was never published. I have continued with the work from time to time as the opportunity presented itself, but I now feel the desire to place the same before you with the hope that by doing so it will stimulate further research and lead to greater results.

I have found that Menhaden Oil gives with certain acids a reaction which to my knowledge is given by no other oil. Of the acids which produce this reaction, hydrochloric acid seems to be the most efficient. When Menhaden Oil is shaken with this acid, the oil acquires a greenish color and when this mixture is then separated into two layers, by means of suitable solvents, so that all the color principle is concentrated and separated from the rest of the oil, a layer is produced which has an intense bluish green color, apparently due to a lipochrome, similar to the one which produces the purple color in Cod Liver Oil with sulphuric acid. The reaction is given by all grades of Menhaden Oil, whether crude or refined. It is strongest in a fresh oil and gradually diminishes in intensity as the oil becomes old and rancid until it finally disappears altogether. This characteristic is also in accord with the loss of the purple color reaction of Cod Liver Oil when that oil becomes old and rancid. At the present time I am studying the nature of the substance more closely which produces this bluish green color in Menhaden Oil with the hope of being able to isolate the same. It would seem most probable that this substance should be present in the unsaponifiable matter of the oil, but the same fails to give the slightest trace of the reaction. However, I propose to continue my investigations along this line.

In order to carry out the test on an oil, I have found the following manipulation and proportions to give the best results:

Place 5 cc. of the oil to be tested in a test-tube of about ⅝ of an inch in diameter and add 5 cc. of acetone. Mix well so that all the oil dissolves. Then add 1 cc. of concentrated hydrochloric acid and shake vigorously for one minute. After shaking, add 5 cc. of petroleum ether, mix thoroughly and then allow the layers to separate. The separation is generally complete in 5 to 10 minutes and the color of the lower layer can then be noted.

With pure Menhaden Oil this assumes an intense bluish green color, some oils giving nearly a blue and others nearly a green color. With pure Cod Liver Oil the layer assumes a yellow to brown color but without a trace of green or blue. With a mixture of equal parts of Cod Liver Oil and Menhaden Oil, the green color is decidedly predominant but masked to some extent by the brown color given by the Cod. As the amount of the Cod Liver Oil increases and the Menhaden Oil decreases, the intensity of the green color is reduced in proportion. When the quantity of the Menhaden Oil present reaches as low as 20 per cent., the green color is no longer readily detected, being almost completely masked by the brown color given by the Cod Liver Oil. However, one who has had considerable experience with the test will still be able, in many cases, to recognize the green shade present although this is again dependent upon the intensity of the color given by the particular Menhaden Oil used.

This interference of the brown color given by the Cod Liver Oil seriously affects the value of the test and I have been endeavoring to find a way of further separating the lower layer in order to eliminate this objectionable color and isolate the one desired, but up to now I have been unsuccessful. Could this be achieved, the very smallest quantity of Menhaden Oil present could be readily detected. Another bad feature of the test is the comparatively rapid changing of the color produced, which after a little while commences gradually to darken until it finally becomes no longer distinguishable. However, the time elapsing before this change begins is more than ample to allow of a careful observation of the color. An examination of the two layers formed in the test shows that the lower one contains besides the color principle. the hydrochloric acid and some acetone and the upper one the rest of the oil dissolved in acetone and petroleum ether. By the use of other solvents than these, a more permanent color can be obtained, but I have found that by their use a more intense brown color is given by the Cod Liver Oil so that no advantage is gained.

In the April number of the JOURNAL of this Association, in an article entitled "Some Constants for Cod Liver Oil and Menhaden Oil," Mr. W. K. Alsop pointed out the difference in the specific gravity and the acid value of the two oils and the value thereof. These differences are of undoubted value when a very large proportion of Menhaden Oil is present, but when the amount is below 40 per cent. no definite conclusions can be drawn therefrom. Suppose we have an oil to test which shows 0.925 specific gravity and 22 acid value. These values are entirely within the limits of a pure Cod Liver Oil and are frequently obtained. Now the oil might be pure and still we might be dealing with an oil consisting of a mixture of 70 per cent. Cod Liver Oil with 0.923 specific gravity and 28 acid value and 30 per cent. Menhaden Oil. Such a mixture would give the same results, namely, 0.925 specific gravity and 22 acid value. It is especially in such cases where my test is of great value, in deciding whether Menhaden Oil is present or not and I have applied it to many of such doubtful samples with great success. I sincerely hope that all of you will find the test of great help when called upon to determine the purity of Cod Liver Oil and that through this communication much good may result.

DISCUSSION.

MR. WILSON:—I would like to hear from those on this subject who have had considerable experience with the analysis of oils. I don't think I can do better than to call upon Doctor Levi for remarks on this paper.

MR. LEVI:—I am so little versed in Menhaden and Cod oils—of course we always give Cod—; but I should say that if Mr. Hoppenstedt would go further into this matter it would be awfully interesting, because the coloration might be due to the esterfication, so to speak, of the free and hydroxide blues in the

Menhaden oil with the hydrochloric acid. It might be due to that. Of course it would be hard to say. The oil is very reactive, and the adding of the acid there would probably form some esters, and the coloration might be due to the peculiar organic formations formed from the oil. The investigation and analysis of oils is very interesting, but it is a work which should be undertaken by a man who can give plenty of time to it, because undoubtedly he will have plenty to do, and it is a very difficult subject to handle; and when we get to that point where we can determine and say, "You have got so much Menhaden oil in your Cod," we will take off our hats to Mr. Hoppenstedt for the beautiful work he has done.

MR. BALDERSTON:—I wish to testify to the beauty of the test Mr. Hoppenstedt has described, because I have seen it several times, and I want to say just a word about another line of investigation that might give results. I spent about three weeks this past summer on the question of the differences between Menhaden and Cod liver oils, along the line of trying to determine the oxidation values, which certainly do not have anything like the same relation that the iodine values do. Iodine values overlap as between Menhaden and Cod oils, but the oxidation values do not; the oxidation values on all the Menhaden oils I have tried being far higher than those of Cod oils. I failed to get any satisfactory method of determining the oxidation value, I tried to do it by heating simply,—that is, keeping them at oven temperature for varying lengths of time, but the value sought in that case is masked by the fact that the Cod oils lose so much more rapidly at the start than the Menhaden. The Cods contain volatile matters of various kinds, as you know, due to incipient decay, (medicinal Cod loses hardly at all at the start), but all the leather Cod oils lose heavily at the beginning in consequence of the volatile matter present; and when you have heated them until approximate constant weight is reached and they begin to oxidize, the oxidation of the Cod is far less rapid than that of the Menhaden and far less complete. And if any independent method of determining this oxidation value can be found so as to eliminate the evaporation results which mask the true oxidation value, it seems to me that might help us out.

CONSERVATION IN THE LEATHER INDUSTRIES.[1]

By F. P. Veitch.

The word "Conservation" has been so frequently employed in the past few years that I hesitate to entitle what I have to say "Conservation in the Leather Industries." No other word, however, so clearly and conveniently expresses the function of the chemist; especially in these industries, where his efforts are largely directed to the rational use of raw material and the finished product. Rational use, to my mind, is the highest type of conservation.

The time was, when we might more properly than now regard tanning as largely an agricultural industry; the processes were simpler, the plants smaller and more distributed throughout the farming districts. While the relations of to-day are not so intimate between the farm and the tannery, agriculture, nevertheless, remains as deeply concerned in this industry as formerly. The reason is not far to seek. Agriculture supplies the tannery with nine-tenths of the raw material, approximately 180,000,000 dollars worth and buys from the leather industry approximately 150,000,000 dollars worth of its finished products. We may go a step farther and say that the nation has a deep interest in these as well as in other industries, and may reasonably demand that the products shall be of the highest quality that the raw materials will economically yield.

Conservation in leather making begins with the forbears of the animal from which the skin is obtained; the characteristics of breed together with the proper nourishment, age and health of the animal are primary factors which help determine the quality of the finished products of leather making. Climatic and soil conditions also play their part in determining the quality and character of the skins, but are much less within human control than other and more important factors. Within a year two thoughtful and practical men, Vogel in this country and Seymour-Jones in England, have called attention to the insufficiency of the hide and skin supply to meet the needs of the leather market. We are familiar with the fact that more and more largely vegetable tanning materials are being imported and that we are threatened

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[1] Read at the A. L. C. A. Convention, Chicago, Oct. 8. 1910.

with an inadequate supply of these materials. We imported in 1908 approximately 55,000,000 dollars worth of the hides and skins, and three to four million dollars worth of the tanning materials employed in the manufacture of leather.

There are two viewpoints from which we may consider conservation in the leather industries; increasing the supply of raw material and their more complete utilization, coupled with the production of better products. The latter aspect should receive our most serious attention, both as chemists and tanners. The ultimate supply of raw materials is, to a large extent, far beyond our control, as these are, as has often been said, the by-products of other industries and are affected only to a minor extent, by the demands of the leather industries. The most rational and economic use of raw materials with the production of an article of the best quality furnish a field sufficiently wide for the exercise of all our talents. From the moment the animal is killed until the finished product made from its skin leaves the factory, knowledge, judgment, and vigilance are necessary.

Probably no other single operation connected with the making of leather has so much influence on the product as the take-off, cure, preservation and disinfection of hides and skins. The loss of material and lowering of quality, which may occur through poor take-off are too familiar to need further consideration here. Undoubtedly, this condition can only be remedied by making it profitable for the small local skinner to do his work properly. From the viewpoint of quality, the cure and preservation of hides is much more important than their disinfection; indeed, the processes of curing and tanning have themselves decided disinfecting properties, and were it not for the danger to the health of the workmen and the infection of others who come in contact with them with very serious diseases, the dangers from infected skins could be dismissed without further consideration. The improperly cured skin yields less and poorer leather than the properly cured skin, indeed at times the product from poorly preserved hides could hardly be called leather. As between the dry and green cured skin there can be no question as to which, other things being equal, is the better. The green or undried skins are more easily and economically handled in the tannery, and make the best leather. The ideal way, of course, would be for the skins to start through the tannery soon after their removal from the animal,[1] and while this is practicable with quite a proportion of our native output, it is out of the question with the majority tanned in this country. In the curing and preservation of skin, our efforts should be directed to methods which are, at once, simple, cheap, effective and permit the skin to remain as nearly as may be in a loose, supple condition. All the operations of the tannery may be hastened on such skins, and the resultant leather be of high quality. The underlying principles of the methods of cure now in vogue are undoubtedly good. As in most lines of technical industry, a wider, more careful application of the knowledge we now have would result in marked improvements. The question of hide disinfection is also of moment to the tanner, because of the possible effect on subsequent tanning processes and on the quality of the leather. This principle may, I think, be laid down for our guidance on this question. The disinfectant employed must be effective but not injurious to the hide. A priori, we may dismiss certain well known disinfectants because they cannot fulfill both of these conditions. The subject is receiving the attention of the Department of Agriculture and also of the International Commission for the Cure, Preservation, and Disinfection of Hides and Skins, and we may hopefully expect its satisfactory solution at an early date.

In the earlier processes in the tannery, the enemy which must be fought from the moment the animal is dead, bacteria and moulds, is still the greatest cause of loss and of poor quality. Here again, it is only when we become careless and fail to apply the knowledge which we have, that the injurious effects of the organisms are of serious moment. It is their unregulated, undirected action which does damage. Certain ones, when controlled, are beneficial and leather is most economically made when their products are intelligently employed. Do not forget that it is by-products or refuse from the life processes of the bacteria which are useful. In other words, it is the chemicals, acids, alkalies and enzymes which the bacteria make that produce

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[1] Some of the most intelligent and experienced tanners think that this is not true.—ED.

the results, rather than the bacteria themselves. It should be added that the weight of evidence favors the production of these chemicals when properly regulated in the presence of the hide during certain processes, rather than the addition from an outside source. In other operations, however, as in deliming and in plumping during tanning, the addition of the proper quantities of acids has given excellent results. It is almost an axiom of tanning, that the quality of the leather is largely determined before the pelt reaches the tan pits and this is due almost entirely to the chemical effects of bacterial action on the hide from the moment it leaves the animal until it reaches the yard. A thorough chemical control of the before-tanning processes would do much, I am persuaded, to make the tanning industry more profitable, increase the output and improve the quality of the leather. And just here the greatest advance will come with the entire elimination of mineral acids for deliming and plumping, and the substitution of suitable mild organic acids. It has been proven that mineral acids, once introduced into hides, can never entirely be washed out, nor is it practicable to completely neutralize them. A varying quantity of these acids remains indefinitely, and sulphuric acid especially, materially shortens the useful life of the leather. In my opinion, there is rarely justification for the employment of mineral acids on leathers. It is against the interests of the tanner and the ultimate consumer of leather, who should see to it that the use of these materials is discontinued. In the utilization of tanning materials, there are vast opportunities through chemical control for the conservation of raw material, and the improvement of quality. No one can say how great is the loss of tanning from the tree to the yard. We do know, however, that there are losses in the forest from leaching, in the shade from the action of bacteria on improperly cured bark and in the leaches from imperfect extraction. Here too, the ideal procedure is to carry the bark immediately from the peelers to the leaches. This, however, is impracticable, but our efforts should be devoted to devising means for reducing to a minimum the elapsed time from the felled tree to the leaches, to the protection against moisture, bacteria and mould. Bark which has been in the shed several years has lost much of its value and has tied up capital to no purpose. The question is simply one of business policy. It can be readily seen that it is more economical to pay $12.00 per cord for 10 per cent. bark for immediate use than to use that same bark which two years before had been bought for $10.00 and has lost in the meantime 2 per cent. of tannin. Though tannin costs practically the same per unit in each case (based on the original cost per cord of bark) : it actually costs more, owing to the additional cost of storing, interest on invested capital. etc. The capital required to operate a tannery is largely increased by the practice of storing tanning materials for long periods.

The grinding and leaching of tanning materials, as generally practiced is, I am convinced, a needlessly expensive and wasteful operation; and while we may reasonably hope that the chemist's researches will give us much needed information on the leather making value of reds or difficultly soluble tannins, he has already supplied us with information, which, if more generally used, would lead to improved results. Information which, even when the value of the aforesaid difficultly soluble tannins has been determined, will still have a practical value.

The more rational utilization of that other essential tanning material, water, would undoubtedly be profitable to the tanner and beneficial to the public at large. The chemist has supplied much available and useful data on the effect of water more especially of the dissolved materials in it on the several processes of tanning, and of water borne tannery wastes on public health; and I recall one investigation of the Bureau of Chemistry which revealed the fact that a town was getting its drinking water and its typhoid fever from one well, while an abbatoir ran its polluted water into another, above. The day is not far distant when the waste water from the tannery must be purified before it is run into the streams. It may be predicted that the chemical engineer will ultimately accomplish this, economically if not profitably. A knowledge of the composition of the water used in the tannery is an essential prerequisite to its intelligent operation; and, though it may not be practicable often to change its character, harmful effects may be minimized and advantage taken of any beneficial qualities it may have; indeed it may often happen that a water unsuitable for certain processes, possesses advantages for others. Thus water carrying large quantities of lime in the form of bicarbonate causes losses in leaching and in the yard, and does not delime satisfactorily, but possesses advantages in the soaking of dry salted hides, may be partly purified for leaching, and corrected for deliming purposes. Personally, I am of the opinion, however, that the character of the water effects more the cost of production and appearance than the intrinsic value of the product.

The operations in the tan-yard proper will always be the most interesting of all the processes of the tannery. Here it is that the most striking change from pelt to leather is observed. There is opportunity here also for greater economy and improvement in quality. There is much information on the importance of proper sequence in strength of liquors on the ratio of acids throughout the system, on the ratio of non-tanning to tannins, on the effect of the kind and quality of salts in liquors and on the action of bacteria in the yard. But it is doubtful, if the correct adjustment of all these factors has been carefully worked out for many yards; or if indeed, the interdependence of the resultant effect of these various factors is at all understood. Although much remains to be learned, a more extended application of our knowledge on these subjects would be advantageous. The most important economic problem of the tanning process proper is to materially shorten the time now required and, at the same time, maintain the highest obtainable quality of the leather. If the interest on invested capital could be reduced one half the saving to the tanning industry would approximate 15,000,000 dollars per year. This problem, we may confidently hope, will, with the chemist's help, be solved at no far distant day. When this occurs, I anticipate material departure from the processes now in vogue, or being experimented with and possibly in what are considered essential qualities in leather. In short, new methods of hastening tanning may be expected.

Turning to the after-tannage or finishing processes, what have we learned regarding them and what changes may be hoped for here? It is the almost universal custom to scour, strip and bleach the grain of certain leathers in order to improve the color, while certain other leathers are dyed, greased or loaded as the case may be. Let us consider first what may properly be termed the legitimate after-tanning operations. How essential are scouring, rolling, greasing and evenness of color, what is the cost of each operation, to what extent may it be eliminated and what is the effect of each on the suitability of the leather, on which it is employed, for the purpose to which the leather is put? Does the leather serve its purpose better and longer, because of these operations? Many straight tanned, scoured and finished harness and sole leathers contain from 15 to 20 per cent. of water soluble material, half of which is tannin. In other words, the finished leather contains half as much uncombined and useless tannin as hemlock or oak bark does. The amount of such tannin contained in the sole leather produced in this country alone would make many million pounds of leather. Does this material add to the ultimate intrinsic value of the leather? It is very doubtful. If it can be economically recovered as it surely can, the better policy would be to use this material in tanning other hides, and thus add to the actual values produced, and proportionately decrease the consumption of raw material. In the last analysis all that has been done is to make the ultimate consumer pay for material useless to him which the tanner could use to advantage. Can we not find better use for our tannins than to throw 15 or 20 per cent. of them away? Has the quality and intrinsic value of sole and harness leather been raised by heavy rolling and other operations of finishing beyond the straightening and evening the leather? In stuffing and greasing there is a point beyond which the leather is not improved, and the use of larger quantities is a waste and fraud pure and simple.

The dying of leather is one of the most delicate operations and it has long been established that much leather is materially lowered in quality and durability, primarily by the mineral acids so frequently employed. Though we have some general information on the importance of leather finishing processes there is need of very careful investigation along these lines, that leathers of the greatest value may be produced at minimum cost.

If some of these legitimate finishing processes as executed are of questionable utilitarian value, what shall be said of the practice of bleaching and loading? Briefly, it is robbery. It may be that the practice started thoughtlessly and in ignorance; but no tanner, shoemaker of other manufacturer of leather goods can to-day plead ignorance of the uselessness and harmfulness of the practice nor persuade himself that the finished product does not cost more when the leather is so treated. It is argued, that the loading of leather is occasioned by the demand for cheaper leather, and that more pairs of soles can be cut from a loaded side. Though such leather is sold by weight, it is used by area; and it takes as many square inches of loaded leather to make a pair of soles as it takes of the unloaded, and the loaded leather costs more per square inch. It is safe to say that neither the tanner nor the manufacturer of leather articles can fool himself with such specious arguments. The public is only fooled because ignorant of the facts and because it is impracticable for the individual to protect himself. In the examination of one hundred samples of sole leather in the Bureau of Chemistry, approximately 58 per cent. of them found to be loaded with glucose, epsom salts or both. This loading varies from 1 per cent. to 7½ per cent. of epsom salts and 15½ per cent. glucose, and to a total loading, when both are present, of 19 per cent. The average amount of epsom salts in the adulterated samples is 3 per cent., of glucose 8 per cent., while the average loading in all loaded leather was 9 per cent. If it be assumed that these results are representative of the sole leather made in this country, by these means, approximately half the production, or 125 million pounds of leather, have been lowered in wearing values; the public has been made to pay for not less than 12,000,000 pounds of harmful material in the leather it bought, at an additional cost, above the legitimate cost of leather, of not less than $4,000,000 per annum.

Is it strange that there is a demand for a law prohibiting the loading of leather, or that the suggestion has been sarcastically made in England that imported American leather should be charged duty at proportional sugar rates? But this is not enough; the shoe manufacturer also lowers the wearing value of the sole leather by buffing off the grain and subsequently makes it impossible to determine the quality of the leather by painting it. Undoubtedly, the public is itself partly to blame for the practice as it is governed more by the appearance of the article than by anything else. As a first step in hastening the abandonment of these harmful and misleading finishing practices, I would earnestly urge the public to buy those shoes, the soles of which show the natural grain and color of the leather on the bottom and the edge.

These, in general, are some of the ways in which leather making materials may be more rationally used, and the quality and utility of the leather improved. You will observe that most of the problems involved in the tanning industry are entirely or chiefly chemical in their nature, and it is needless to state that they will be more economically and rapidly solved through the harmonious coöperation of the chemist and the tanner.

On some of the problems of making better leather more economically the Bureau of Chemistry is already at work, and it is hoped through the coöperation of the tanning industry, to extend the work in the study of underlying principles which the tanner has not had time to investigate for himself. Such cooperation will lead to practical results in the shortest time and at minimum expense. I believe I would promise that the Bureau will coöperate earnestly and vigorously with you in determining the losses incident to the several tanning processes, and in devising ways of reducing such losses to a minimum, and also in experiments looking to the improvement of the quality of leather of all kinds.

DISCUSSION.

(We give here an abstract of the long discussion which followed Mr. Veitch's paper.)

Mr. Yocum remarked that Mr. Veitch's estimate of the loss of tannin in storing bark is too high and said that some tanners prefer to have the bark in the shed a year before grinding, the drier bark giving stronger liquors.

Several speakers took exception to the sweeping character of Mr. Veitch's statements about the loading of leather. Mr. Wallin pointed out that the treatment of sole leather described in Mr. Russell's paper, soaking the leather in strong hot liquors after it has been tanned and dried, is loading, according to Mr.

Veitch's definition. Yet this treatment is necessary in order to give the firmness, thickness and resistance to water penetration necessary for a good sole leather. Sole leather is essentially a loaded leather, and wears much better than leather which has absorbed only enough tanning materials to tan it completely.

Mr. Healey described an experiment on water penetration of heavily and lightly tanned leathers. The pieces of leather were clamped to the end of a flanged pipe, the pipe placed upright so that the leather formed the bottom of a cylindrical vessel a foot deep. The vessel was then filled with water. A leather heavily loaded with extract subjected to this test was not penetrated by the water in 28 days, while other samples made from the same kind of hides and completely tanned but not loaded were penetrated in a few minutes so that the water dropped through. This water-resisting property, Mr. Healey remarked, is very necessary to sole leather, and even if the soft leather were water-proofed with rubber or wax, it would not make desirable soles for use on rough ground. The materials crowded into the sole leather make it firm as well as water-resisting.

Mr. Veitch called attention to the fact that glucose and Epsom Salts have not the same value in rendering leather firm and impervious to water, since they are so much more easily soluble in water than the tanning materials which constitute the load in the better qualities of sole leather. Several speakers assented to this point and deplored the use of an excess of soluble materials. Mr. Eisendrath illustrated the matter by stating his experience in testing pig-skin strips with and without added glucose. He believed that the glucose detracted from the value of the leather, and expressed the opinion that in general glucose is used to give weight and that the practice is not fair to the user of the leather.

Attention was called to a point which had been mentioned by Mr. Vogel in the tanners meeting the previous day, that the way to prevent injurious loading is to sell leather on analysis, as tanning extracts are sold. The difficulty at present in the way of this method is the fact that there is no agreement among leather buyers in regard to what they want. In fact it is doubtful in the case of many buyers whether they know what the analysis of a good leather should be, and certainly most wearers of shoes know absolutely nothing about it.

Mr. McCandlish alluded to some experiments of Dr. Parker, which indicated that glucose and epsom salts in leather hastened water penetration.

Mr. Veitch, admitting that excess tannin put into sole leather increases its resistance to penetration, said he was not satisfied that the total wear was increased by such excess, and expressed the opinion that sole leather treated with grease would give better service than that loaded with excess tan.

Mr. Kerr brought up the subject of frictional tests of sole leather. Mr. Veitch said he knew of no effective method of making such tests. Mr. Dickerson mentioned some tests which had been brought to his notice tending to show that solid loaded leathers wear better than loose ones. Another speaker spoke of wear tests which had the same result.

Mr. Holder expressed the opinion that the rolling of sole leather is injurious to it, and that French hammered sole wears better than rolled sole. He hoped that a method of finishing by pressing instead of rolling would be tried, and believed that the resulting leather would be better.

Mr. Veitch, in answer to the question "When is leather loaded?" said "In my judgment any unusual or even regular process which lowers the wearing quality of the leather or which increases its cost without commensurate return is loading."

THE NECESSITY OF PROPER SAMPLING.

By T. A. Faust.

It is evident that the analysis of a sample of any material is practically worthless if the sample is not truly representative of the entire lot; in fact, it is impossible to make a true analysis of a lot from a sample which has not been properly drawn. However, if you review the Journals of this Association, or read the proceedings of the Conventions, you will find very few references to sampling. If you go outside of the sphere of leather chemistry, you will notice the same condition, especially abroad, where sampling has received very little attention.

In fact, the only man who has taken up this proposition thoroughly is Martin Griffin. In an address delivered before the New York Section of the Society of Chemical Industry in 1905, he characterized sampling as a matter of practical mathematics, mean values and theory of errors. He called attention to the work done by the American Institute of Mining Engineers, and also the Association of Official Agricultural Chemists, as being more thorough than that of other Associations. The same gentleman at a meeting in Boston in 1909, read a paper on "A Mathematical View of Sampling with Reference to the Degrees of Accuracy to be Obtained."

Besides these two articles by Mr. Griffin, there are a few articles published on the sampling of Ores, Coal and Fertilizers, but in the last ten years there have not been more than seven or eight articles published on the entire proposition of sampling.

This Association has paid more attention to sampling in the few years of its existence than the majority of the older organizations in their career. But even with us, the importance of proper sampling has been disregarded, our efforts being to make the methods of analysis concordant and trustworthy.

The American Leather Chemists Association has done more work on the subject than the International Association of Leather Trades Chemists. So far as the writer knows, no mention has been made of sampling for some years in the latter Association, until the Conference at Paris, a few weeks ago, when Dr. Gordon Parker read a paper on "Proposed Changes in Rules of Sampling."

The official method of the A. L. C. A. was drawn up at the Convention held four years ago, by a committee of which Mr. Haley was chairman. The methods were patterned after those used by the I. A. L. T. C. The committee realizing that there would be constant improvements, suggested that they be made provisional and not official. The following year at Chicago, the methods were discussed fully, but no changes were made and they remained provisional. At this meeting, Mr. Wallin called attention to several instances where improper sampling had caused large differences in the analysis, and that all members should adhere to the rules.

Last year, the Association made the methods official, and a few weeks ago they were revised. Some of the clauses, however, seem rather impractical, and I hope you will not consider me as a younger member of the Association, too free in expressing my opinion on these methods. My statements are borne out by practical experience in sampling.

In sampling liquid extracts, the most convenient instrument to use is a thief, which is merely a long glass tube, the upper part of which is shaped like an elongated separatory funnel, the lower part tapered to a ¼ inch bore. After proper rolling or mixing, the thief is inserted into the extract, the aperture at top is closed and the instrument quickly removed. This will give you a good average sample. Knocking the heads out of barrels and stirring with a plunger is impossible at the docks or railway siding where a great deal of the sampling is done. In England, most liquid extracts are sampled with a similar instrument, but having the advantage of a valve at the lower end, which can be closed from the top when the container is full.

Solid quebracho and cutch are nearly always sampled by chopping a triangular piece from surface to center of the bag with a chisel and hammer. The suggestion has been made of using a cast iron pipe, sharpened at one end, and a cap on the other, this tube to be driven through the entire bag, and the contents emptied into a closed receptacle. However, this method is not practical in the summer when cutch and most solid quebracho becomes very plastic. The wrapping of the extract in paraffine paper, as advocated in this year's revision, is an excellent idea, as it minimizes the loss of moisture, although wrapping the cork in paraffine paper answers the purpose equally well.

For sampling sumac, a copper tube shaped like a skyrocket is used, the upper part being cut open at the side, the lower part serving as a handle. This can readily be pushed through the bag; a few turns will fill the tube with sumac taken uniformly from the surface to the center of the bag, and the instrument then withdrawn. I think this is superior to the official method, as the latter has a very limited applicability. It is impractical to empty the bags in uniform horizontal layers on the docks or in the warehouses, where the greater part of sumac sampling is done. In addition, sampling can be done by this method in a small fraction of the time necessary for the official method. This instrument can also be advantageously used for sampling valonia crystals and chestnut extract in powdered form.

I also consider it impractical to sample barks and woods by sawing and using sawdust. I think it better to chop off small pieces of the material from various parts of the lot, and then grind in a suitable grinding machine.

In reference to the sampling of materials, other than tanning materials, used in the leather industry, nothing has been said as to the method to be pursued. I would mention greases, oils, moellons, coal, water, paints, lime or any chemical used, or even the proper sampling of leather for analysis. I will not speak of the sampling of any chemicals, as that is more a matter of common sense and is of minor importance. The sampling of water is a comparatively easy matter, although in the case of running water, certain precautions must be taken.

Standard methods of sampling coal are used by all chemical engineers. Mr. A. Bennett published an article on this subject in the Journal of the American Chemical Society, May, 1908. in which he states that the sampling of coal is fully as important, should be conducted under as reliable auspices, and safeguarded as much as the analysis. Of course, the tanners realize the importance of buying coal with the highest B. t. u. value.

The sampling of oils, greases and leather, deserves more consideration, however; while not as important as the tanning materials, just as serious mistakes may be made.

For sampling oils, or in fact any liquids shipped in barrels, carboys or drums, the most convenient instrument is the thief, to which I have referred. This instrument is used by the Government samplers in sampling oils. Moellons should be stirred very thoroughly, as the unoxidized oils will rise to the top, and the oxidized fatty matter and water remain at the bottom when standing for any length of time.

For hard greases, stearine and tallow, an instrument on the order of a tallow tryer is found most suitable and gives a representative sample. I might also mention that block or paste Gambier can be sampled with this instrument to great advantage; in fact, this is the official method of the I. A. L. T. C.

Even the sampling of leather should not be neglected. A great many sample leather by simply cutting a few strips off the back, but this is not at all representative of the entire piece. The back contains less grease than the belly; in harness leather the difference may be 5 per cent., while the hide substance and the combined tannins ate higher in the back; consequently, to obtain a representative sample, pieces should be cut off the back, shoulder, flanks and belly.

In all extracts, all other conditions being equal, an increase in the moisture content will cause a corresponding decrease in the tannin. The tanner who sends solid extracts in a paper or pasteboard box will not obtain a true valuation of his extract, as the extract will dry out in shipment, causing a corresponding increase in tannin. The same applies to any ground fresh bark, also sumac, moisture being lost if not kept in glass bottles. Sumac is sold on a close basis of tannin, and the loss of two or three per cent. moisture will cause an increase of about one per cent. of tannin. In such cases, the tanner is misinformed, as the analysis shows more tannin than he really has in the sumac at the time of sampling. Of course, this is avoided where the official methods are adhered to, but very many tanners underestimate the importance of proper sampling, and do not take proper precautions.

Very often, the importer brings in a shipment from which he draws a sample, and the tanner to whom the goods are sent draws a sample. Now, unless both these men adhere to the prescribed methods, a variance in the analysis will very often occur.

I think it important that every tanner should have a copy of the official methods, and follow these rules, in order to obviate any chance of error in the tannin result. I believe the majority of disputes since the practical perfection of the methods of analysis, are due to variance in sampling, and if this matter can be adjusted, there will be very little occasion for any differing results. Moreover, the tanner will then have more confidence in the chemist's ability to make an analysis beyond question, thereby strengthening the position of the A. L. C. A. in the eye of the tanner.

ETHYL TANNATE.[1]

By R. J. Manning.

Of the naturally occurring tannins gallotannic acid, obtained from gallnuts and many other sources, is the most important and best known. Strecker[2] claims that gallotannic acid is a glucoside of gallic acid as it yielded gallic acid and glucose on hydrolysis. Schiff[3] synthesized digallic acid from gallic acid by means of phosphorus oxychloride and claims that digallic acid and gallotannic acid are isomers. If this were so, gallotannic acid would have a formula $C_{14}H_{10}O_9$ and on hydrolysis would yield no glucose. On account of the difficulty in purifying the tannin, determinations of its composition vary with different experimenters. I have prepared a crystalline ester and through it have obtained satisfactory analyses giving the composition of gallotannic acid and considerable information about it.

DESCRIPTION OF THE GALLOTANNIC ACID USED.

The material used in these experiments was obtained through Lyman Bros., Toronto, from the German firm of Schering, and came in the form of light whitish brown flakes; extracted with ether in a Soxhlet, all dissolved, leaving a slight brown stain in the shell, soluble in boiling water. It was purified by the method described by Walden:[4] 100 grams of the commercial tannin were dissolved in 250 grams of amyl alcohol (which must contain a little water) and 350 grams of ether were added; no precipitate appeared. The tannin was then thrown down by gasoline, filtered and dried in a vacuum desiccator over sulphuric acid. So purified, it formed a whitish, rather heavy powder.

The crude sample of tannin contained a trace of gallic acid detected by the potassium cyanide method;[5] the purified product was free from this if excess of gasoline were not added during purification, and in every respect, except solubility, behaved like gallotannic acid as described in Allen's "Commercial Organic Analysis."[6]

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[1] *The Journal of the American Chemical Society*, October, 1910.

[2] *Ann.*, 90, 340.

[3] *Ibid.*, 170, 49.

[4] *Ber.*, 31, 3167 (1898).

[5] S. Young, *Chem. News*, 48, 31.

[6] Vol. III, Part I, pages 35-38 (1900).

Hydrolysis.—A dilute aqueous solution, after boiling for half an hour, reduced Fehling's solution (glucose) and gave a distinct red with potassium cyanide (Young's test for gallic acid); the same result is obtained by boiling for a moment with dilute hydrochloric acid. After long boiling with calcium carbonate while a current of air passed through the solution, the blue coloration changing to red with acids (which is characteristic of gallic acid) was observed.

Behavior with Reagents.—*Arsenic acid* in 5 per cent. alcoholic solution warmed with its own volume of a 10 per cent. solution of the tannin, solidified to an insoluble jelly, which on standing in the air dried up to a garnet colored mass. *Ammonium molybdate* and *potassium ferricyanide,* reddish colorations; *lime water,* white precipitate quickly turning blue; *ferric chloride,* blue-black precipitate, soluble in much water; *lead acetate or nitrate,* white precipitate in not too dilute solutions; *silver nitrate,* silver mirror on warming; *copper sulphate,* greenish blue gelatinous precipitate turning black on warming; *potassium permanganate* in alkaline solution, red brown precipitate, dissolving on warming to a yellow brown solution which becomes wine-red in the air; dilute *sulphuric acid* and dilute *hydrochloric acid,* and *concentrated salt* solutions form precipitates in moderately concentrated solutions of the tannin, which dissolve again on adding water.

Solubility.—My preparation was soluble in water, glycerol, ethyl acetate, and acetone; slightly soluble in anhydrous amyl alcohol, ether or ethyl alcohol; very slightly soluble in carbon disulphide, benzene and gasoline. It is quite insoluble in chloroform (the gallotannic acid and chloroform were shaken together and filtered, but the filtrate gave no coloration whatever with ferric chloride).

Allen[1] says that gallotannic acid is soluble in six parts of cold water; my preparation was much more soluble. In an experiment in which the tannin and water were shaken together in a thermostat at 0°, many successive portions of tannin kept dissolving until the liquid was a thick sirup, and further addition of the solid balled together and dissolved with extreme slowness. In the end the perfectly clear brownish sirup con-

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[1] *Commercial Organic Analysis*, 3d Ed., Vol. III, Part I, page 34.

tained less than one and a half grams of water to one of tannin. At 32° the saturated sirup was still thicker and contained more than two grams of tannin to one of water.

The solubility of tannin in ether, amyl alcohol, and ethyl acetate, is greatly increased by the addition of a trace of water, as shown by the following data:

One gram of	Dissolved at 15°
Ethyl Acetate (Kahlbaum)	0.2 gram tannin
Ethyl acetate with 5 per cent. water by volume	2.5 " "
Amyl alcohol normal (Kahlbaum)	0.1 " "
Amyl alcohol with 5 per cent. water by volume	0.84 " "

The solubility of mannose, glucose, galactose, cane-sugar and of the glucosides, saponin, salicin, and amygdalin in amyl alcohol, acetone, and in ethyl acetate, is also much increased by the addition of a trace of water but not so markedly, as in the case of tannin. The solubility of the alkaloids, strychnine and brucine, in ethyl acetate and in acetone, on the other hand, is not markedly increased by the addition of water.

In these solubility determinations the method of analysis for gallotannic acid was that described by F. Jean,[1] involving titration with iodine in alkaline solution.

ANALYSIS OF GALLOTANNIC ACID.

To insure perfect dryness the tannin was heated in a hot air-bath at 110° for two hours.

(*a*) The elementary analysis gave the following results:

Calculated for $C_{41}H_{32}O_{26}$ .... C, 52.35; H, 3.40.
Found .... C, 52.4, 52.25; H, 3.45, 3.49.

(*b*) To estimate the glucose in tannin, the following procedure was adopted: 0.2 to 0.5 gram of the tannin was boiled with 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid for an hour. As gallic acid has a marked reducing action on Fehling's solution, it was removed by extraction with ether, and as glucose itself is somewhat soluble in water-saturated ether, the extraction was carried on quantitatively and a correction applied as follows:

From 0.1 to 0.5 gram glucose was mixed with 0.5 to 1.2 grams ethyl gallate and the mixture dissolved in 200 cc. water and 25 cc. of 10 per cent. hydrochloric acid. After boiling the solu-

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[1] *Chem. Centr.*, 1900, I, 1107.

tion for an hour, it was made up to 100 cc. and extracted six times by shaking up for ten minutes each time with 50 cc. of ether. After the sixth extraction, all the gallic acid formed by the hydrolysis of the ether except a slight trace had been removed. The following percentages of the original glucose were found by analysis in the aqueous layer:

Glucose	78.9	79.0	78.8	78.6	per cent.

Hence the boiled solution of tannin was extracted six times with ether, the free hydrochloric acid neutralized with sodium carbonate, the glucose estimated and the results multiplied by 100/79.

The analysis gave glucose: 19.0, 18.79 per cent. Calculated on the assumption that one formula weight of the tannin on hydrolysis gives one formula weight of glucose: 19.1 per cent.

(*c*) Formula weight determination from the boiling-point of solutions.

Water as solvent	813	843	922	1025	1500
Acetone as solvent	1672	2023	1500	1450	....
Water as solvent (from freezing point)	1957	1942	1769	1956	1972

Calculated for $C_{41}H_{32}O_{26}$: 940.

PREPARATION OF THE ETHYL ESTER OF GALLOTANNIC ACID.

50 grams of the tannin were dissolved in 250 cc. of Kahlbaum's 99.8 per cent. ethyl alcohol. After introducing the light brown solution into a 500 cc. flat-bottomed flask, hydrogen chloride gas, dried by passing through 18 inches of pumice stone moistened with sulphuric acid, was bubbled through for at least two and a half hours. During the operation the temperature of the liquid rose to about 60°. By cooling the solution during the passage of the gas through it, the yield was diminished, while applying heat to the flask did not noticeably increase the amount of the ester formed.

The dark brown sirup left after the passage of the hydrogen chloride gas was evaporated in a large porcelain evaporating dish until quite thick, and Kahlbaum's lime-free barium carbonate added in excess. The sticky mass was extracted three times with anhydrous ether, the resulting greenish brown ethereal liquid allowed to evaporate, and the residue heated for some hours in a water-bath. A dark greenish brown powder remained.

The crude ethyl tannate so obtained was purified by extraction with chloroform in a Soxhlet for two days. This leaves behind the coloring matter and unaltered tannin but dissolves any ethyl gallate as well as the ethyl tannate; hence the necessity of using tannin as free as possible from gallic acid. During the extraction the ethyl tannate separated out of the chloroform in the form of pale yellow spherical nodules of about 2 mm. in diameter. The yield was about 40 per cent. of the tannin used.

In the hope of obtaining a better yield, 50 cc. of benzene[1] were added to the dark brown solution through which the hydrochloric acid gas had been passed, the whole well shaken and the benzene distilled off. After three successive treatments with benzene, the liquid left in the distilling flask was evaporated and treated with barium carbonate and ether as before. This method gave no better yield and was therefore not used again.

DESCRIPTION OF THE ETHYL TANNATE.

On splitting open these nodules, they were seen to consist of a mass of light yellow shining crystals radiating from a common center. Their melting-point was 157° (ethyl gallate melts at 141°).[2] They were readily soluble in ether, alcohol and water; slightly soluble in chloroform; insoluble in gasoline and in carbon bisulphide. Their aqueous solution resembled a solution of tannin in its reactions with ammonium molybdate, lead nitrate or acetate, silver nitrate, copper sulphate, and potassium permanganate. With potassium cyanide the aqueous solution of ethyl tannate always gave a slight red color indicating the presence of traces of gallic acid or its ester.

ANALYSIS OF THE NODULES.

(*a*) *Elementary Analysis.*—The substance was mixed with a little carefully dried red lead and ignited in a porcelain boat.

The analysis gave: .... C, 52.3 52.4 52.35; H, 5.25 5.11 5.25
Calculated for $C_{51}H_{62}O_{31}$: 52.30 5.30

(*b*) *Loss of Water on Heating.*—To estimate the percentage of water, the nodules were heated in an air-bath to 125-135° for two hours. On first heating they became rather sticky, but

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[1] *J. Chem. Soc.*, **88**, 852 (1905).

[2] Etti, *Ber.*, **11**, 1882.

did not melt completely, and on continued heating became drier again but showed a tendency to turn brown and to sublime. Hence care had to be taken not to allow the temperature to rise over 135°.

The analysis gave: 7.6, 7.5, 7.8 water; calculated for $C_{51}H_{52}O_{28}.5H_2O$: 7.69 per cent.

(*c*) *Ethoxyl Determination.*—The method used was that of Zeisel as described in Meyer and Tingle's "Estimation of Organic Radicles," pp. 34-48. In some of my determinations the precipitate of silver iodide was brownish instead of yellow. The results with these colored precipitates varied widely, being too large, and hence were rejected. It was found afterward, however, that if the brown silver iodide precipitates in these high results were boiled for five minutes with 100 cc. of 15 per cent. nitric acid, filtered and weighed, the precipitates regained their normal color and the new results agreed with those not rejected. This treatment with nitric acid does not perceptibly affect the pure silver iodide.

OC_2H_5 found: 19.24, 19.32, 19.39, 19.55, 19.55 per cent.; calculated for $C_{41}H_{27}O_{23}(OC_2H_5)_5.5H_2O$[1]: 19.23 per cent.

(*d*) *Hydrolysis of the Ester and Estimation of the Glucose.*—2 grams of the ester were boiled with 100 cc. water for two hours with a return condenser and then 25 cc. distilled off. This distillate gave no trace of alcohol when tested by the iodoform method.[1] If, however, previous to the distillation, 10 cc. of dilute hydrochloric acid or of dilute caustic potash were added to the distilling flask, the distillate then gave, especially in the latter case, a distinct deposit of iodoform.

The freshly prepared solution of ethyl tannate reduced Fehling's solution slightly; but the solution which had been boiled with acid or with caustic potash reduced Fehling's solution readily and gave a marked potassium cyanide test for gallic acid. The products of the hydrolysis are therefore ethyl alcohol, glucose, and gallic acid.

The glucose was estimated by the same method as was used for the estimation of glucose in the gallotannic acid and the same correction was applied.

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[1] *Z. anal. Chem.*, **9**, 492.

The analysis gave: 15.37, 15.42, 15.51, 15.13 per cent. glucose. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives one formula weight of glucose: 15.38 per cent.

(*e*) *Estimation of the Gallic Acid.*—0.2 to 0.3 gram of the ethyl tannate was hydrolyzed by boiling with dilute hydrochloric acid as in the estimation of the glucose. The boiled solution was then diluted to 250 cc. and the gallic acid estimated by the iodine titration method of Jean.[1]

Gallic acid found: 72.56, 72.66, 72.8. Calculated on the assumption that one formula weight ($C_{51}H_{62}O_{31}$) of the ester on hydrolysis gives five formula weights of gallic acid: 72.64 per cent.

(*f*). *Formula-weight Determinations from Boiling-Point of Solutions.*—

Acetone as solvent: 255, 280, 257.
Ethyl acetate as solvent: 362, 275, 300.
Chloroform as solvent: 1,335, 1,000, 1,200, 1,467.
Water as solvent (from freezing point): 301, 309.
Calculated for $C_{51}H_{62}O_{31}$: 1,170.

Comparing these results, it is seen that those given by the chloroform solution are several times greater than those given by the other solutions. The lower numbers might be explained by assuming that in all the solvents but chloroform there is a dissociation into anhydrous ester and water. To test this, 0.5 to 1.0 gram of ester was dissolved in 50 cc. acetone and the solution dehydrated carefully by introducing 10 grams anhydrous calcium chloride. After filtering and washing the calcium chloride carefully with acetone, the filtrate was diluted up to 100 cc. and its boiling-point determined, giving the following results:

Formula weight found: 950, 1,050. Calculated for $C_{51}H_{52}O_{26}$: 1,080.

Moreover, on evaporating this solution to dryness, an amorphous dark brown, sticky mass was left, instead of the crystalline substance before obtained.

A HIGHER HYDRATE OF THE ESTER OF GALLOTANNIC ACID.

On the evaporation of solutions of ethyl tannate in ether, chloroform, alcohol, acetone, and ethyl acetate, only minute crystals were obtained. To get large crystals, a cold (15°) saturated aqueous solution of ethyl tannate, obtained without

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[1] *Chem. Centr.*, 1900, I, 1107.

heat, was allowed to evaporate in a round-bottomed evaporating dish by being placed in the sunlight. Even at that temperature a partial decomposition of the ester into ethyl gallate and glucose took place. The ethyl gallate, being less soluble, crystallized out first as a top ring of pale yellow, steep rhombic crystals around the sides of the evaporating dish. At the bottom of the vessel, on almost complete evaporation, were found large, light brown crystals, many between one and two centimeters in length, with a sticky fluid containing the glucose.

An aqueous solution of these crystals behaved like a solution of the lower hydrate of ethyl tannate. They melted at 132°[1] and effloresced readily over sulphuric acid and slowly in the air. They lost their water of crystallization on being heated at 125-135° like the lower hydrate.

Analysis gave: 20.5, 20.7, 21.0 per cent. water. Calculated for $C_{51}H_{52}O_{24}.15H_2O$: 20 per cent.

SYNTHESIS OF ETHYL TANNATE FROM ETHYL GALLATE AND GLUCOSE.

20 grams ethyl gallate prepared according to Schiff's method[2] were ground up with 5-6 grams glucose and mixed to a thin paste with phosphorus oxychloride. After heating this paste in a water-bath for two hours, during which time great quantities of hydrochloric acid were given off, a dark sticky mass remained. This was further dried by heating at 120° for a couple of hours, extracted with anhydrous ether, the ether solution evaporated, and the residue again extracted with chloroform in a Soxhlet for twenty-four hours. At the end of that period a light colored mass had settled out of the chloroform. By the fractional crystallization of its aqueous solution as previously described, the higher hydrate of the ethyl ester of gallotannic acid was obtained. This gave all the reagent tests for tannin, for glucose, and ethoxyl groups. It melted at 132°. The maximum yield I obtained was only about 5 per cent. of the theoretical.

SUMMARY.

1. Two crystalline derivatives of tannin have been obtained.

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[1] Hydrated ethyl gallate melts at 90°.

[2] Schiff, *Ann. Chem.*, 163, 215; 170, 72.

They are ethyl esters of gallotannic acid differing in the amount of water of crystallization. The previous analyses of gallotannic acid varied because crystalline derivatives were not known and therefore pure material was very difficult to obtain.

2. These esters were synthesized from alcohol and gallotannic acid and one of them was also synthesized from ethyl gallate and glucose.

3. Various analyses show that the formulas for these esters are $C_{41}H_{27}O_{21}(OC_2H_5)_5.5H_2O$ and $C_{41}H_{27}O_{21}(OC_2H_5)_5.15H_2O$, and that they are glucosides of gallic acid in which one formula weight of glucose and five formula weights of gallic acid are represented in one formula weight of the ester. This gives the formula $C_{41}H_{32}O_{26}$ for gallotannic acid.

4. Dissociation of the hydrated ester into water and anhydrous ester would account for the low formula-weight determinations in acetone, etc.

This work was done under the direction of Professor W. Lash Miller.

ABSTRACTS.

Determination of Acids in Tanning Liquors. GEORG GRASSER. *Collegium,* 1910, pp. 406-10. The usual method consists in determining CO_2, acetic, lactic and gallic acids as a sum, or by distillation separately determining the volatile acids, CO_2 and acetic. The author figures and describes an apparatus for determining the separate acids in one operation. The assay flask, an Erlenmeyer, is provided with a 3-hole cork. Through one hole passes an inlet tube to the bottom of the flask; outside it is branched by a T-joint to admit either CO_2—free air or live steam. An other opening carries a dropping funnel, while the third, an outlet bears a T-tube connected with both inverted and downward condensers. There are therefore 5 independent passages to the flask, which may be closed by cocks or screw clips. The top of the invert condenser is connected with a train of $CaCl_2$ and KOH absorbtion tubes terminating in an aspirator. Before analysis, a current of air freed from CO_2 is drawn through the apparatus for some time and then the assay liquor is introduced through the dropping funnel, heated to boiling to expel the CO_2 which is collected in the KOH bulb for weighing. When this is completed the inverted condenser is shut off and the acetic acid expelled and collected in a beaker beneath the direct downward condenser for titration. The residue in the flask, after removal of the tannin by gelatine (Koch's method) is titrated with baryta and phenol-phthalein for lactic acid plus gallic acid. In case it is desired to separately determine gallic acid, the author has obtained good results by the following method. The sample is divided into 3 aliquot parts, and in one the sum of lactic and gallic acid determined as above. The second is titrated with 1/50 N. iodine solution until one drop gives with starch paste in a porcelain dish a weak violet permanent for ½ minute. The iodine solution is standardized on pure gallic acid (say 7 grams per liter) to the same end-point with dark colored solutions, the spotting test is best observed at the contact zones of the two drops. To the third portion, a few cc. of dilute H_2SO_4 (1:20) are added and the titration made similarly. In this case, the iodine is fixed by the tannin alone, the acid preventing absorption of iodine by the gallic acid. The difference between the second and third titrations in iodine equivalents, represents the equivalent of the gallic acid. Larger amounts of H_2SO_4 may precipitate part of the tannin and withdraw it from action of iodine. Some practice is required for accurate results.

Chestnut Extract. U. J. THUAU. *Le Cuir*, 1910 (3) 541-2.—The European chestnut, *Castanea vulgaris* grows principally in France, Italy and Spain. In Australia there are tannin yielding trees of the cupeliferous family, resembling the chestnut, but the extracts are much redder. In North America the species is *C. pumila,* rich in tannin. In France there are over 30 factories of chestnut extract producing 40 million francs worth annually. This consumption threatens an exhaustion of the chestnut forests and it behooves the State to reforest. Fresh cut wood contains about 75 per cent. H_2O, 4 per cent. tannin; after 3 months seasoning the barked wood contains 30-35 per cent H_2O. The dry wood contains from 7 to 11 per cent. tans, and that from Corsica even 12 to 13. Besides its tannin of the pyrogallol class, chestnut wood contains large amounts of sugar and resins. The dried roots contain 5 to 7 per cent. tans while the bark contains only 2 to 3 per cent. The ash of the wood extends to 5 per cent., composed chiefly of phosphates of lime and potash. Chestnut wood is of a grayer color than oak and it is easy to recognize leather which has been layered with chestnut wood by its yellowish gray color. Extracts, because of the decolorization in manufacture, show this less. Chestnut wood has increased in price in recent years, reaching 20 to 23 francs per ton. The small branch wood yields an extract richer in sugar and non-tans; 6 per cent. glucose was found in such an extract of 25° B. Although suited for the first vats, it is harmful in the drum. Medium wood should yield an extract of under 3 per cent. sugar which gives sufficient acid.

The Mimosa Barks and their Significance for the Leather Industry. JOHANNES PAESSLER. *Ledertechn. Rundschau,* 1910, pp. 321-3, 329-31.—Although the importation of this valuable material rich in tannin increases from year to year, the author believes it could be used with advantage in greater amount and the object of the paper is to point out its useful properties and to promote its utilization. The varieties of interest in the tanning industry are derived from several acacias native to Australia but later introduced into other lands. In English they are called "wattles" probably from the use of the tree in making wattled structures. The principal species are: *Acacia decurrens,* also var. *A. molissima,* the black or green wattle of New South Wales which flourishes even on the poorest soil; *A. pycnantha* and *A. penninerris,* the gold wattle which grows in South Australia in the coast regions; *A. deal bata,* the silver wattle growing in Tasmania, Victoria and New South Wales. Of these the black wattle, containing 25-45 per cent. tannin and the gold wattle, 20-30 per cent., are valued highest; the silver wattle is poorer. Formerly the tannin content of the commercial bark fluctuated greatly but since its value has become known, the richest varieties have been selected and cultivated and a ware of less than 30 per cent seldom appears. The cultivation of tannin-yielding acacias was introduced into South Africa (Natal) some 30-35 years ago and has been maintained with the *A. decurrens,* van. *molissima,* this being the richest. A very sandy stony soil is unsuited for the tree, likewise a lime soil; the best is a deep soil of medium adhesiveness, a sandy clay. In Natal the tree grows at elevations of 300-1,100 m. above the sea, and flourishes best at a medium annual temperature of 10-15° C. and not less than 400 mm. rainfall. A detailed account of the sowing and cultivation is given. The tree grows rapidly and in 5-10 years gives a bark of 6-10 mm. thickness. In Natal the trees are felled and stripped when 6-7 years old. The best results are obtained by drying the bark under cover.

(To be Continued)

PATENTS.

Process for Detanning Chrome Leather. U. S. Patent No. 967,215. ALBERT G. MANNS, Oconomowoc, Wis., assignor to A. O. Trostel.

The patentee is a recently elected member of the A. L. C. A. His process consists in soaking the leather scrap in clear lime water, then in a weak acid solution, then in a weak alkaline solution and finally washing it. The material so treated is said to be good glue stock.

Process of Forming Glue from Leather. U. S. Patent No. 967,762. HENRY G. HALLORAN, Brighton, Mass.

The leather scrap is subjected to electrolysis in a solution of salt. The current forms caustic soda and chlorine which decompose the leather. The material is then washed, soaked in chlorine water and again washed.

Process of Coloring Leather and Products Thereof. U. S. Patent No. 970,326. MARGARET M. GREGG, Brooklyn, N. Y.

Apparatus for Treating, Dehairing, Swelling and Tanning Hides. U. S. Patent No. 971,126. A. FAY, Louisville, Kentucky, assignor to G. F. Seiser and W. J. Cogle.

The hides are suspended in the liquor in a closed tank, from which the air is then exhausted. During the treatment a little warm air is permitted to enter below the surface of the liquor.

Bark-Rossing Device. U. S. Patent No. 973,494. CHARLES FRIEDLUND, Mountain, Wis.

Roll for Leather-Dressing Machines. U. S. Patent No. 973,675. W. F. LUCKE, Champlain, N. Y., and JESSE C. BLAKE, Beverly, Mass., assignors to T. W. & C. B. Sheridan Co.

Formic Acid. U. S. Patent No. 975,151. MAX NEUMANN, Wiesbaden, Germany, assignor to General Chemical Co., New York.

Formic acid is made by the action of phosphoric acid on a formate in the cold.

Process of Tanning. English Patent No. 26,040. C. W. NANCE, London.

The hides to be tanned, separated by wooden frames, or by other means, are placed in a closed pan and treated with thin milk of lime. A high vacuum is maintained in the pan, the liquid contained in it being occasionally boiled. After 24 hours the hides are taken out, scraped free from hair and washed in the usual way. They are then placed in a pan in which a high vacuum is created and weak tanning extract is sprayed over them until they are well covered, the liquid being occasionally boiled. As the liquor evaporates, further weak liquor is run in until the extract is fairly concentrated, after which it is not again boiled. From time to time a little of the liquor is withdrawn and fresh liquor passed in. In about two days the hides are tanned and may be withdrawn, washed, air-dried, and finished, or they may be washed and dried in the vacuum-pan in which they were tanned.—Abstract from *J. S. C. I.*