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Association

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COUNCIL MEETING.

A meeting of the Council was held at New York, December 3, 1910. The following members were present, Messrs. Russell, Reed, Teas, Hoppenstedt, Griffith and Alsop.

The National Tanners Association desiring that two members serve on their Advisory Committee for the tanners institute. J. H Russell and J. H. Yocum were appointed in accordance with their suggestion.

The Secretary was requested to send out a form to the active members and endeavor to secure from them information that would be of use in making up committees and lead to better support of this important part of the Association's work.

The following committees have not presented reports as yet.

On the Detection of Tanning Materials in Mixtures, A. L. Dean, Chairman.

On the Cure and Disinfection of Hides, V. A. Wallin, Chairman.

"Chrome" Committee, S. S. Sadtler, Chairman.

The following subjects were chosen for committee work.

Analysis of Leather, F. P. Veitch, Chairman.

Acidity of Tanning Liquors, W. K. Alsop, Chairman.

Rapid Cooling of Tannin Solutions for Analysis, H. C. Reed, Chairman.

Disposition of Tannery Waste, J. H. Russell, Chairman.

Analysis and Detection of Sulphite Cellulose Extracts, P. H. Small, Chairman.

Plumping Effect of Acids, Lloyd Balderston, Chairman.

Oil Analysis.

Analysis of Extracts—C. W. Morris was appointed to secure collaborative analyses from the active members of three samples of extract, one chestnut, one unclarified quebracho and the other one to be selected by him.

PROPOSED CHANGES IN METHODS.

At a meeting of the Council held December 3, 1910, the following proposed changes in methods were submitted in writing. In accordance with the By-Laws these are published in this issue of the JOURNAL.

Official Method for Tannin Analysis, Analysis of Extracts, Section 9, *Non-Tannins.* Third line commencing with "Digest" to read "ten times" instead of "twenty-five times." (This refers to the proportion of water to hide powder.)

Official Method for Tannin Analysis, Crude Materials. To Section 4, *Extraction of Sample,* shall be added the following:—4(a) *Fresh Materials; Woods and Barks, 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.

Official Method for Tannin Analysis, Crude Materials, Section 4, *Extraction of Sample.* Fifth line commencing with "At least" to be altered to read "500 cc. etc."

METHODS OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR 1911.

OFFICIAL METHOD FOR TANNIN ANALYSIS.

I. Crude Materials.

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of Sample for Extraction*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of

water for extraction should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatine salt solution fails to give a precipitate. At least 400 cc. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

(4A) *Sumac and Kindred Materials*:

Put the material (the amount should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water and allow to soak one hour. Then extract by collecting 2,000 cc. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand over night and analyze the following day by the Official Method for Extracts.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Method for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts.

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35-0.45 gram tannin per 100 cc. of

solution. Dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir and pour on a 590 S. & S. 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

(9) *Non-Tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with twenty-five times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand overnight. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary; so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the original solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the filtrate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning until clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE.—In order to limit the amount of dried hide powder

used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 per cent. to 75 per cent. water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatine 10 per cent. salt solution.

(10) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

III. Analysis of Liquors.

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-Tannins*:

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 table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
0.35——0.45 gram	9—— 11 grams
0.25——0.35 gram	6.5—— 9 grams
0.15——0.25 gram	4——6.5 grams
0.00——0.15 gram	0—— 4 grams

Solutions to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

IV. Evaporation and Drying.

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer,"

at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor greater than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(17) *Reagents*:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter, is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS.

General:—

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture, it is apparent that the sampling in all its details

should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air-tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of the liquor which have set around with no preservative in them for some time do not represent the condition of the liquor when sampled.

(1) *Number of Packages to be Sampled*:

When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to sampled, 1 per cent. of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10 per cent. of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9 per cent. of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8 per cent. of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7 per cent. of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6 per cent. of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5 per cent. of the number of barrels shall be sampled. When from 421 to 500 barrels are to be sampled, 4 per cent. of the number of barrels shall be sampled. When more than 500 barrels are to be sampled 3 per cent. of the number of barrels shall be sampled.

(2) *Liquid Extract in Barrels*:

The heads shall be removed from the number of barrels

specified in (1), the contents of each barrel stirred until homogeneous, and a sample of equal size taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples shall be drawn for analysis. These samples shall be preserved in air-tight glass containers, labeled with the date of sampling and such distinguishing marks as may be necessary. When a considerable period of time is likely to elapse between the sampling and the analysis, each individual sample shall be weighed when prepared and the certified weight of the sample be marked on the label.

(3) *Liquid Extract in Bulk*:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) *Liquid Extract in Tank Cars*:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE: As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge 3 minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container so soon as taken, be thoroughly mixed and sampled as in (2).

(5) *Solid Extracts*:

The number of packages specified in (1) shall be selected, as nearly as practicable, of equal size. Whenever possible every n^{th} package shall be set aside for sampling while the extract is being unloaded. When this is not possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up till it will pass through a sieve of 1 inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of the required size shall be taken, be wrapped in paraffine paper, and be enclosed in the smallest clean dry air-tight glass receptacles that will hold them, labeled, etc., as in (2).

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least two pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(6) *Crude Tanning Materials*:

A. Shipments in bags, mats, barrels or other similar packages.

The number of packages specified in (1) shall be emptied in uniform horizontal layers in a pile on some clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than two quarts each shall be preserved in air-tight containers properly labeled.

When the number of packages to be sampled is so great as to make one pile impracticable, two or more piles may be made, and the samples from the several piles properly mixed.

B. Shipments in bulk.

1. Nuts, Beans, Pods, Ground Materials, etc.

Equal portions shall be taken from at least ten uniformly

distributed parts of the bulk, be mixed and sampled as in "A."

2. Bark, Wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least one quart in size be preserved in air-tight containers, as in "A."

(7) *Spent Material from Leaches*:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(8) *Tanning Liquors*:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint be taken for analysis. The addition of 0.03 per cent. of thymol of other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than one pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) *Preparation of Sample*:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

(2) *Moisture*:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats*:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) *Ash*:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material*:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose*:

To 500 cc. of the solution obtained by extraction according to (5), add 20 cc. of normal lead acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry Na_2CO_3 and filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry Na_2CO_3 until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than 0.25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with

water to 145 cc. if necessary, cover with a watch-glass, bring to boil and set in a boiling water-bath for exactly 30 minutes. Filter through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol, dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by 0.8883 and calculate to glucose according to the following table: (Published this JOURNAL, May, 1909, page 125, et seq. from J. S. C. I., **13**, 1227 et seq.)

(7) *Nitrogen*:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107, (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling-point of the acid

from 5 to 15 minutes, or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHOD FOR COLOR VALUATION OF TANNING MATERIALS.

Immerse a piece of thoroughly wetted white broadcloth, three inches by four in size, in a solution of the material to be tested, containing 3 per cent. of tannin, and allow to remain with frequent agitation for 45 minutes. The solution previous to immersing the cloth is heated on a water-bath to 50° C. and the heat then turned off, the coloring being effected 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. in diameter and 4 in. deep, and the beaker immersed at least 2½ in. 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.

PROVISIONAL METHODS FOR THE ANALYSIS OF OILS AND FATS.

Saponification Value.

Preparation of the Alcoholic KOH.—Purify the alcohol as follows: To ordinary alcohol add potassium permanganate in very fine powder or saturated solution until the pink color holds for about ten minutes; allow to stand over night, filter and distil over a fixed oil and sodium hydroxide, the first portions of the distillate, about a quarter, being rejected. Dissolve the KOH in the alcohol thus prepared, filter, and make up to half normal strength.

Determination.—Weigh off accurately in a flask holding 150-200 cc., 1.5-2.0 grams of the fat, or oil, purified and filtered if necessary. Next run into the flask 25 cc. of the alcoholic potash, attach a long cooling tube or invert condenser, and heat on the water-bath for thirty minutes, frequently imparting a rotary motion to the contents of the flask until complete solution has been effected, which can always be done unless there is considerable unsaponifiable material present. After this allow to simmer, but not to boil vigorously, for the remainder of the time. Next add 1 cc. of a 1 per cent. phenolphthalein solution prepared by dissolving 1 gram phenolphthalein in 100 cc. 90 per cent. alcohol and titrate back the excess of potash with half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, the same influence on the final result, and is thus eliminated. The difference in the number of cubic centimeters of acid used for the blank test and the real test corresponds to the quantity of potash required, and is calculated to milligrams of potash to 1 gram of fat.

Acid Value.

Weigh accurately a convenient quantity of the material to be tested into an Erlenmeyer flask, and treat with about 25 cc. of a mixture of alcohol and ether, previously rendered slightly pink with alcoholic KOH after the addition of 1 cc. 1 per cent. phenolphthalein solution. Then titrate the mixture to the same point to which the solvent had been brought. Use tenth-normal alcoholic KOH for this and from the number of cubic cen-

timeters required, calculate the amount of KOH absorbed. This expressed as the number of milligrams per gram of substance is the acid value.

Iodine Value.

A. O. A. C. Official Method—The Hanus Method. Bulletin No. 107.

(*a*) *Preparation of Reagents—Hanus Iodine Solution.*—Dissolve 13.2 grams of iodine in 1,000 cc. of glacial acetic acid (99.5 per cent.) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration—3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal Sodium Thiosulphate Solution.—Dissolve 24.8 grams of chemically pure thiosulphate, freshly pulverized as finely as possible and dried between filter- or blotting-paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

Solution of Potassium Iodide.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

Decinormal Potassium Bichromate.—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

(*b*) *Determination*—(1) *Standardizing the Sodium Thiosulphate Solution.*—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

(2) *Weighing the Sample.*—Weigh about 0.5 gram of fat or 0.250 gram of oil[1] on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour into the crystal and allow to cool. Introduce the watch crystal into a wide mouth 16-ounce bottle with ground-glass stopper.

(3) *Absorption of Iodine in Hanus Method.*—Add 25 cc. of the iodine solution to the fat or oil dissolved in 10 cc. of chloroform. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent. of the amount added.

(4) *Titration of the Unabsorbed Iodine.*—Add 10 cc. of the potassium iodide solution and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(5) *Standardizing the Iodine Solution by Thiosulphate Solution.*—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

[1] Use from 0.100 to 0.200 gram in case of drying oils which have a very high absorbent power.

Per cent. of iodine absorbed:

Weight of fat taken	1.0479	grams
Quantity of iodine solution used	40.0	cc.
Thiosulphate equivalent to iodine used	62.1	cc.
Thiosulphate equivalent to remaining iodine	30.2	cc.
Thiosulphate equivalent to iodine absorbed	31.9	cc.
Per cent. of iodine absorbed (31.9 × 0.012697 × 100) divided by 1.0479	38.65	

Unsaponifiable Matter.

Wherever possible use the following method: Saponify 5 grams, or its equivalent, with 5 cc. of a 50 per cent. by volume aqueous KOH solution and 25 cc. alcohol. Heat on the water-bath for half an hour, frequently agitating at the beginning until as complete solution has been effected as is possible. Then transfer to a shallow porcelain dish, using alcohol to rinse the flask. When the alcohol is about half evaporated off, mix 10 grams of sodium bicarbonate and 25 grams of clean quartz sand, previously washed with HCl and distilled water and dried thoroughly. Add this mixture to the soap and stir together with a glass rod. Evaporate to dryness and continue the drying for several hours or over night. The mixture is then pulverized and placed in a Soxhlet extraction apparatus, where it is extracted with a low-boiling petroleum ether for four or five hours. The ether solution, containing the unsaponifiable matter is then transferred to a separatory funnel and washed with distilled water. Then filter into a tared flask, and distil off the solvent. The last traces may be removed by passing a current of air through the flask over the residue and finally drying in an oven at 98°-100° C. for four hours. The residue is weighed as unsaponifiable matter.

For oils that cannot be treated in this way on account of their forming a glutinous mass with petroleum ether, proceed as follows:

Saponify in the same manner as above and transfer to a shallow porcelain dish. Evaporate to dryness and continue to dry for several hours, or over night, but without adding sand and sodium bicarbonate. Next add about 30 cc. petroleum ether and rub it up with the soap by means of a glass rod flattened at one end. Then decant off the ether, with whatever soap may be in suspension in a finely divided condition and repeat the operation

several times until the soap is thoroughly extracted. No less than 200 or 300 cc. in all should be used. The soap in suspension, as well as in solution is next washed out with distilled water in a separatory funnel, using a little alcohol to break up emulsions. The washing should be proceeded with cautiously at first, and the clear ether transferred to another funnel as fast as it is formed, where it may be vigorously shaken. The aqueous soap solution should also be shaken out with petroleum ether as some of the unsaponifiable matter is apt to pass into the aqueous part together with the soap. When thoroughly washed, all the ether solutions are filtered into a tared flask, the solvent distilled off, the last traces being removed by passing a current of air through the flask and drying in the oven for four hours, as above. The residue, however, may contain small amounts of fatty acids which can be determined from the acidity and a correction made.

Maumené Test.

In a tall 100 cc. beaker weigh out such a quantity of oil as when made up to 50 grams with mineral oil will not give a rise in temperature above 60° C. Make up to 50 grams with mineral oil and place in a large beaker well lined with hair. Add 10 cc. concentrated sulphuric acid of the same temperature as the oil mixture, taking one minute to add and always allowing the pipette to drain the same length of time. Stir constantly with the thermometer during the addition of acid and continue stirring until the temperature has reached the highest point. Run blank, using the same amount of mineral as for test. Deduct this rise from the total rise for the mixed oil. For specific temperature, run 50 grams of water in the same way as the sample was run. Divide the rise in temperature per gram of oil by rise in temperature per gram of water and multiply the result by 100.

Specific Gravity.

Specific gravity should be determined at 20° C., both the substance and the distilled water with which it is compared being at that temperature.

Titer Test—Provisional.

A. O. A. C. Provisional Method.

Bulletin No. 107.

(*a*) *Standard Thermometer.*—The thermometer must be grad-

uated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be made at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about fifteen inches over all. The thermometer is annealed for seventy-five hours at 450° C. and the bulb is of Jena normal 16-inch glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched in the stem, the graduation to be clear cut and distinct but quite fine.

(*b*) *Determination.*—Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free the fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam-bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 × 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce saltmouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 × 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermometer, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury.

The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Melting-Point.

Take a tube of thin glass 2½ inches in length, and of such size that when the thermometer is inserted there will be about 1 mm. space between it and the glass. Fuse one end of the tube in the flame until the edges are drawn in slightly, forming a smooth, round hole. About half an inch from the other end make a small hole, either by fusing and blowing, or by filing. The tube is then ready for use. Draw a rubber band tightly over the end that was partially closed by fusion and bind on with a rubber ring. Pour such a quantity of the melted fat into the tube that when the thermometer is inserted the bulb will be a little more than covered by fat. The column of fat should then be about one and one-fourth inch in height. The thermometer, which is inserted to near the bottom of the tube is firmly secured with a perforated cork. The fat is now cooled well down below its melting-point by immersing in cold water. When this is done, take the apparatus from the cold water, remove the rubber band, and wipe dry. Then suspend the thermometer with the tube and fat attached, in an Erlenmeyer flask, or other convenient air-bath, securing it by means of a cork. Place on a water-bath and as the temperature slowly rises note the point at which the fat begins to protrude quite perceptibly, also the point at which the first drop falls and the point at which the fat becomes clear. For the latter, a small cork is inserted to prevent the fat from running out. Then remove the cork, and as the fat runs out notice its consistency, whether thin or viscous.

Cold Test—Millwood.

Warm the oil until the stearine is dissolved and filter through several thicknesses of filter-paper, into a *dry* 4-ounce wide-

mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia, asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the thermometer, and at every degree rise in the temperature the bottle is inverted; continue until the oil runs to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

Cloud Test—Manns.

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding-point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding-point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice and water. The test is conducted as follows; the oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is transferred to a 4-ounce bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the dry body of the oil, the temperature at which this cloud occurs is noted.

With care, results concordant to within 1 degree Fahrenheit can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit. The oil must be tested within a short time after heating to 150° C., and a retest must always be preceded by reheating to that temperature. The cloud-point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

COLLOID CHEMISTRY AND TANNING.[1]

By H. R. Procter.

The manufacture of leather may be considered as a problem almost purely of colloid chemistry, since the hide-fibers are merely an organized colloid jelly, and not only the tannins themselves, but the basic mineral salts used in tanning possess marked colloid character. It must be admitted, however, that up to the present, the many attempts to explain the conversion of hide into leather have been by no means wholly satisfying; and I do not propose in these pages to add another to these incomplete theories, but rather to summarize what has already been accomplished, and to distinguish between ascertained facts and assumptions which may take their place in the future explanation, but which are as yet unproved.

The hide-fiber is, as has been stated, a colloid jelly capable of swelling largely in water, and chemically most closely allied to ordinary gelatine, into which it rapidly changes on heating with water. The other constituents of the hide, such as yellow elastic fiber, and albumins, if they cannot be altogether disregarded in a theory of the tanning process, at least play a very subordinate part in it. Practically the greatest complication in this respect arises from the organized structure of the fibers, which are bundles of extremely tenuous fibrils of about 0.001 mm. diameter. The material by which these fibrils in the unaltered hide are cemented into bundles has been the subject of much discussion[2] and it is yet uncertain whether it differs from the

[1] Reprinted from the "*Gedenkboek—van Bemmelen*," 1910.

[2] Rollet, *Sitz. ber. Wien. Akad.*, 39, 305; Reimer, *Dingl. polyt. Journ.*, 205, 153 *et seq.*; Van Lier, *Hoppe-Seyler's Zeitschr. für physiol. Ch.*, 61, Heft 2.

fibrils themselves in any other way than by a greater degree of hydration; but for the purposes of the present enquiry its nature is of secondary importance, since in practice it is largely if not wholly removed previous to tannage by the solvent action of alkaline or acid liquors. It may be mentioned, however, that even in the dissolved condition, it enters into insoluble combination with the tannins, and with most other tanning substances; in this respect resembling the earlier hydrolysis-products of gelatine.

When placed in cold water, the hide-fiber swells; but like gelatine, not indefinitely, but to a fixed maximum. During the earlier stages of the swelling considerable mechanical pressure is exerted; and judging by analogy, heat is evolved; though the author is not aware that it has been experimentally determined. As the swelling approaches its maximum, the mechanical energy becomes very small, and the heat evolved is insensible. It is clear that we have here a case of osmotic pressure of an ordinary character, in which the attraction of the fiber-matter for water is balanced against that of its own cohesion; and both forces must diminish as swelling proceeds. In order that there may be a maximum, the attraction for water must diminish more rapidly than the cohesion. At higher temperature this ceases to be the case, and the swelling proceeds to complete colloid solution. The position of the maximum is not a fixed one, but may be varied by the previous history. It has been shown by the author that that of gelatine is partially dependent on its original setting volume, and both in this case, and that of hide it is influenced by the temperature and possibly by other conditions of the previous dehydration, since both hide and gelatine after drying at high temperature show very little tendency to swell, and even in hot water are dissolved with great difficulty.

Both in acid and alkaline solutions the swelling is greatly increased, and the maximum is much raised. In acid swelling, which has been specially investigated by the author, gelatine which will absorb 7 or 8 times its weight of pure water may swell to over 50 times in very dilute acid; and in the stronger acids, and typically in hydrochloric acid, a maximum swelling is obtained at a dilution of below 0.01 millimolecular concentration; and gradually diminishes with increasing concentration till actual

solution begins; and hide-fiber behaves in quite an analogous way, though the maximum is lower owing to its greater cohesion. It is clear that in both these cases two separate kinds of absorption are concerned; firstly the direct attraction of fiber for acid, and secondly the mechanical absorption of acid liquid by osmosis. It is not possible at present accurately to determine what proportions of the actual acid absorbed are due to each of these forces, but that they are of different character is proved by the fact that while the whole of the absorbed acid can be estimated by titration with caustic alkali using phenolphthalein as an indicator, a considerable part is no longer capable of reddening methyl-orange, indicating that it does not ionize to a greater extent than about 10^{-6} millimolecular hydrion concentration. The actual quantity of hydrochloric acid fixed in this way increases with increase of concentration, at first rapidly, and afterwards more slowly, tending to a maximum of about 1.25 mols. per 1,000 of dry gelatine. The osmotic swelling of acid gelatine can be almost wholly inhibited by the concentrated solution of an alkaline chloride (though on neutral gelatine such solutions slightly increase swelling); and under these conditions the total maximum absorption is somewhat greater than that not indicated by methyl orange. The behavior of sulphuric acid with concentrated sodium sulphate solution is almost identical, taking into account its dibasic character.

If the provisional assumption be made that the acid solution absorbed osmotically is of the same concentration as that of the exterior solution, an almost constant excess is absorbed, amounting with most acids to about 0.8 mols. per 1,000 of dry gelatine. It is, however, quite clear that the underlying assumption is only approximate, as the very fact that chloride solutions exert an external osmotic pressure on the gelatine when acidified with hydrochloric acid proves that the acid gelatine must inversely expel chlorides, (including hydrogen-chloride) from the absorbed solution, and consequently, the latter must be weaker, and the amount of fixed acid larger than that shown by the calculation; and it is quite probable that if an adequate correction could be applied, the results would agree closely with those of the two methods already mentioned. The quantitative results are in

agreement with the ordinary equations for the hydrolyzable salt of an acid with a weak base.

The results of alkaline swelling so far as they have been investigated are very similar in character, suggesting a definite hydrolyzable compound of a weak (amphoteric) acid with a strong base, and the evidence in both these cases points strongly to ionic chemical combination, though it cannot be said to be yet actually conclusive.

The swelling in the case of acids is obviously dependent in general terms on hydrion concentration, and in the case of alkalies, on that of hydroxyl-ions, but in both cases perplexing anomalies occur, and it is pretty clear that with acids the anions, and with alkalies the kations also have their share in the reaction. Thus the swelling by hydrochloric acid is repressed by alkaline chlorides, while that caused by sodium hydrate is unaffected by neutral sodium salts but repressed by excess of hydroxides; but on the other hand it has been shown by Stiasny[1] that the swelling produced by different hydrates varies in character and firmness, and that these differences continue even when the different hydroxyl concentrations due to differences of ionizability are compensated by varying the strength of the solutions.

Investigations of the absorption of vegetable tannins, as well as of the metallic basic salts capable of producing leather, while somewhat inconclusive, point rather to adsorption than to chemical combination as the leading factor, at least in the first stages of the process.

It should not be forgotten, however, that the tanning action of salts such as those of chromium and aluminium is a complex one, in which both effects are probably involved, the acid combining chemically, and the colloid salt physically with the hide-fiber. Thus in the case of ordinary tawing with alum and salt, the hydrolyzed acid of the mixture is rapidly absorbed by the fiber, leading to further hydrolysis and production of a basic and more or less colloidal aluminium salt which is itself absorbed, while the common salt present in the mixture dehydrates the fiber osmotically, preventing swelling, and enabling the fiber to carry a larger quantity of acid. It is clear that if this be ad-

[1] *Gerber*, 32, 200 *et seq.* (1906).

mitted, investigations as to the salt primarily absorbed, such as those of Reimer[1] and Krutvig[2] are useless, since, though on the whole the acid and base is absorbed in the proportions present in the mixture, their exact relation is dependent largely on physical conditions. In the case of aluminium tannage the action is usually allowed to stop at the point of equilibrium with the solution, and the resultant leather is in part a true aluminium tannage, and in part a mere physical product of the action of the acid and salt, which by dehydrating the individual fibrils prevents their adhesion on drying. This view is strongly supported by the effect of water on this kind of leather, which by removing the common salt, permits the swelling action of the acid, and at the same time dissolves a considerable part of the absorbed aluminium salt, leaving, however, a permanently hydrolyzed and basic portion so that while the washed leather dries hard and horny, it does not completely return to the condition of untanned pelt. In basic chrome tannage, the process is usually carried a stage further. The primary absorption of chrome is favored by the use of a solution already made basic, so that the fixation of a given quantity of acid corresponds to that of a larger proportion of base, and the resultant leather next undergoes so-called "neutralization," which consists in the removal of the excess of absorbed acid by a weak alkaline bath, and the consequent permanent fixation of the chrome in a basic and colloid form. In most other tanning processes a more or less complete fixation is obtained either intentionally, or as a result of natural changes in the absorbed matter, the nature of which is often difficult to explain. Even in alum tannage considerable fixation takes place on "aging" or keeping for some weeks, after which a much smaller proportion of the alumina salt can be washed out. It is possible that, in some cases of organic tannage, oxidation takes part in this fixation, as has been supposed by Dr. Fahrion,[3] but it seems to the writer too much to assume that this is universally the case. Owing to the fixation just spoken of, the tanning process is usually irreversible, and no definite absorptive equilibrium can occur, since

[1] *Dingl. polyt. Journ.*, 205, 153 *et seq.*

[2] *Rev. univ. des Mines*, 1899; *Collegium*, 1902, 161.

[3] *Zeits. f. angew. Ch.*, 22 (1909); Comp. Meunier and Seyewitz, *Collegium*, 1908, p. 195 *et seq.*

the insoluble portion no longer takes part in it; and this irreversibility is of course essential in most cases to the production of commercially valuable products, since otherwise on exposure to water, the tanning matter would dissolve out, and the fiber return to the condition of raw pelt. In many cases, however, the fixation is very incomplete and much of the tannage may be washed out, as for instance with alum and with some vegetable tannins. It may be supposed, therefore, that the original absorption of the tanning matter is usually a physical adsorption either by the mechanical surfaces of the fibers, or of a more intimate nature within the substance of the jelly;[1] while the fixation may in some cases be due to chemical action, but is often analogous to the change from sol to gel, or to the mutual precipitation of two oppositely charged colloids. It appears that a neutral gelatine free from electrolytes possesses no electric charge[2] and does not precipitate a pure tannin solution, but in acid solution takes a positive charge as compared to the liquid, and in an electric current wanders to the kathode, while tannin particles are negative. All practical tanning operations must be carried on under acid conditions, the only marked exception being that of formaldehyde, which acts best in alkaline solution, but obviously presents little analogy either to the organic tannins, or to the more or less acid solutions of basic salts. Apart from its effect in cataphoresis, the exact function of the acid in vegetable tanning is not easy to explain. Mr. Arnold Seymour-Jones, working in conjunction with the author, has investigated the subject but the results are somewhat ambiguous, and vary with different tanning materials and acids. It is obvious that the function is a complex one, related not only to the electric charge, but to the swelling of the fiber; and the time occupied in diffusion through it; and it is purposed to carry on the investigation, in the hope of clearing up these points. In this connection, what has been said of the osmotic effect of salt solutions on acid gelatine and hide-fiber should not be overlooked. By the mere action of acid and salt, the pelt can be so altered as to possess all the physical properties of white leather so long as it is kept dry; and Knapp[3] has shown that a similar

[1] Comp. Herzog and Adler, *Collegium*, 1908, p. 178.
[2] Hardy, *Journ. of Physiol.*, 24, 288-304 (1899).
[3] "Natur und Wesen der Gerberei," Braunschweig, 1858.

effect may be produced by mere dehydration with alcohol.

Knapp's theory developed in the brochure just cited that all tanning was due merely to surface-coating of the hide-fibers which prevented their adhesion, has proved insufficient to explain all the known facts, and there is little doubt that not only actual chemical changes occur, but also physical absorption which is rather molecular than merely mechanical, but there can be no question that in certain cases actual coating of the fibers does take place. Knapp showed that by treating alcohol leather with an alcoholic solution of stearic acid its softness and permanency was much increased, and in many fat-tanning processes, mechanical coating though not the sole action concerned, yet plays its part. It must also be mentioned that in the later stages of sole-leather tanning, when the fiber has fully absorbed its fill of soluble tannin, the deposition of ellagic acid and other difficultly soluble products of the tanning materials on and between the fibers still continues and contributes much to the solidity of the finished product.

Finally, it must be repeated that no single explanation will cover all the very various ways of making leather, and that while Knapp's original dictum that the essential condition is the isolation and non-adhesion of the fibers remains true, there are many ways in which this can be brought about.

Leeds, Aug., 1910.

THE VALUATION OF MINERAL LEATHER OILS—LABORATORY TESTS.

By Charles R. Oberfell.

The value of mineral oils in the leather industry has been proved, and they are coming into more extended use every year. Some, of course, are of very fine quality while many are unsatisfactory. It devolves upon the chemist for the leather manufacturer to determine the suitability of these oils, and it has been his task up to the present to select whatever tests he deemed would give him the value of the oil, and to use any of a number of methods to obtain results on these selected tests.

Many of the characteristics obtained on an oil used for lubrication can be interpreted in the valuation of a leather oil. For example the viscosity, gravity, cold test, evaporation, etc., are

determined on leather oils and are of value when the chemist has collected sufficient data to make proper comparisons.

This Association might consider whether or not this is a suitable field for investigation. Methods for the analysis of mineral leather oils should be standardized, in order to forestall the possibility of confusion with which the oil chemist is dealing to-day. One illustration will show the necessity of this. If a sample of lubricating oil is sent to say six chemists for viscosity test the results will more than likely all be different, because the probability is that they will use different forms of apparatus to determine this characteristic. How simple and desirable it would be for the Association to prescribe a viscosimeter on which all mineral oils used in the leather industry would be tested and thus help to eliminate differences between buyer and seller, and make possible the accumulation of data whereby an oil could be readily valued.

Chemically, mineral leather oils do not differ from mineral lubricating oils, but in the case of the lubricating oils the exact conditions under which they find service can be ascertained, as area of surface to be lubricated, character of bearing, speed and load, while leather oils are subject to any number of unknown factors; character of leather and tannage, condition of leather when oiled, atmospheric conditions during drying, etc. On account of this difference there is a greater latitude in the interpretation of the chemist's report and necessarily some modifications in analytical procedure is made. The flash test of an oil to be used as a lubricant can be taken as indicating the class of work on which the oil can be used, while for greasing leather the same will probably be used to indicate whether or not the oil might impart a harshness to the finished product.

The following tests suggest themselves as being useful, but all are perhaps not essential.

A.—Specific gravity.
B.—Viscosity.
C.—Evaporation.
D.—Flash point.
E.—Burning point.
F.—Acidity.
G.—Alkalinity.
H.—Color.
I.—Cold test.
J.—Cloud test.
K.—Purity.
L.—Asphaltic bases and tar.
M.—Saponification matter.
N.—Sulphur.
O.—Penetration.
P.—Emulsification.

A. *Specific gravity.*—The gravity is essential as from it the weight per gallon of an oil is obtained. It may also be useful in forming an idea as to the source of the oil; whether Texas, Pennsylvania or Mid-Continent crudes were used. The methods for determining the gravity are too well known to discuss, but there are certain forms of apparatus in use which have inherent faults and these must be guarded against.

B. *Viscosity.*—This test is of importance as it gives the body of the oil, which when considered with the weight leads to an idea of how the oil will remain on the leather. An oil which is heavy and of low viscosity will obviously "drip" more than an oil in which these characteristics are not so far apart. The viscosity also tends to determine the penetrating ability and will be considered under penetration test. For viscosity determination there are many forms of apparatus. The essential points to be considered in its selection are uniformity and cost. The viscosity should be taken at a normal temperature; one at which the oil is generally used.

C. *Evaporation.*—This test will indicate the completeness of refining or the amount of matter present which is volatile at low temperatures. The effect of these "light ends" must be determined, but present knowledge points to their imparting a harshness to the finished grain. As to its determination it is essential that a uniform procedure be in use, for widely varying results can be obtained by different methods. It is necessary to specify the amount of oil to use, temperature, time of heating and form and size of dish in which the oil is exposed.

D. *Flash point.*—In a manner this supplies the same information obtained by the evaporation test, for an oil of high percentage of volatile matter will have a low flash point. The relative value of these tests must be determined, and here also a choice of apparatus is possible. Whether an open or closed cup with mechanically timed test flame is used it is to be decided, but it should be the same in all cases. Here too, the cost of the apparatus is a factor after uniformity is secured. The open cup is in general use.

E. *Burning point.*—At present this test finds no useful application unless it may enable the analyst to form an idea of the source of the crude petroleum.

F and G. *Acidity and Alkalinity.*—The presence of either indicates an imperfectly refined product. Their effect is well known and a high class oil should be free from both. Their detection is largely qualitative which presents no difficulty.

H. *Color.*—Whether a perfectly refined, well balanced oil of dark color will impart a less desirable color to leather than one of lighter shade is a matter of speculation. The writer believes that other things being equal, unless the oil is very dark or black, the color has little influence.

I. *Cold test.*—The values for this may vary over a comparatively wide range and make little difference. Unless the oil congeals at a very high temperature the leather manufacturer is not interested. If the test were of greater importance it should receive careful attention at the hands of the leather chemist. Great variation exists in the methods in use. The amount of oil, rate of chilling, time the oil remains in the chilling mixture, etc., are all points in which uniformity is needed.

J. *Cloud test.*—The amount of paraffines present or the behavior of the oil during chilling may be of importance in applying oil to leather during cold weather. The remarks under cold test equally apply here.

K. *Purity.*—An oil which contains water or is turbid can not have the same value as a clear, moisture free oil. The methods for use here are optical.

L. *Tar and asphaltic bases.*—Their presence in any amount may lead to poor color or smeared appearance. A clear solution with 84-88° gasoline readily settles the matter.

M. *Saponifiable matter.*—Whether or not a mineral oil is adulterated with inferior animal or vegetable oils is a matter of importance. Their detection and estimation is well known.

N. *Sulphur.*—If sulphur is of importance it can only be in determining whether or not an oil refined from a crude containing sulphur is suitable for leather dressing. Sulphur in itself should have no reaction and the oxidation of the sulphur is not probable. This point is open to discussion and the writer considers it well worth determining. The sulphur-lamp method where the products of combustion are taken up in sodium carbonate solution is in common use among oil chemists, but is very

tedious and has constant sources of error. A proposed method follows.

O. *Penetration.*—The less body an oil has the easier it will penetrate, but this is not an arbitrary property as the weight of the oil determines how thin it may be. No methods are known for this property, but it is hoped that the leather chemists can develop a substantial one as it will greatly aid in valuating an oil for leather dressing.

P. *Emulsification.*—A mineral oil which forms a creamy emulsion will penetrate the leather fibers well, and in addition on its ability to hold the emulsion depends its remaining in the leather during drying. If a test can be developed which will give the emulsifying property of an oil, a solution of the penetration test will be at hand.

The following methods, collected from various sources, are in use in the writer's laboratory and are submitted not in the thought that they are the best, but because they have served a useful purpose and may form a nucleus from which other and better methods may be developed.

SPECIFIC GRAVITY.

The Westphal balance, on account of its convenience, is used when there is sufficient sample. The oil is cooled to 15.5° and placed in a water-bath, at this temperature, during balancing. When sample is small a pyknometer having a capacity of 25 grams is used. The pyknometer is filled at about 14.0° the stopper inserted and then placed in a bath which is kept at 15.5° until no more oil rises from the capillary tube. The weight of the oil is obtained by multiplying the gravity by the weight of a gallon of distilled water at 15.5°.

EVAPORATING TEST.

Weigh approximately 0.2 gram of oil into a flat bottom heavy glass dish; 8 mm. deep and 50 mm. diameter. Place in an air oven, the temperature of which is nearly constant at 60-65°, and heat for 8 hours. It is then cooled and weighed. The loss is calculated in percentage.

FLASH POINT.

Set a porcelain crucible, 60 mm. top diameter, 25 mm. bottom diameter and 50 mm. in height in a sand-bath so that the top of

the crucible is below the rim of the sand-bath. Fill the crucible with oil to within ¼ inch of the top, adjust the thermometer in the center of the liquid. Apply heat so that the temperature of the oil rises 8° per minute and apply test flame first at 150° and then at every rise of 2.5°. A jet flame can be obtained by using a glass tube drawn out until it gives a flame 8 mm. long and 3 mm. diameter. Apply the flame by passing it slowly and completely across the crucible about ½ inch above the level of the oil and just in front of the thermometer. The flash point is the lowest temperature at which the vapors of the oil flash and go out.

BURNING POINT.

Continue the heating after the flash point is determined. Applying test flame as before until the vapors catch fire and burn over the surface of the oil.

VISCOSITY.

For a cheap and thoroughly reliable instrument for leather work the Dudley pipette used by the chemists for the Pennsylvania R. R. is used. This pipette is graduated to hold 100 cc. at 70° F. and will deliver 100 cc. of water at 70° F. in 34 seconds. The pipette should be enclosed in a box with a sliding glass front and metal bottom for heating the oil contained in a metal beaker. A thermometer passes through the top of the box into the beaker and another one extends into the box so that the oil and the temperature of the interior of the box will be the same. Bring the oil to 20°. See that temperature of the box is the same. Allow the oil to flow and record number of seconds required. Report in number of seconds or in degrees obtained by dividing the number of seconds by 34.

REACTION OF OIL.

Heat about 15 grams of the oil with 50 cc. distilled water, draw off the water and test its reaction with litmus. If the reaction is acid it is probably due to sulphuric acid which is tested for with barium chloride.

ASPHALTIC BASES AND TAR.

Place 5 cc. of the oil in a pear shaped separatory funnel of about 200 cc. capacity, add 95 cc. 84-88° gasoline, shake well and allow to stand 15 minutes. No precipitate should appear.

COLD TEST.

Place 50 cc. of the oil in a 4 ounce vial bottle, provided with a stopper through which passes a short stout thermometer. Place in a chilling mixture and stir occasionally until the oil has solidified. Insert the stopper and allow the bottle to remain in the chilling mixture one hour. Remove, wipe dry and place in a beaker containing dry asbestos wool to insulate the bottle. Stir the solid oil with the thermometer, invert the bottle frequently and note temperature at which the oil flows from one end to the other in 15 seconds. For chilling mixture use ice and salt or if necessary crystallized calcium chlorid and snow or shaved ice.

CLOUD TEST.

Use bottle, amount of oil and thermometer as in cold test. The cloud test or chilling point is the temperature at which flakes or scales begin to form in the liquid. It is determined by cooling the oil 5° at a time with occasional stirring and constant watching.

SAPONIFIABLE MATTER.

(Qualitative)

Heat 5 cc. of the oil in a test-tube with a piece of sodium hydroxide for 15 minutes at 230°-250°. Cool. Saponifiable matter is indicated by the gelatinization, complete or partial of the contents of the tube.

(Quantitative)

For all practical purposes determine unsaponifiable matter (Mineral Oil) by the A. L. C. A. Provisional Methods for the analysis of oils and fats. The difference between this and the amount of original oil taken represents the portion saponified.

SULPHUR.

(Tentative method)

To 25 grams of the oil in a porcelain dish add 2 grams of dry sodium carbonate and evaporate cautiously to a thick syrup. Ignite with the gradual addition of small amounts of ammonium nitrate until the ash is white. The residue is taken up with dilute HCl, filtered and the sulphuric acid estimated in the filtrate as barium sulphate. A preliminary test for free sulphuric acid is required.

Harrisonburg, Va., Nov., 1910.

ABSTRACTS.

Chestnut Extract. U. J. THUAU. *Le Cuir*, Nov. 15, concluded from Nov. 1.—Two methods of extracting are used. In the first the vats are open; in the second, closed vats called autoclaves are used, and the extraction takes place under a pressure of two atmospheres or more, at temperatures ranging up to 130° C., (266° F.). Experiment has shown that the yield of extract increases with pressure up to two atmospheres, (121° C., 250° F), but decreases at higher pressures and temperatures. Excepting mimosa bark, valonia and sumac, whose tannin decomposes at temperatures above 60° C., (150° F.), almost all tanning materials may be extracted at the boiling temperature without sensible decomposition of the tannin. Above this temperature a part of the tannin decomposes into pyrogallic, gallic and ellagic acids, into pyrocatechin, into anhydrides of tannin, or into glucose.

When the extraction is done under pressure, there is a larger yield of tannin and a little more non-tannin, but a part of the tannin which has been extracted is converted by the heat into non-tans, and this results in an extract differing materially in composition from that made in open vats. An average analysis of chestnut extract of 25° Baumé made in open vats is as follows: Tannin, 32 per cent., non-tannin, 7.3 per cent., insolubles, 0, water, 60.7 per cent., while an extract made under a pressure of two atmospheres gave an average of: Tannin, 29.8 per cent., non-tan, 12 per cent., insolubles, 0, water, 58.2 per cent.

Some extract factories use green chestnut wood, but because of the high moisture content of the wood, they obtain a poor yield. Most manufacturers, however, pile the wood to dry before using it. The extracting vats are grouped in series of 5, 7, 9 or even 12, containing from 6,000 to 12,000 liters (1,500 to 3,000 gallons) each. The open vats are made of wood or copper, the autoclaves of copper or bronze. An autoclave of 12,000 liters holds from 4,500 to 6,000 kilos (5 to 6⅔ tons) of wood. The liquor passes in succession through all the vats, over wood less and less spent, and finally over new wood, the fresh water passing into a vat in which the wood is nearly spent. The temperature is highest in the first vat, containing nearly spent wood, and diminishes gradually. The strength of the liquors thus obtained is from 3 to 4½ degrees Baumé, (22° to 33° barkometer).

They are clarified and decolorized by special methods, blood being much used.

The liquors are then concentrated in vacuum evaporators, multiple effect apparatus being employed, sometimes with as many as six effects. The yield of 25° Baumé extract from different chestnut woods varies from 15½ per cent. to 23 per cent. for wood which has been in storage a year.

Chestnut extract is used chiefly by sole leather tanners. It costs from 75 to 85 centimes per kilo of tannin, (7 to 7¼ cents a pound). It is not, properly speaking, cold soluble, but dissolves readily at 60° C.

Chestnut extracts treated with sulphite or Solvay soda are not very desirable, as they oxidize in the air and give a dark color. The best extracts are those which, rich in tannin, remain clear under the oxidizing action of the air.

It is to the interest of the makers to use the pressure-extraction method because of the greater yield. :Some makers, however, continue to use open vats, encouraged by the higher price of the product.

A chestnut extract rich in non-tans penetrates slowly, while the penetration is more rapid if the non-tan content is less. The conditions in the case of vat tannage are different from those of drum tannage. In the former case the proportions of tannins and non-tans absorbed by a hide from chestnut extract are about 20:1, while a drummed hide will absorb one-fourth as much non-tan as tan. This latter proportion is near the average of that found in chestnut extract, so that in drum tannage the hide absorbs the extract whole, so to speak. Since non-tans in leather are easily extracted by water, a high percentage of them tends to lower the quality of the leather. It may be stated, therefore, that for drum tannage the better extract is that which for a given tannin content has the lower proportion of non-tans.

For vat tannage, however, the conditions are different. An extract rich in non-tans, while it penetrates more slowly, plumps better because of its larger proportion of glucose and organic acids, and a part of the anhydrides of tannin may be hydrolyzed and transformed into tannin, thus giving a high yield. Extract poor in non-tans has the advantage of penetrating more quickly, but it gives a lower yield, and because it furnishes less non-tans to the leather, the leather ought to be better.

Acid in Chrome Leather; Determination of Free ——. G. GRASSER. *Collegium*, 1910, pp. 381-382.—The qualitative test for free acid in chrome leather by pressing test-paper against its cut surface is not always conclusive owing to the strong affinity which the acid has for the leather fiber. The following method for determining free acid in chrome leather is stated to be reliable and quick and also shows any excess of alkali in de-acidified leather. 20-30 grams of the finely divided leather are made into a thick paste with distilled water in an Erlenmeyer flask. 30-40 cc. of N/1 hydrochloric or sulphuric acid are added, the flask connected with a reflux condenser, and warmed with the naked flame until the leather particles are completely dissolved (½-1 hour). The interior of the condenser is then washed into the flask, which is cooled and the contents titrated with N/1 alkali using methyl orange as an indicator. Any access of alkali required over that necessary for neutralization of the N/1 acid used represents the free acid derived from the leather and in a similar way any access of alkali in the leather is shown. If the presence of green chromium salts renders the determination of the end-point difficult, litmus is used as an external indicator. Through the decomposition of the leather all chromium is brought into solution and chromic acid and chromates are reduced to chromium salts. The chromium origi-

nally present in the leather can therefore be determined in the solution, but a volumetric process must be used, since the presence of organic matter hinders the precipitation of chromium as hydroxide.—Abstract from *J. S. C. I.*

Employment of Cold in the Leather Industry. W. EITNER. *Der Gerber,* Oct. 15 and Nov. 1, 1910, pp. 279-293.—The rapid cooling of hides immediately after removal as carried out in the packing houses of America and Argentina, is an advantage because it tends to prevent the incipient decay due to the blood, etc., in the hide, which would otherwise take place before the salt could arrest the action of bacteria present in and on the hide. The temperature for this purpose should be below 10° C. (50° F.) but the hides must not be frozen, as the expansion of the water in freezing tears apart the hide-fibers and weakens the leather made from such hides.

Wet salted hides keep more perfectly in cool storage-houses than in warm ones. The stone vaults formerly used for hide storage were admirably adopted to keep the hides at a nearly uniform temperature.

Dry salted hides after the sweating process were formerly hung in cold running water for some weeks, to sterilize them. This is now done in a few hours by chlorine, sulphurous acid or formaldehyde.

In the tanning process, low temperatures are not desired, as the reaction between hide substance and tanning material, whether vegetable or mineral, does not go on below 12° or 15° C., (44° or 50°F.). Formerly, however, owing to the unclean conditions in the tanneries and the failure to destroy the germs of unfavorable fermentations before the tanning was begun, the high temperatures of summer sometimes caused the hides to decay in the tan pits, so that ice had to be used to prevent the liquors from becoming too warm.

One strange use of cold in the making of leather was the so-called "tanning of the Holy Simon." Leather tans slowly and poorly in the winter, and if it was necessary to hasten the finishing of stock to fill orders the half-tanned hides were laid out to freeze. After this the tanning materials penetrated quickly, but the quality of the leather was much lowered.

An important use of cold is in the clarification of extracts, a process which is being patented by the firm of Dr. A. Redlich. Quebracho extract, made under pressure, is immediately cooled rapidly to below 10°. The heavy resinous dyes soluble above 100° are thus separated in the form of large flakes, and they carry down with them the materials which would othewise deposit slowly and be difficult to remove. By this method a bright, clear, rapidly penetrating extract is produced.

Scientific Investigation as Applied to Tanning. L. JABLONSKI of Berlin. In *Shoe and Leather Reporter* of Sept. 22, 1910, p. 41.—The writer calls attention to the importance of analyzing the waters used in the beam-house, in order to determine what substances should be put into the soaks, and of careful experiment to determine what treatment here

gives the best results. He recommends the analysis of the lime used, in order to avoid introducing into the limes argillaceous earths, which partially tan the hides, and spoil the quality of the leather. The time requires for liming should be determined as closely as possible, in order to avoid loss of hide substance by liming too long.

He recommends testing with phenolphthalein to determine when deliming is finished, and calls attention to Professor Procter's suggestion to use sal ammoniac or sulphate of ammonia in the last stages of deliming in order to avoid danger from free acid.

Constituents of Candelilla Wax. G. S. FRAPS AND J. B. RATHER. *Journal of Industrial and Engineering Chemistry,* November, 1910, p. 454. —This hard opaque, nearly white wax is from the candelilla or Mexican wax plant. Suggested uses for it are:—Candles, shoe polish, phonographic records, electric insulation, beeswax substitute.

Its constants as determined by Deiler, and by Hare and Bjirregaard, and the corresponding constants of beeswax are given in the table.

	—Candelilla wax—		
	Deiler	Hare	Beeswax
Specific gravity at 100° C.	0.87	.....	.....
Specific gravity at 15° C.	....	0.98	.....
Iodine number	14.0	36.8	6—13
Acid number	19.0	12.4	19—21
Ester number	40.7	....	73—76
Saponification number	59.7	64.9	.....
Melting point	66° C.	67°-68° C.	.....
Unsaponifiable matter, per cent	.....	91.17	.....

The wax is completely soluble in chloroform and carbon disulphide.

By extraction with ether for 40 hours, 40 per cent. of the wax was extracted and the dissolved matter was purified and crystallized. It seems to be the hydrocarbon hentriacontane. The crystals are small and white; melt at 68° C.; soluble easily in carbon tetrachloride and in chloroform, but not in cold alcohol.

Further extraction with boiling ether gave another white crystalline substance, probably also a hydrocarbon, melting at 85° C.

Rapid Saponification of Fats for Titer Determination. CHAS. V. ZOUL. *Journal of Ind.* and *Eng.. Chem.,* Nov., 1910, p. 479.—The method substitutes glycerine for water or alcohol as a solvent for the potash. 95 per cent. glycerine was found unsatisfactory, especially with neutral fats, it being necessary to boil off the 5 per cent. of water before saponification began.

120 grams of H. G. glycerine are placed in a 6½ in. porcelain casserole, 25 grams of KOH added and heated over a flame. The potash dissolves easily. The fat (100 grams) is now added and stirred with continued heating. The fat dissolves in 1 minute, with slight foaming in the case of refined fats. Heating is continued until the liquid becomes quiet and homogeneous, indicating complete saponification. The melt is now taken off the flame and from 15 to 30 cc. of water added from a

wash-bottle, a little at a time, waiting each time for the foaming to subside. Dilute acid is then added to break up the fatty acids, which precipitate in a milky form and separate into a layer on slight heating. The acid must be added in small quantities, with repeated stirring. Hot water is added, and the whole placed on a steam-bath for washing. The whole time consumed may be as little as 10 minutes. The method is less satisfactory with low grade fats.

Improvement on the Wiley Method for Determining the Melting-Point of Fats. HARRY STEENBOCK. *Jour. Ind. and Eng. Chem.*, Nov., 1910, p. 480.—A serious difficulty with the Wiley method is due to occluded bubbles of air in the fat discs, which expands and carry the discs to the surface.

The author dropped melted fat on cold mercury. The discs were removed when thoroughly hardened, by means of a cold steel spatula, and thrown into cold 50 per cent. alcohol. The vessel of alcohol is then set in a vacuum desiccator and exhausted until bubbles cease to be given off.

Scott Oil Tester. *Jour. Ind. and Eng. Chem.*, Nov., 1910, p. 482.—This instrument is made by E. H. Sargent & Co. under the direction of Mr. D. G. Scott of Chicago. It substitutes an electric spark for the usual flame jet in testing for flash-point. It may be used over a wide range of temperatures. The instrument is self-contained occupying only 8 x 10 inches of space, and is 16 inches high. The sample required is very small and danger from fire is precluded.

A New Indicator for Alkalimetry and Acidimetry. PROF. DR. R. MELLET. Lausanne; *Chemiker Zeitung*, No. 121, 1073.—The author has investigated the 4-amino-*m*-oxybenzoic acid and its derivatives, of which only the methylester (orthoform) and the ethylester had up to this time been produced, in the endeavor to prepare the corresponding diazo-derivative, and to unite it with phenol and naphthol products, in order to obtain red or violet azo-dye. Among the azo-dyes analyzed, the combination of 4-diazo-*m*-oxybenzoic acid with β-naphthol, proved very sensitive to acids and bases, as it yielded highly characteristic red and violet coloring. The alkali salts of this dye are very soluble in water (violet color), while the acid itself (red) is insoluble in it.

If a mineral acid is added to the alkaline solutions, as for example dilute hydrochloric acid, the color changes to a bright red, remains for a few minutes in a colloidal form and then precipitates. It is not therefore recommended to use the β-naphtholazo-*m*-oxybenzoic acid as an indicator, at least not for titrations which require a certain amount of time. In order to obtain a soluble product the β-naphthol was replaced by one of its sulpho derivatives, forming sulpho-β-naphtholazo-*m* oxybenzoic acid which is easily soluble in water (with a red color) and whose alkali salts give a violet solution. The diazotizing of the 4-amino-*m*-oxybenzoic acid results in a yellow powder of great instability which is an anhydride.

The union of this diazo-acid with 6-sulpho-β--naphthol results easily in an alkaline solution: the tri-sodium salt is immediately formed. In this form the new substance is most easily produced pure. The acid itself can be easily freed from its sodium salt by hydrochloric acid.

Properties and use as an indicator in Alkalimetry and Acidimetry.—The 6-sulpho-β-naphtholazo-*m*-oxysodiumbenzoate produces a deep violet powder which is very easily soluble in water, and gives an intense violet solution. With excess of alkali this solution becomes cherry red with acids, it changes quickly to red, without forming a precipitate. The 6-sulpho-β-naphtholazo-*m*-oxybenzoic acid is likewise very soluble in water with an intense brilliant red color (in very dilute solutions the color is orange red). Alkalies change this red liquid immediately to dark violet as soon as the neutralization point is reached. This indicator cannot be used like litmus in the form of test-paper, because the red paper on contact with concentrated alkali changes directly from deep red to cherry red; therefore shows no sufficiently clear color change. As test-paper it is therefore only sensitive to acids or to very dilute alkalis. On the other hand it is very good to use for titrations of alkaline and acid solutions, and because of its great dyeing ability and its sensitiveness it appears to be superior to most indicators now in use except phenolphthalein. Its solution does not become moldy like litmus solution, but remains unchanged. It is sensitive to all mineral acids, most organic acids and all bases, including ammonia. A few preliminary results are given which have to do with the sensitiveness of this new indicator as compared with those commonly used. The indicator used for these titrations was a 1 per cent. solution of the sodium salt, to which N/10 HCl was added drop by drop until it showed a clear red color.

In comparison with a litmus solution of the same weight this possesses thirty times as much color.

Determination of sensitiveness and comparison with a few common indicators.—It is well known that the color change of an indicator does not depend only upon the absolute quantity of acid or base to be titrated but also upon the amount of dilution. Methylorange, entirely loses its usefulness with solutions more dilute than N/10. This loss of sensitiveness is due principally to the hydrolization and electrolytic dissociation of the indicator, which can be recognized by the intermediate colorings appearing in the course of the change. Investigation of the sensitiveness of indicators with different concentrations, which were carried on by Robert Thomson[1] in 1883 and then by Glasser[2] in 1901, gave the following results. 1. That the various indicators could not be used without distinction when solutions are to be titrated whose concentration deviates noticeably from that of the normal solution. 2. That the same indicator when used for the neutralization of a like quantity of acid requires an entirely different quantity of base according to the dilution

[1] *Chem. News*, 1883, **47**, p. 123.

[2] Glaser, *Indicatoren der Acidimetrie und Alkimetrie*, Wiesbaden, 1901.

of the base, and *vice versa*. 3. That neutralization cannot be reached in both directions with an equal quantity of normal solution.

1. Titration of N/100 HCl with N/100 NaOH.

	For 10 cc. HCl			For 20 cc. HCl			For 40 cc. HCl		
	a	*b*	*b—a*	*a*	*b*	*b—a*	*a*	*b*	*b—a*
Phenolphthalein...	10.0	..	..	20.0	..	..	40.0	..	..
Litmus.....	9.5	9.9	0.4	19.6	20.05	0.45	39.8	40.5	0.7
Methylorange.....	9.0	9.7	0.7	18.3	19.5	1.2	36.2	38.7	2.5
New indicator.....	9.8	10.0	0.2	19.7	20.05	0.35	39.8	40.1	0.3

2. Titration of N/100 NaOH with N/100 HCl.

	For 10 cc. NaOH			For 20 cc. NaOH			For 40 cc. NaOH		
	a	*b*	*b—a*	*a*	*b*	*b—a*	*a*	*b*	*b—a*
Phenolphthalein...	9.85	..	..	19.8	..	..	39.4	..	..
Litmus.....	9.75	10.5	0.75	19.8	20.8	1.0	39.9	41.5	1.6
Methylorange.....	10.4	10.85	0.45	20.8	21.6	0.8	41.4	43.2	1.8
New indicator.....	9.85	9.95	0.1	19.8	19.95	0.15	39.8	40.0	0.2

The new substance which I propose as an indicator, possesses as will be shown, an exceptionally great sensitiveness (which nearly equals that of phenolphthalein in the transition from acid to base) and can be advantageously used even with N/100 solutions.

For all the determinations normal, N/10 and N/100 solutions of sodium hydroxide, and of hydrochloric acid, adjusted with phenolphthalein were used. The new product shows its superiority to other indicators especially in the N/100 solutions. The figures in the accompanying table are the average of a great number of titrations. In order to be able to recognize clearly the beginning and end of the color change two control experiments were conducted, one in acid, the other in alkaline solution.

In the table *a* represents the number of cubic centimeters which were necessary to cause the beginning of the color change, *b* the number of cubic centimeters required to complete it. Then *b-a* represents the number of cubic centimeters during the addition of which the indicator takes on transition colors.

From these determinations the following conclusions may be drawn about the new indicator. 1. It possesses a fully satisfactory sensitiveness toward N/100 solutions. 2. The amounts of normal solution correspond to the required amounts with phenolphthalein (colorless to red) if the color change is carried out to the point of extreme coloration. These two indicators can therefore be used interchangeably. 3. Whatever concentration is used, the indicator shows practically the same sensitiveness (up to a total volume of liquid of about 80 cc.). 4. The titration can be followed out in both directions with the same exactness if it is carried out to the point of deepest color. 5. The change from deepest red to deepest violet, and vice versa, requires less normal solution than other indicators. The transition colorings are therefore confined to narrower limits than with the others.

The Mimosa Barks and their Significance in the Leather Industry (concl.). JOHANNES PAESSLER. *Ledertechn. Rundschau*, 1910, pp. 337-8. 345-7, 354.—Eitner mentions a South American mimosa bark from Brazil, which he also calls "Bohano" bark; he finds 30-32 per cent. tannin. This bark is not a market ware.

The tannin-bearing acacia has been introduced with success in German East Africa in the mountainous regions. In Usambara, at 1,300-1,700 m. (4,000-5,500 ft.) above the sea, maturity is reached in 5 to 6 years and the yield of bark is higher than in Natal. The tannin content is high, 40-45 per cent.

The view was formerly held that Natal mimosa was poorer in tannin than the Australian bark. As the result of many analyses for years the author finds that the average is about the same from either source. Since 1901, 260 samples of mimosa bark have been analyzed at the Freiberg station with the following average (limits in parenthesis):

	Filter method	Shake method
Tans	33.0 (22-48)	31.5 (20.5-46.5)
Non-tans	9.5	11.0
Insoluble	43.0	43.0
Water	14.5	14.5

The trunk bark of the mimosa contains somewhat more tannin than that of the branches; v. Schroeder found 39.2 and 35.9 per cent. respectively. The author likewise found 33.5 and 29.6 per cent. in Australian barks.

The ratio of non-tans to tans in mimosa is considerably less than in domestic tan barks. To 100 parts of tannin there are about 30 and 35 parts non-tans according as the filter or shake methods are used. The sugar, according to v. Schroeder amounts to 3 parts which is slight compared with 26 for oak and 32 for pine. Mimosa has therefore slight acid-forming power which agrees with practice. The bark (ground) costs 22 marks per 100 k. or 0.67 and 0.70 m. per kilo of tannin (filter and shake methods). This is about equivalent to $55 per ton, and 8½ cents per pound of tannin.

Mimosa gives leather a light, somewhat reddish color which darkens by action of light. The tannin is readily soluble so that the bark can be readily extracted without leaving more than 3 to 4 per cent. of the tannin in the residue. The bark extracts well because of its fibrous structure and may yield liquors of 8 to 10 per cent. Mimosa liquors do not diminish in tannin content on standing as shown experimentally by the author in 1904. A liquor containing in 100 cc., 2.85 grams tans and 0.63 non-tans, after 60 days analyzed 2.79 and 0.41 grams, the small loss in non-tans being due to formation of volatile acids. Recent experiments at the Freiberg station have shown that mimosa has high weight-giving power, being taken up by leather in marked quantity; almost equal to quebracho. Mimosa is properly rated as adapted for sole-leather, giving a solid product. It is incorrect, however, to assume that it is unsuited for harness and upper leathers.

The author has tanned calf-skins in pure mimosa and obtained a good full leather, soft to the touch.

Caution is necessary in employing mimosa as dusting material for lay-aways. In the first place, if there has been an insufficient fore-tannage, a dead tannage (Zugerben) results and secondly, like all materials rich in tannin, mimosa tends to produce spots when in direct contact with the hide. Mimosa should not be used in dusting the first lay-away and only gradually, mixed with other materials, in the following layers. To avoid spots, the mixture with the tannin-poor materials should be uniform. On the whole it is better not to employ mimosa for dusting, but in liquors for the handlers and lay-aways.

Commercial mimosa extracts are liquid or pasty, of density 21 to 28° B., corresponding to 63-53 per cent. water; solid extracts are not made. The average composition of the extracts is (filter method):

	Mean	Limits
Tans	31.5	27-36
Non-tans	9.5	5-12
Insoluble	1.0	0-3
Water	58.0	63-53
Mineral	1.5	1-3

The shake method gives 1 to 3 per cent. less tannin. If in the manufacture too high a temperature has been used in the extraction or unsuitable clarification, the ratio of non-tans may increase. Such a product analyzed 29 per cent. tans, 12.5 non-tans, and had a gravity of 27.5° B. High density therefore does not always imply high tannin. It dissolving mimosa extract, it is necessary to heat the water to 40-50°: the conditions are therein less favorable than with oak, chestnut or treated quebracho though better than with untreated quebracho. Very little sediment separates on cooling. The price of 1 k. tannin in extract is 84 pfennigs compared with 67 pf. in the bark. Considering the cost of extraction, and loss in the bark, it would appear best to use extract.

Extract mimosa D. manufactured according to the patents of Lepetit, Dollfus and Gansser of Milan is not a mimosa extract but sulphited quebracho. In analyses tans 38, non-tans 8 per cent. and is characterized by its high ash of 6.5 per cent.

The Valuation of Logwood. GEORG GRASSER. *Collegium*, 1910, 461-3. —The best gravimetric method is that of Schreiner which is similar to the official method of tannin determination. The total solubles in the extract are determined on evaporation, and the dyestuffs by difference on treatment with hide powder which absorbs them. The results are somewhat uncertain with varying hide powder and the method laborious. The author has therefore worked out a simple method which gives accurate enough results for valuation. The principle is to precipitate the dyestuff with lead acetate and measure the volume of the precipitate. Absolute values cannot be obtained, but various brands may be thus compared and a standard assumed. Five grams logwood are extracted

with 200 cc. water in the author's apparatus lately described (ante, p. 526), 1½ hours sufficing. The extract is made up to 250 cc., 50 cc. of this mixture with 20 cc. of lead acetate solution (1:20) and a portion of the mixture centrifuged in a hand apparatus for 5 minutes when the settling is complete. The volume of the precipitate is not proportional to the concentration in strong solutions but the ratio becomes fairly constant when a dilution of 0.3 per cent. is reached as shown in the table.

Grams extract in 100 cc.	Cc. precipitate in 10 cc.
16	6.35
8	5.50
4	5.30
2	4.00
1	3.00
0.5	2.50
0.25	1.20
0.125	0.60
0.0625	0.30
0.0312	0.15

Since logwood averages 10 per cent. dyestuff, 4 to 6 grams should be extracted in 200 cc. for accurate work. To obtain the greatest accuracy, the standard and the sample test should be centrifuged at the same time.

The Occurrence of Osyritrin (Violaquercitrin) in Osyris Abyssinica. S. J. M. AULD. *Proc. chem. Soc.*, 1910.—A. G. Perkin separated the glucoside osyritrin from Cape Sumach (*Osyris compressa*) and showed it to be identical with viola-quercitin isolated by Mandelin from *Viola tricolor*. The author has separated the same substance from the leaves of *Osyris abyssinica* from the Transvaal. The extract from this material produced a darker and poorer leather than the Cape Sumach. The leaves contained 23 per cent. tannin. The concentrated aqueous extract was fractionally precipitated with lead acetate and the last fraction decomposed with H_2S yields a reddish brown catechol tannin. By extracting the leaves with alcohol and recrystallizing, greenish yellow crystals in needles were obtained melting at 185-6°, agreeing by analysis with the formula of osyritrin, $C_{27}H_{28}O_{16}$, $3H_2O$. On hydrolysis, it split up into a dextro-rotary sugar (osazone melting at 204-5°) and an insoluble coloring matter having all the properties of quercitin, $C_{15}H_{10}O_7$.

The Manufacture of Lacing Leather. *Ledertechn. Rundschau.*, 1910, 347-8.—For sewing and lacing leathers only large flat hides of 20 to 30 k. green weight are suited. Silesian hides are best, but even light pips may be used. When croupons (butts) are used, these are best separated after soaking, the waste going to the limes and the croupon being "geschwödet." For this, one-half k. sodium sulphide is dissolved for each croupon, of three-fourth k. for each whole hide and sufficient slaked lime added to make a thin paste. The hides are spread out flat, hair upwards, and the cold paste applied evenly with a broom. They are then folded so that the flesh is as little in contact with the liquor as possible. After one-

fourth hour, the unhairing may begin; if by hand, rubber gloves are indispensable for protection. Washing in fresh water immediately follows, 6 hours when running, 12 hours in suspenders. After shaving and stretching the hides are again left in fresh water an equal time. If alum tanned leather is to be made, a bran bate is advisable; for colored and fat tanned leather, one-fourth hour's washing in luke-warm water is sufficient. For the alum liquor, 15 k. alum, 4 k. salt, and one-half k. wheat flour are used to 100 l. water; the bath should not be over 25° C. The first day the hides should be turned 2 to 3 times, the second day once, the liquor being stirred up each time. Old liquors may be used again when strengthened with 6 k. alum, 1½ k. salt, one-fourth k. flour to each 100 k. white hide, but should not be used more than 3 or 4 times. To tan through, 7 to 8 days are required; if complete, a thick portion of the hide when folded remains white. After drying, the leather is softened by machine or hand work, and should then be of a fine white color, mild to the touch. The greasing is done in a warm room by burning in or dipping, the fat being at 60-70° C.; the leather should first be warmed. A more practical method is to apply the grease in a drum which can be heated. The mixture is generally equal parts of stearine and tallow. For colored leathers, the dye is applied before tannage, using any water-soluble aniline dyes. The colored hides are not tanned in alum liquor, but rubbed on both sides with a mixture of 2 parts alum, 1 part salt and a little flour, then laid together in a wooden tub. Care is taken that the hides do not dry, they being turned every 2 days; the tannage is complete in 7 to 8 days.

PATENTS.

Method of Unhairing and Tanning Hides or Skins. U. S. Patent No. 976,036. GEORGE D. BURTON, Boston, Mass.

The hides are placed in a solution of sal soda, and an electric current is then passed through, intermittently, the solution being kept agitated. This process removes the fat from the hides. They are then taken out and fleshed and washed in a weak acid solution. They are then placed in a tanning solution and again subjected to the action of electric current.

Process of Electrolytically Treating Tannic Infusions of Plants. U. S. Patent No. 975,835. H. DAMKÖHLER AND H. SCHWINDT, Bremen, Germany.

Leather-Working Machine. U. S. Patent No. 975,628. GEORGE MCKEEN, Peabody, Mass.

Pressure Device for Leather-Skiving Machines. U. S. Patent No. 975,495. CHARLES H. BAYLEY, Boston, and BENJAMIN F. MAYO, Salem, Mass., assignors to United Shoe Machinery Co.

Leather-Wringing Machine. U. S. Patent No. 976,968. ROBERT F. WHITNEY, Winchester, Mass.

Method of Manufacturing Substitutes for Leather-Board. U. S. Patent No. 976,827. A. J. OSTBERG, Australia.

The method consists in cutting leather scrap into thin shavings and then mixing them with some adhesive and subjecting them to pressure.

Table for Leather-Working Machines. U. S. Patent No. 978,120. E. Y. B. ENGELMAN, NOXEN, PA.

Formic Acid. U. S. Patent No. 975,866. HENRY HOWARD, Boston, Mass.

Sulphur trioxide in gaseous form is passed into water containing a formate.

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A SUGGESTION FOR COLLABORATIVE WORK ON COLOR VALUATION.

By W. S. Loud.

During the past few years I have been particularly interested in the work of the Association in respect to color tests, especially concerning those employing pelt, and I believe that it is possible for these tests to be of much more practicable use than at present. The man experienced in handling leather undoubtedly prefers the tanned hide as a medium of comparison of color valuation and probably those of us who advocate so strenuously the color measurement method would resort to the pelt to really *know* something concerning the extract with which we are working.

I think it is because of the fact that a good piece of leather really *proves something* that a method involving color measurement as a valuation is not always desirable. I have seen extracts which were apparently all right by the analysis, but color tests proved them worthless; had we used the tintometer or cloth method instead of pelt these extracts might have caused considerable trouble.

A color test made on sheep skiver should have a thickness of at least one thirty-second of an inch when finished, in order that it may be worthy the name of leather and also because of the fact that skins of this sort can be stretched but very little; thus the color imparted to the pelt by the tannin remains. Color tests made on very thin skivers can be stretched and worked until the resulting color is many shades lighter than the original. Many of the color tests accompanying reports at the present time are thin nearly to the degree of transparency.

We have tried to work out a scheme of processing heavy sheep skivers by which comparative results can be obtained, and think, in so far as our own laboratory is concerned that the results have been very good, although it is only possible to determine the practical value of the method by collaborative work. For this reason we would like to get results from other chemists who might desire to process skivers according to the following scheme.

If a laboratory is making color tests every day, and a bottle drum holding two gallons is available, eight hundred grams of the heavy skivers (pickled weight) cut in pieces four inches square may be processed at one time, as they will keep in good condition for three months or longer. After weighing the skins cut up for washing, place under the tap in a screen and wash for one-half hour, wring well, and drum in distilled water at 90° F. for fifteen minutes. Rinse well under the tap, drum for ten minutes, wring and place in a solution containing borax equal to 10 per cent. of the pickled weight of the skivers. Drum this solution for eight hours, wash thoroughly under tap, drum twice for twenty minute periods in distilled water at 90° F. Wring and rinse after each operation and then drum in a solution containing one per cent. of acetic acid based on the pickled weight. Drum for one-half hour and keep skivers in a glass stoppered jar.

In this slightly acid solution the skins will keep for an indefinite period and require no washing previous to tanning, as the small amount of acetic acid present does not seem to influence the color of the finished test. Skins preserved by this treatment are much superior to those kept in borophenol or formaldehyde, as the acetic acid plumps but little and keeps them in a soft and pliable condition for tanning.

The procedure is somewhat tedious, but because of the fact that so many can be treated at one time, together with the fact that the skins will keep well, there is undoubtedly a great saving of time over a method involving washing or preparing the skins each day.

I believe that interesting results would be obtained if collaborative work were done on the method as outlined above.

ACIDS IN TAN LIQUORS.[1]

By Prof. H. R. Procter and A. Seymour-Jones.

The present great interest in the subject of this paper, as shown in the recent conference of the I. A. L. T. C., has rendered its early publication desirable, a fact which we somewhat regret since the recent important paper of Sörensen on "Enzymes" bears largely on a similar subject. In the present paper we have devoted much attention to indicators, and have had necessarily to accept certain of the views of other chemists who have worked on this subject; and Sörensen's work promises to throw fresh light on many points that we had regarded as settled. As we have as yet had insufficient time to digest his work and none to perform further experiments, much that follows must be regarded as more or less provisional.

For the past twenty-five years the question of the acidity of tan-liquors has been prominent in the chemistry of leather manufacture, and during that period upwards of twelve methods have been devised to estimate it, none of which have proved wholly satisfactory. On the other hand, the effect of the acids on the absorption of tannin by the skin and the rôle which they play in the production of sound leather, has only been studied empirically by practical tanners, and has received no attention from the research chemist.

It therefore seemed advisable to study both these questions; but in the present paper, we only propose to give an account of our work on the estimation of the acidity of tan liquors, leaving the study of its effects to a later publication. As the whole question largely depends on facts in physical chemistry which are of somewhat recent elucidation, it may be well to preface the account of experimental work by some remarks of a theoretical character.

The distinction has long been made in practice between "strong" and "weak" acids, without any very clear conception of the nature of the difference. Equal molecular quantities of either will neutralize or saturate equal quantities of base; but if a "strong" acid, such as hydrochloric, is added in excess to the salt of a weak acid such as acetic or carbonic, the weak acid

[1] *Journal of the Society of Chemical Industry*, December 15, 1910.

is liberated and the strong takes its place in the salt. Corresponding to this, salts of strong bases with weak acids often exhibit in solution marked alkaline properties, though chemically neutral (*e.g.*, sodium carbonate). The acid "strong" in this sense does not become "weak" by dilution with water, but rather the "weak" acid when diluted approaches the properties of the "strong" acid of the same concentration.

While the alkali-saturating power of all acids of equivalent molecular concentration is the same, their other effects are often widely different, and though their swelling effect on hide cannot be said to vary directly with their "strength," it is yet closely connected with it, and acids of a very weak character have no appreciable swelling power, though they still neutralize lime. As to the nature of "strength" and "weakness," the following may be stated. All acids may be regarded as compounds of the hydrion H′ and an anion or acid forming group, and all alkalis as hydroxyl, OH, and a kation or basic group. When the two are brought together the H and OH unite to form water, while the anion and kation constitute the salt. The more loosely the hydrogen is held and the more readily it reacts, the stronger the acid is; and the same holds of a base with regard to its hydroxyl. In modern chemical theory the strong acid is supposed in dilute solution to be already almost wholly separated (ionized) into hydrion (the single H′) and anion, while in the weak, only a small proportion, which, however, increases with increasing dilution is so dissociated. Whether this percentage of ionization is actual, or only represents a certain average freedom, is unimportant—it is at least a convenient numerical way of stating what in some sense or other is an established fact.

The strength of an acid is therefore dependent on the amount of hydrogen ions in a given volume of the solution, or, in other words, on the hydrion concentration of that solution. Just as we measure the concentration of an acid or an alkaline solution in normal, decinormal, centinormal, etc., so we measure the hydrion concentration in the same way. A normal solution of hydrion would contain one gram molecule of hydrogen ions per liter, and such a solution would correspond approximately to a 1.35 normal hydrochloric acid solution.

We have thus two meanings for the strength of an acid solu-

tion, firstly the total molecular quantity of acid which it contains, *i.e.*, its value as measured by the quantity of "normal" alkali required to saturate it; and secondly its acid strength as measured by its sourness and other "acid" properties, and more strictly by its hydrion concentration. In the case of N/10 HCl. these two quantities are nearly the same, since almost all the acid hydrogen is present as free hydrions; while in an N/10 solution of gallic acid they are extremely different, as nearly the whole of the hydrogen remains attached to its anion, and the solution is not perceptibly sour. If, however, caustic soda is added, the small percentage of free hydrions unite at once with its hydroxyls to form water; more hydrions are evolved from the undissociated acid to take their place, and in turn are used up. The hydrogen ions which thus remain in reserve in the undissociated acid molecule are known as "potential" hydrogen ions. In the end the whole of these are combined to form water and the soda is neutralized; though at no time has the solution been more than feebly acid. The importance to the tanner of this difference of behavior is obvious, since by the use of a chemically weak acid he is able to neutralize lime and other bases in the hide without producing undesirable swelling, while on the other hand for swelling purposes the acid employed must have a certain concentration of free hydrions. In discussing the very great dilutions which have to be considered in some cases, it is to be remembered that water itself is not wholly devoid of acid and basic properties, but contains free hydrions and free hydroxyl ions in equal quantities and each to the extent of about 10^{-7} normal (N/10,000,000). Therefore in neutralizing an acid the point of true neutrality is not 0 as might be supposed, but 10^{-7} normal; even alkaline solutions contain free hydrions, though balanced by larger amounts of free hydroxyl ions.

As before indicated, we may directly determine the "acidity" in two ways; the first method is to measure the "actual" hydrion concentration; the second, to determine both "actual" and "potential" hydrogen ions by direct titration. In the latter we have to use indicators, and with regard to these there are certain points which technical chemists often fail to realize. Firstly, the color change of the large majority of indicators is grad-

ual, extending over a considerable range, although between definite limits of hydrion concentration, which vary with the nature of the indicator. Phenolphthalein has a fairly sharp color-change at 10^{-8} to 10^{-9} normal hydrion concentration, while methyl orange has a gradual color change extending from 10^{-3} to 10^{-5} normal. In the light of these facts the discussion of haematein later in the paper should prove interesting.

It should now be obvious that as different indicators change their distinctive property, color or other characteristic, at definite though different hydrion concentrations, varying amounts of strong and weak acids will be estimated according to the indicator used. This raises an interesting point, as some chemists lay great stress on the "accuracy" of a method; that is to say that they take an artificially acidified liquor and endeavor to estimate the same amount of acid as that put in. Let us suppose that to 95 cc. of a neutral solution of tannin they have added 5 cc. N/1 acid, this latter having been prepared by standardization against N/1 alkali and phenolphthalein, the color-change of the latter taking place at 10^{-8} normal hydrion concentration. In estimating the acidity of this liquor unless the color-change of the indicator used takes place at the same hydrion concentration as phenolphthalein, the amount of acid estimated will always differ from the amount originally added, by amounts varying with the strength of the acid used and the neutral salts of weak acids present. Thus the search after a method which will estimate the same amount of acid as that put in, is futile so long as the indicators are mixed and the relationship between them is not specified.

One other point requires discussion before proceeding to a consideration of the work accomplished, viz., the effect of extensive dilution of the acid solution. It can easily be seen that dilution with water would, in most cases, affect the hydrion concentration. If all the acid were not dissociated then addition of water would cause a certain number of "potential" ions to be converted into "actual" ions, while if the acid were wholly ionized then addition of water would decrease the hydrion concentration. Thus if to an acid solution which has a hydrion concentration of 10^{-4} normal, *i.e.*, just sufficient to turn congo red blue, we add water until the hydrion concentration has fallen

to 10^{-5} normal, the solution will no longer affect congo red. Thus dilution of an acid solution always tends to alter the amount of acid estimated, and is in most cases highly undesirable.

Under the same heading we may speak of the effect of the presence of neutral salts on the hydrion concentration. It must be accepted by the layman as a fact that the presence of neutral salts, especially those which have an ion in common with the acid (*e.g.*, sodium acetate and acetic acid) always tends to prevent the dissociation of an acid into its ions, and while the determinable acidity of such a solution may still be high, the actual hydrion concentration may fall very low.

The first step in our experimental work was the examination of the published methods for estimating the acidity of tan liquors. All these methods were carried out in their most recent published details. *Procter's lime-water method* depends on the principle that tannin and many allied phenolic bodies form insoluble calcium (or possibly lime) salts on the addition of a clear saturated solution of calcium hydroxide to the liquor, while the organic acids usually present in the liquors form soluble calcium salts. In this way is determined the actual "lime dissolving" power of the liquor, and an important piece of information conveyed to the tanner.

In Procter's Textbook of Tanning the following passage occurs: "A liquor may have acidity equal to several cc. of lime-water and yet react absolutely alkaline to methyl orange. Hence the acidity of a liquor available for plumping may be taken as represented by the lime-water required to change the red of methyl orange to yellow, and if the liquor does not redden methyl orange then it is incapable of plumping."

These words were written thirty years ago, and we can now show them to be perfectly true. Methyl orange changes color at a hydrion concentration of 10^{-4} normal, and although solutions of about 10^{-5} normal showed a slight tendency to plump, it was found that the limit might be more correctly fixed between 10^{-4} and 10^{-5} while that of the lime-water method is nearer 10^{-6}.

Theoretically the lime-water method is good as it involves no detannization or dilution of the liquor, but it has to be used very carefully to give concordant results, and apparently the

experiences of the American leather chemists with it have been far from happy ones. They state that with tail liquors which contained very little tannin no end point was obtainable as only a darkening of the liquor took place without any turbidity. This difficulty could no doubt have been overcome by the addition of some neutral tannin solution as indicator, though it may be remarked in parenthesis that absolutely neutral tannin solutions, especially of the pyrogallol variety, are difficult to obtain. The presence of acids giving insoluble lime salts in acid solution, such as oxalates may be met by the addition of some calcium chloride before filtration.

The real objection to the method lies in the uncertainty of the indicator, viz., the insoluble calcium tannin compounds. This involves two main defects, since certain tannins give somewhat soluble lime salts, and some organic calcium salts are insoluble; and secondly, the indefiniteness of the end point. It is not easy to obtain exact concordance between two observers, for difference of opinion nearly always exists as to what constitutes "a trace of turbidity," which marks the commencement of the formation of the calcium tannin compounds. The results of five observers are given in cc. of saturated lime-water per 10 cc. of liquor:—

Observer	1	2	3	4	5
Liquor X	14.7	14.9	14.6	15.05	15.0
Liquor Y	11.6	12.0	11.7	12.1	11.8

Fifteen readings taken by one observer on two favorable liquors at intervals of five minutes were as follows:—

Liquor X	14.7	14.65	14.65	14.7	14.6	14.7 all others	14.7 cc.
Liquor Y	11.6	11.6	11.5	11.55	11.5	11.65 "	11.6 cc.

Abnormal liquors were, however, examined, which did not yield such concordance. For example, a very dark, strong handler liquor was examined and, though filtered clear, five titrations had to be made before concordance to 0.3 cc. could be obtained. More concordant results could be obtained by dilution of the liquor with distilled water, though as has been stated dilution is never desirable. It is, however, apparent that if the observer and the concentration of the lime-water be kept constant, and if trouble be taken to obtain brilliantly clear filtrates

and with the aid of printed matter underneath the titration vessel, the method is useful for all practical purposes.

The method of Kohnstein and Simand (Ding. Polyt. Jour., 1885, cclvi. pp. 38, 84) depends on the treatment of the tan-liquor with magnesia free from carbonate and lime, and upon the difference in solubility of the magnesium salts subsequently formed, and only estimates those acids with soluble magnesium salts, and if a tannin chances to have a soluble magnesium salt then that tannin will be estimated as an acid.

This method is very laborious, and we have been unable to obtain the accuracy and concordance which have been claimed for it. The following are the results of experiments on six liquors, stated in grams of acetic acid per liter. Although the various sub-divisions of the method were carried out only the total acid results are given, as their accuracy did not seem to justify further detail.

	First titration	Second titration	Third titration
Liquor 1	0.0477	0.0504	0.0450
Liquor 2	0.0292	0.0346	0.0308
Liquor 3	0.1471	0.1393	0.1309
Liquor 4	0.3684	0.3418	0.3777
Liquor 5	1.4518	1.5822	1.5200
Liquor 6	3.8670	3.0920	4.4878

A defect pointed out by Bennett and Wilkinson (this J., 1907, 1186) was confirmed by the present experiments, viz., the inconstancy of composition of some of the magnesium compounds with organic acids, excess of magnesia forming basic salts. A theoretical advantage of the method is that it involves no dilution of the liquor, but in the author's opinion it is too elaborate and too little reliable for general use.

A method suggested by Bennett and Wilkinson in this Journal (*loc cit.*) involves the use of lead oxide (litharge) both as a precipitant for tannin and as an absorbent for acids, only those acids with soluble lead salts being estimated.

The details of this method as laid down in the J. S. C. I. were most carefully carried out, but it does not appear that lead oxide is a satisfactory means of differentiating acids and tannins, and the compounds formed with both are apparently of irregular composition and uncertain solubility. Results obtained with the

method show that lead salts of the acids are formed of varying range of basicity, and this seriously affects the final estimation.

A comparison of the above method with the lime-water method is interesting. Results are given in grams acetic acid per liter:—

	Liquor A	Liquor B	Liquor C	Liquor D
Lime-water method	1.34	1.50	3.63	2.44
Bennett & Wilkinson	2.17	1.62	2.41	1.98

The method published by Koch (Ding. Polyt. Jour. 1887, page 395) and subsequently modified by Paessler & Spanjer (*Collegium,* 1903, pp. 10 and 17) depends on the removal of tannin by precipitation with a 0.2 per cent. aqueous gelatine solution, and subsequent titration of the supernatant liquor with standard alkali and an indicator. The method which has been largely adopted, was very thoroughly examined with no very satisfactory results. Theoretically azo-litmin should be a good indicator for the purpose, as its main color change takes place at a hydrion concentration of $10^{-7.8}$ normal, which includes most bodies with any claim to acidic properties, but the color change is gradual and the end point difficult to determine, so that the personal equation enters largely, and concordance between observers is not usually good. Examples are given of six liquors and five observers. Results in cc. N/10 alkali for 25 cc. liquor:—

Observer	1	2	3	4	5	
	cc.	cc.	cc.	cc.	cc.	
Liquor A	19.4	19.1	19.3	19.8	19 4	N/10 alkali
Liquor B	21.7	21.2	21.45	22.1	21.3	"
Liquor C.....	15.9	15.0	15.9	15.5	15.15	"
Liquor D	17.3	17.1	17.8	17.4	17.9	"
Liquor E	17.0	16.8	17.4	16.5	16 9	"
Liquor F	24.55	24.0	24.1	23.8	24.4	"

A very serious objection may be advanced against nearly all methods involving detannization, *i.e.,* that certain amount of acid is co-precipitated with the tannin. It will be shown later that in every case of detannization so far examined varying amounts of the bodies otherwise estimated as acids are carried down with the tannin.

Another objection to the method is that even an experienced observer usually has to make about five titrations before concordant results can be obtained.

Results in cc. N/10 KOH for 25 cc. One observer:—

	Results in cc. N/10 KOH for 25 cc. One observer. Liquor A cc.	Liquor B cc.	Liquor C cc.
1st titration	21.1	23.4	12.7
2d titration	20.6	22.8	12.1
3d titration	20.2	22.6	12.1
4th titration	20.0	22.45	12.0
5th titration	20.0	22.40	12.0

A zinc oxide and hide powder method proposed by the commission (A. L. C. A. Jour., 1906, p. 223) appointed by the American Leather Chemists Association was carefully examined, though without much hope of good results.

The working details were the following:—

Sixty cc. of the liquor were diluted to one liter. To 200 cc. of this solution 20 grams of moist hide powder and one teaspoonful of chemically pure zinc oxide were added. These were shaken in a shake machine for five minutes and then filtered; 100 cc. of the filtrate were titrated with decinormal alkali in the presence of phenolphthalein, adding a little zinc oxide to give a sharper end reaction. The requisite correction was made for moisture in the hide powder, and a blank sample run to determine free acid in the latter.

The results obtained were not concordant, and in every case were much lower than with any other method. This was due not only to the fact that hide powder very readily absorbs acids, but that zinc oxide combines with most acids to form neutral salts.

A few corrected results are compared with the lime-water method below, the results of the latter having been calculated into cc. N/10 alkali.

Liquor	1 cc.	2 cc.	3 cc.	4 cc.	5 cc.	
ZnO + hide powder	10.9	12.7	12.5	8.8	9.8	N/10 alkali
Lime-water	15.4	16.1	16.8	12.4	10.3	"

For some years past the American Chemists Association has been particularly persevering in its endeavors to find an accurate and concordant method for the estimation of acidity of tan liquors. The charcoal method of Simand was first of all adopted as official. This method consists in detannizing a measured volume of the liquor by animal charcoal, and estimating the acidity of the remaining solution by titration.

Although the animal charcoal used was labeled C. P., we found it an altogether unsatisfactory agent for the removal of tannin and coloring matters in the presence of acid. Very varying results were obtained and a number of blank experiments showed that the errors were due to the unequal amounts of acid absorbed by the animal charcoal together with the tannin; varying in six blank experiments from four to fourteen per cent. of the total acid. This serious defect has also come under the notice of the American chemists, who universally condemn the method.

In 1906, A. W. Hoppenstedt tried to solve the problem by removing the tannin by means of an alcoholic solution of quinine, and then titrating the filtrate consisting of the quinine salts of the acids with caustic alkali in the presence of phenolphthalein. (J. A. L. C. A. for September, 1907.) In experiments carried out in this way the precipitation of quinine and tannin filtered well, but on titration the dense precipitation of the liberated base considerably masked the end reaction. This could, however, be remedied by a number of titrations. Instead of titrating 100 cc. of the filtrate it was found more convenient to work with smaller volumes, and more concordant results were obtained by titrating 20 cc. of the filtrate at a time. The following figures show the concordance of the method:—

	cc.	cc.	cc.	cc.	cc.
Liquor A	31.3	31.2	31.2	31.2	31.25 N/10 KOH
Liquor B	28.4	28.3	28.2	28.25	28.3 per 20 c.c.
Liquor C	24.9	24.8	24.7	24.8	24.75 liquor.
Liquor D	10.7	10.5	10.35	10.55	10.2

Although the method involves detannization and considerable dilution of the liquor, both of which tend to lower the results, it gives higher results than most other methods; although quinine co-precipitates quite an appreciable percentage of acid. This fact is probably due to the production of weak acids by oxidation, and the use of phenolphthalein, which estimates many bodies of very feebly acid properties.

Comparison was made between this method and a direct titration with N/10 alkali and phenolphthalein paper, working in an atmosphere of coal gas to avoid oxidation of the liquor:—

Liquor	1	2	3	4
Detannized	31.2	28.3	24.8	27.7
Undetannized	31.75	28.5	25.1	27.9

The method has to be worked quickly and the filtration must be very rapid to prevent oxidation and darkening of the filtrate. This renders the method awkward to manipulate, and an undesirable and laborious condition, in which a considerable error is possibly introduced, is the necessity of making yard liquors up to the same strength as that used in tannin analysis.

Phelan and Fiske have suggested a means (J. A. L. C. A., 1908, pp. 99) whereby the method ordinarily employed to determine CO_2 in carbonates is so modified as to be available for determining the acidity of tan liquors. A definite volume of liquor is mixed with calcium carbonate, the carbon dioxide driven off, dried, and collected in U tubes containing soda lime. The increase in weight of the tubes is taken as proportional to the amount of acid in the original liquor. In this case only those acids which, at boiling temperature, will liberate carbon dioxide from calcium carbonate are estimated. The method is ingenious, but requires a somewhat elaborate apparatus and is quite as laborious as the Kohnstein-Simand, neither the additional labor nor the additional apparatus being justified by accuracy or concordance of results. It should be stated that a similar apparatus was given an extended trial at Leeds some years prior to the above publication and did not prove successful.

In the J. A. L. C. A. for March, 1908, p. 85, Reed describes two new methods for the estimation of acids in tan liquors based on the precipitation of tannin by an alcoholic solution of gelatine, and subsequent titration of the filtrate from the tanno-gelatine precipitation with standard alkali, using an alcoholic solution of haematein as indicator. In the second method he merely modifies the first by substituting a basic dye for the alcoholic gelatine solution, and titrating the solution as before in the presence of the same indicator.

Both these modifications were thoroughly investigated, and the first as a practical works control method is certainly good; the second method is in no way promising. As indicator a pure sample of haematein was obtained from the University Tinctorial Chemistry Department, of which a fresh solution had to be prepared each day, as haematein in solution rapidly undergoes change.

In his original paper, among other observations, the author

makes the following:—"It is not necessary that the supernatant solution from the tanno-gelatine precipitation should be clear, nor is it imperative that there should be an entire absence of tannin in the solution, as haematein is practically neutral to tannin." Reed also states that "where a water solution of gelatine or salted solution of gelatine was used, a much bulkier precipitation was obtained and an appreciable loss of acid resulted. When alcohol is used there is perhaps a trifling loss of acid. It was observed that the alcoholic gelatine solutions gave a better precipitation on standing than when freshly made." He also admits that a correct end point determination with haematein requires much practice, and trusts "that the method will not be condemned if the analyst fails immediately to make successful determinations." It is also noted that "haematein is affected to a much less degree by salts of gallic acid in the presence of alkalies than is phenolphthalein. In the titration of acetic, lactic, and gallic acids and their mixtures, it will give with standard alkali practically the same calculated acid as will phenolphthalein, perhaps a shade less as it is more susceptible to alkalies." These statements may be confirmed and the method was found convenient to work and gave fairly concordant results, combined with rapidity of execution, but the end point with haematein is never easy to determine. The best results obtained were:—

Titration	1	2	3	4
Liquid A	10.7	10.65	10.6	10.5
Liquid B	15.2	15.2	15.25	15.25
Liquid C	15.6	15.5	15.45	15.45
Liquid D	20.9	20.8	20.8	20.8
Liquid E	17.55	17.40	17.35	17.40
Liquid F	21.4	20.9	20.5	20.2

Results are given in cc. N/10 KOH required for 25 cc. of liquor.

Liquors A, B, C, D, and E, represent the best results and F one of the worst, and the method is open to one or two objections. Detannization with alcoholic gelatine solution is little, if any, more advantageous than that with aqueous gelatine, in so far as the extent of the co-precipitation of acid is concerned, but filtration is much easier since the precipitate is less bulky and more compact, probably because of the dehydrating power of the alcohol. A second difficulty is the character of the indi-

cator used. While other indicators change color more or less sharply at a definite hydrion concentration, haematein is practically always changing color from a hydrion concentration of twice normal (= 6.034 × N/1HCl) to 10^{-15} normal (= 6.8 × N/1KOH), but the authors estimate that the particular color change taken as end point by them took place at about 10^{-7} normal. The question of the haematein indicator is gone into more fully later, but the following is a comparison of two observers using the gelatine haematein method on five liquors:—

Liquor	1	2	3	4	5
Observer 1	10.65	15.2	15.6	20.9	17.45
Observer 2	10.8	15.6	15.85	21.2	17.7

The basic dyes recommended in Reed's second method are lemon-yellow "O" (sold by the Berlin Aniline Works), thioflavine F, methyl violet, and auramine. Only the latter pair were tried by the present authors, but the precipitation of tannin seemed very imperfect. Clear liquids were never obtained by a single filtration and were always highly colored, which absolutely precluded the use of haematein as an internal indicator.

In the J. A. L. C. A. for June, 1910, Yocum and others propose a modification of the gelatine haematein method by removing gallic acid by precipitation with gelatine in the presence of gum arabic. They state that the one serious defect of the original method is that it includes the non-plumping acids in the estimation, and where a large proportion of the tanning materials used are of the pyrogallol variety, the amount of gallic acid thus estimated is very considerable.

Experiments show, however, that the reaction is by no means a quantitative one, and considerable amounts of gallic acid are found in the liquor after treatment; while gum arabic itself is usually quite acid in solution. A much more convenient and scientific method is to select an indicator such as congo red paper, which is not sensitive to hydrogen-ion concentrations too weak to plump.

Haematein is scarcely affected by tannins, and if the titration is conducted under petroleum ether as described in a subsequent part of this paper, and the liquid spotted on haematein paper freshly blued by very dilute ammonia, well washed, and

used on a tile in a moist condition, very good results are obtained, though it is still not easy to fix on a definite end point.

An incomplete and unpublished method by Procter and Law consisted in the direct titration of the unfiltered and undetannized liquor with N/10 NaOH, using haematein paper as an external indicator.

Probably the best method for detannization which was examined, was that of Stiasny, which involves the precipitation of the tannin by formaldehyde in the presence of hydrochloric acid, but is unfortunately restricted to the catechol tans, which alone are completely precipitated. The details of the estimation were as follows:—

Twenty-five cc. of the tan liquor were pipetted into a flask, 20 cc. of N/2 HCl and then 10 cc. of carefully neutralized formaldehyde were added, and the whole boiled with a reflux condenser for ten minutes. The whole of the tanning and coloring matters were precipitated, leaving the 20 cc. N/2 HCl and the unknown quantity of acid in a brilliantly clear solution. The flask was rapidly cooled under the tap, the solution filtered, and the precipitate well washed. The filtrate and washings were then titrated with N/2 KOH and phenolpthalein, when any cc. of N/2 KOH above the 20 cc. required to neutralize the HCl added, represented the acid previously present in the liquor.

This method was thoroughly tested on quebracho, mimosa and gambier liquors. It was shown that in this case, owing possibly to the unusual character of the tannin precipitation, very little co-precipitation took place. The results were somewhat high, as the indicator used was phenolphthalein. It was found convenient instead of performing the whole titration with N/2 KOH, to add 20 cc. of the latter to neutralize the 20 cc. of N/2 KOH, and then titrate with N/10 KOH. Unfortunately the reaction with pyrogallol tans is neither complete nor quantitative.

A method which was formerly in use at the Vienna research station, though not tested in the present work, is interesting in that while theoretically wrong, it gave in many cases fair practical results. The principle of the method was to run into the acid liquor excess of standard caustic soda, and then utilize the excess of soda to liberate ammonia from ammonium sulphate,

the gas being collected in standard acid in the usual way. This of course would enable the operator to calculate the concentration of acid in the original liquor.

We have not had time to examine the complicated method and apparatus of Georg Grasser (*Collegium*, October, 1910, p. 406), but many difficulties and at least theoretical objections present themselves to anyone familiar with the problem, and in the final estimation of non-volatile acids it relies on the method of Koch, which we have already criticized. With regard to volatile acids, we need only point out as a well-known fact, that in steam distillation considerable quantities of lactic acid are invariably carried over with the acetic.

This completes the list of published methods. It will be seen that the great difficulty lies in the fact that a tan-liquor may contain any acid from strong acids like formic to phenolic bodies with feebly acid functions, and that if we estimate the acidity by titration with an alkali we always have to make an arbitrary choice of the end point by specifying a certain indicator. Thus no one method can give the tanner all the information he requires. If he wants to know the lime dissolving power of his liquors, probably nothing can give it better or more directly than the lime-water method. If he requires the actual present acidity of his liquor it can only be given in the form of the hydrion concentration, but this point will be discussed later. If he requires the total acid, he must, by choice of a suitable indicator, decide at what point he will draw the line between acid and non-acid bodies. Phenolphthalein, for instance, will include not only all trade acids, but some substances which are really not acids at all, though they have a feeble power of combining with bases; while methyl orange or congo red exclude many of the weaker true acids. It must also be remembered that in presence of the excess of alkali, which is required to influence such indicators as phenolphthalein, many really neutral bodies are hydrolyzed to bodies of a more acid character, as for instance tannin to gallic acid; and in the presence of oxygen still more profound changes take place, mostly in the direction of increased acidity.

Several of the methods which have been described involve the previous detannization of the liquor, and it has been pointed out that this in almost all cases is accompanied by marked co-

precipitation of acid. A rather considerable series of experiments was therefore made to test the effect of different methods of detannization, using throughout each series the same indicator. In each case 25 cc. of the liquor was titrated under petroleum ether to avoid oxidation, and the figures given are the number of cc. of N/10 KOH required for neutralization. To prevent or lessen oxidation, petroleum ether was used as described in a later part of the paper.

Series I.

Indicator	Moist haematein paper				
Liquor	A	B	C	D	E
Strength (grs.tan.)	0.70	1.5	2.3	2.8	3.04
Gelatine, aqueous	16.4	15.5	10.9	18.7	19.4
Gelatine, alcoholic	16.2	15.7	10.8	19.05	19.6
ZnO and HP	14.3	14.1	8.2	15.6	16.55
No detannization	16.7	16.05	11.1	19.2	19.85

Series II.

Detannization with gelatine salt solution as used in the Loewenthal method. Indicator moist haematein paper:—

Liquor	Before detannization	After detannization
Handler A	14.45	13.9
Handler B	16.05	15.6
Gallotannic	6.7	6.4
Mixed mimosa	10.3	10.1
Quebracho	10.05	9.6
Mixed liquor	11.3	11.05
Light leather suspenders	16.5	16.05

Series III.

Comparison of the Stiasny formaldehyde method of detannization of catechol tanning liquors with the Simand animal charcoal method:—

Indicator—Phenolphthalein paper.

Liquor	Stiasny cc.	Simand cc.	No detannization cc.	
Quebracho	10.70	10.40	10.65	N/10 KOH
Mimosa	7.45	7.30	7.45	"
Gambier	14.1	13.75	14.0	"
Mixed catechol	9.9	9.70	10.0	"
Mimosa	10.95	10.7	10.95	"

It will be seen from these results that in every case except Stiasny's method, detannization lowers acidity, through mostly

not to a serious extent for works control. The tannins themselves are either non-acid, or of such feeble acidity that for practical purposes it may be disregarded, and it is not difficult to choose indicators on which they have no observable effect, so that probably the most accurate results are obtained by direct titration without detannization, but with a suitable indicator. We have therefore made a somewhat detailed study of the possible indicators, not merely as regards the possibility of a rapid and accurate estimation of the total acid, but with a view of determining the proportion of acids of different "strengths;" and while our efforts to find ideal indicators have not been wholly successful, details of our results are given, in the hope that they may at least save others from useless investigation.

Since rapidity and ease of execution is often of equal importance to extreme accuracy in technical work, it is clear that a liquid internal indicator would present considerable advantages, but in most cases this is precluded from the dark color of the undetannized liquor, and resort must be had to the less satisfactory spotting on paper, which, however, often obviates the necessity of a somewhat tedious filtration. On the whole the greatest difficulties arise from the slow color-change of most indicators which renders it difficult to fix a precise end point recognizable by all operators.

It is well known that gallotannic acid and all other pyrogallol tannins hydrolyze or oxidize rapidly in alkaline solution in contact with air or oxygen to form increased quantities of acid. Consequently when an acid pyrogallol tannin solution is slowly titrated without any precautions to exclude oxidation, the value obtained is much higher than with a rapid titration; and in fact, within limits, the slower the titration the greater the amount of acid estimated. The precautions taken to prevent this have been mentioned, but it may be of interest to give a short account of the work carried out to obviate this difficulty.

In a good many preliminary experiments we attempted to obtain a neutral atmosphere inside the titration flask by bubbling coal gas through the liquor. This had the advantage that the reducing action of the coal gas to some extent counteracted the oxidizing action of the alkali, and gave quite satisfactory results, but the use of coal gas is objectionable owing to its ex-

plosive properties when mixed with air. Petrol ether, boiling below 40° C., which is a neutral liquid with a heavy vapor and sufficiently volatile to produce a neutral atmosphere on agitation, was tried with great success, and a further modification was introduced by the use of a small separating funnel. Into this was run the liquor to be titrated (usually 25 cc.), 2 cc. of the petrol ether were added, forming a layer over the oxidizable liquid, and by judicious agitation the vapor could be made to rarefy the air in the funnel to a considerable extent. The tan liquor was now titrated by dropping the standard alkali through the layer of petrol ether, and vigorously shaking to ensure thorough mixing and the maintenance of a neutral atmosphere. The tube of the separating funnel was cut off just below the tap, so that after each addition of alkali one drop of the liquor could be withdrawn and spotted on the paper indicator. This method was very effective in preventing any rapid oxidation. When the titration was finished and the reading had been taken, the tan liquor was run out from the bottom of the funnel, and the petrol ether left, where, if required it could be thoroughly washed in the funnel with water, and used again.

This method was used on all the following indicator tests:—

Mauvein was found to be only sensitive to acids above decinormal in strength, and was consequently useless for the purpose in view.

Methyl violet did not prove at all useful as the color-change was very gradual, and the only distinct change from blue to violet took place at a hydrion concentration of 10^{-2} normal.

Benzopurpurin has too gradual a color-change, allowing of differences up to 5 per cent.

Congo Red changes color from violet to scarlet at 10^{-4} normal, and as paper is quite the best indicator for this acid concentration. The paper is kept in the red (alkaline) state, as this is the most stable. This indicator may well be used by the separating funnel method to estimate the plumping acids of any liquor. Readings can usually be obtained to 0.1 cc.; it can conveniently be used in conjunction with some indicator of a later color-change to estimate both strong and weaker acids. Sörensen has found that congo red, being a colloidal indicator will not estimate acids in the presence of proteid matter. As we

propose to use the indicator in the form of test paper, by which the congo red is already strongly adsorbed, we believe that this difficulty will be obviated.

Methyl Orange changes color at a hydrion concentration at 10^{-4} normal, and is quite serviceable in the form of paper. It gives approximately the same end point as congo red, but the color-change is not so pronounced, though the results obtained showed excellent concordance.

Gallein is useless as an internal indicator for liquors, and in paper the color-change is not sufficiently definite.

Sodium Alizarin monosulphonate has a rapid color-change at 10^{-5} normal hydrion concentration, and proved fairly useful as paper. It was not so good as congo red or methyl orange for ordinary work but proved very serviceable in the approximate estimation of the actual hydrion concentration.

Carminic and Rosolic acids in pure acid and alkaline solutions have sharp but delicate color changes at 10^{-6} and 10^{-7} normal respectively. The delicacy of the color changes was such as to render it impossible to use the indicators either internally or as paper.

Lime-water. The advantages and disadvantages of using the action of lime water on tannin as an indicator have been discussed.

Lacmoid changes color at a hydrion concentration of 10^{-6} —10^{-7} normal, and in the form of paper is moderately serviceable, but generally inferior to azo-litmin. The color change is neither very distinct nor sharp.

Haematein. Test paper was made by saturating strips of good quality filter-paper in a freshly-prepared 0.1 per cent. alcoholic solution of the purest obtainable haematein, and allowing to dry without heat. The paper had to be kept in the yellow (acid) condition, as in the bluish purple (alkaline) state the color faded rapidly. The paper was rendered blue immediately before use by immersion in a *very* dilute aqueous ammonia solution, washing, and removing superfluous moisture by pressing between filter-papers, and then used in the moist condition. The end point of the titration is seen much more accurately if the paper is moist, as the mere moistening of haematein paper produces a slight change of color. It was also found that

haematein paper, even in the acid condition, did not keep satisfactorily for more than one week. The end point of the titration was supposed to be reached when no yellow color was produced in the indicator paper immediately on spotting with the liquid under titration, since further color-changes almost immediately take place. The greatest difficulty is the extremely gradual nature of the color-change, the yellow color almost imperceptibly gives place to a yellowish pink very difficult to distinguish from it. The following particulars are taken from a paper by Salm, "Studie über Indikatoren" (*Zeit. für Physik. Chemie*, Band LVII., 1907, page 471) to which we are indebted for much of our information on this subject, and represent the color-changes of haematein from a hydrion concentration of twice normal to one of 10^{-15} normal hydrion concentration.

Hydrion concentration		Color
2	normal	raspberry red.
1	"	pink.
10^{-1}	"	green gray.
10^{-2}	"	greenish yellow slowly going gray.
10^{-3}	"	
10^{-4}	"	green yellow.
10^{-5}	"	
10^{-6}	"	brown with a trace of red.
10^{-7}	"	bright lilac.
10^{-8}	"	violet.
10^{-9}	"	red violet.
10^{-10}	"	red violet, turning brown.
10^{-11}	"	
11^{-12}	"	dark red violet.
10^{-13}	"	dark red, later slowly brown.
10^{-14}	"	dark red, later brown, then yellowish green.
10^{-15}	"	blue violet.

Salm remarks that most of the colors are not permanent. The present authors do not claim, of course, that all these variations in color could be observed without the use of a colorimeter, but they are sufficiently obvious in the normal course of experiments to explain certain peculiar color effects and to render haematein a very difficult indicator.

Acetic, lactic, gallic and benzoic acids and all strong inorganic acids are moderately well estimated by the use of haematein paper, while boric acid only produces a slight reddening. Cer-

tain phenols in strong solution turn haematein paper reddish brown, but the color produced by such strengths of these bodies might be found in the liquors is very slight, and is readily distinguishable from the yellow color produced by bona-fide acids. The purest gallotannic acid which could be prepared was distinctly acid to haematein.

Azo-litmin paper was purchased. Changes color at a hydrion concentration of 10^{-8} normal. The color change is somewhat slow, and there are four distinct shades in it, viz.: a pink violet, violet, bluish violet and blue. The indicator did not prove very serviceable, and the readings obtained with the filtered and undetannized solutions were not very concordant. As used in Koch's method the indicator is somewhat unsatisfactory, and on the whole it does not compare very favorably with some others.

Phenolphthalein changes color fairly sharply at a hydrion concentration of 10^{-9} normal and seems to estimate a few bodies not included in the haematein value. It was not very serviceable with liquors either in the solution or as paper. By diluting the liquor and spotting on a tile fairly concordant results could be obtained. Its most prominent defect for our special purpose was the very decided alkalinity required to produce the color-change, which led to hydrolysis and oxidation of the tanning matters.

Alizarin only changes color when the hydrion concentration is below 10^{-11} normal, *i.e.,* in decidedly alkaline solution, and consequently is unsuitable for tan liquors for the same reason as phenolphthalein.

Fluorescein is an indicator which does not depend on an ordinary color-change, but on the appearance of green fluorescence, beginning at a hydrion concentration of N 10^{-5} and increasing to about N. 10^{-7}. It is used as an internal indicator in the solution, and is applicable even with dark-colored liquids. It is therefore an excellent indicator for estimating the total acidity of a tan liquor, and in *Collegium,* No. 419, we ventured to outline a method using the maximum fluorescence as end point. For six months, working with one sample of fluorescein, we obtained excellent results, but recently we have found that the personal equation involved by this method is much higher than we had previously reason to suppose. We have found that the stand-

ard fluorescence obtained by adding excess of alkali to 10 cc. of tan liquor containing five drops of 2 per cent. alcoholic fluorescein solution was not always definite. We tried to overcome this difficulty by using the fluorescence produced by a solution of definite hydrion concentration, viz.: 10^{-7}, as standard, and hoped in that way to obtain perfectly definite results, but ultimately found that different samples of fluorescein gave slightly different fluorescence, and the amount of indicator solution added had a great effect on the result.

It has been found, not only by ourselves, but by colleagues in other parts of England, that the fluorescein method as outlined by us in the *Collegium* is capable of giving good results in the hands of one observer, but as we have previously stated, this is common to many methods. We are very reluctant to abandon fluorescein, as with its use a direct titration of the unfiltered liquor may be made with great accuracy, the real difficulty being to obtain a definite standard of color capable of being reproduced by different observers; and we shall be glad if leather chemists will assist us in making experiments in this direction as it is quite evident that this indicator is well worthy of our attention. We now propose to experiment with the following indicators kindly provided by the University Tinctorial Chemistry Department:—aesculin, methyl red, 1 : 4 amido naphthol benzaldehyde *o*-sulphonic acid, and an unknown fluorescing substance.

A considerable series of experiments was carried out to test the fluorescein method, and in most cases the concordance was very similar to that with haematein; close for any single practiced observer; less good for a variety of observers fixing their own standards, but a few observers seemed regularly to obtain results constant in themselves but differing from the majority. Congo red, methyl orange and haematein papers were also carefully tested by titration under petrol ether with different liquors and each gave results not differing among themselves at the most by more than about 0.2 cc. and usually much closer.

The following table shows the results obtained on a series of liquors containing the material of an ordinary mixed tannage taking that found by haematein which closely indicates the true point of neutrality as 100. Of course the actual relation only

holds good for the individual liquors as it is dependent on the proportion of different acids present.

Indicator. Approx. Hion concentration	1	2	3	4	5	6	7	8
Azolitmin	106	100	104	104	109	..	..	..
Haematein	100	100	100	100	100	100	100	100
Fluorescein	88	89	93	87	62	..	..	..
Rosolic acid	88	93	93	92	66	..	..	..
Lime-water	82	96	93	..	69	49	65	63
Congo red	82	71	74	75	44	32	33	37

The last three liquors contained oakwood extract and oak bark only.

The figures of course represent the percentages of the total acid of the acids reaching the strengths or hydrion concentrations assigned to the various indicators. Acids which are not indicated by congo red have little or no plumping effect though they will still dissolve lime.

Below are given a few comparative results on four liquors from a light leather yard which were tested for acidity by the lime-water, haematein and congo red methods. The haematein and congo red were used as outside indicators with the separating funnel method before described. The big difference between the two latter indicators in all the readings was very puzzling, and can only be accounted for by the assumption that the liquors contained very few of the stronger acids.

Liquor No. I. Oakwood Extract and Oak Bark.

Acidity by
Lime-water = 25 cc. of liquor require 8.0 cc. N/10 alkali.
Haematein = " " " 16.0, 16.05, 16.05 cc. N/10 alkali.
Congo red = " " " 5.9, 5.8, 5.9, " " "

Liquor No. II. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 9.8 cc. N/10 alkali.
Haematein = " " " 15.25, 15.15, 15.10 cc. N/10 alkali.
Congo red = " " " 5.0, 5.0, 4.95 " " "

Liquor No. III. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 10.4 cc. N/10 alkali.
Haematein = " " " 16.5, 16.4, 16.5 cc. N/10 alkali.
Congo red = " " " 6.0, 6.1, 6.0, " " "

Liquor No. IV. Same composition.

Acidity by
Lime-water = 25 cc. of liquor require 10.2 cc. N/10 alkali
Haematein = " " " 16.4, 16.3, 16.25 cc. N/10 alkali.
Congo red = " " " 5.9. 5.9, 6.9 " " "

Handler liquor, Valonia, Myrobs, Oakbark, and Chestnut 22° Bkr.

Acidity by
Lime-water = 25 cc. of liquor require 9.2 cc. N/10 alkali.
Haematein = " " " 14.4, 14.45, 14.5 cc. N/10 alkali.
Congo red = " " " 10.8, 10.7, 10.6, 10.6 " "

The above figures, which appear somewhat inexplicable, are given to show that the use of a number of indicators in the titration of a tan-liquor acidity seems to throw some light on its acidic composition and certainly conveys more information to the tanner. In these cases the haematein result might stand for the total acid value, that of the congo red for the total plumping value, and the lime-water for the lime dissolving power.

A number of interesting phenols and aromatic acids, which if they do not occur in the liquors at least form the basis of many tannins, were examined. We trust to publish more fully on this point at a later date. but it may be sufficient for the present to give the following results. We found that gallic acid was ionized to a much greater extent than protocatechuic acid in equivalent solution, *i.e.*, that gallic acid is the "stronger" acid and there can be little doubt that it possesses a slight plumping power. Both acids turn congo red paper blue.

Of the phenols pyrogallol and resorcinol are both acid to haematein, the former considerably and the latter slightly so. Neither produced any color-change in congo-red. Phlorogucinol did not affect either congo red or haematein.

It may be added that all these tests were performed on the purest obtainable products.

Discussion (at Leeds).

Mr. F. W. Richardson said that many of the suggestions in the paper might be very useful in general laboratory work, such as the determination of organic acids, where the question of dilution and the reagents used were very important. No two

analysts, for instance, used phenolphthalein in the same way, and where very accurate results were required work with it was questionable. His experience with dilution methods was not very fortunate. The proposal to use the inversion of sugar as a criterion, reminded him that curious results were sometimes obtained when complex organic bodies were also present.

MR. A. G. PERKIN said that as yet there was no evidence of the presence of a carboxyl group in the natural catechol-tannins. It was possible that catechol-tannins might exist in nature, which were similar to the artificial product Schiff obtained by the condensation of two molecules of protocatechuic acid, and if so would be expected to possess an acid nature. On the other hand, it was hardly likely that such a compound would give the phlobophane reaction, so characteristic of the well-known catechol-tannins. In his opinion this property was not necessarily due to the presence of a catechol nucleus, but rather arose from the peculiar structure of the compound as in the case of catechin and cyanomaclurin, and this was evidently of a more complex nature than that possessed by gallotannin. According to numerous workers catechin is the parent substance of catechutannic acid and can be very easily converted into this compound, which seems to be a typical catechol-tannin. Such being the case, it was not easy to understand, in the light of (Kostanecki's) formula for catechin, how catechutannic acid could possess a carboxyl group.

DR. L. L. LLOYD said that if solutions contained any neutral salts there was the possibility of the production of mineral acids. Thus a mixture of wool and formic acid at a temperature above 50° tended to produce mineral acid which might hydrolyze tannin. Possibly leather might have a similar action.

DR. H. INGLE said that he always doubted the results obtained on titrating organic substances containing double linkages with alkali unless the atmosphere was absolutely excluded. Thus if saponification values of resins were done in open air there was a tendency to get an inaccurate result. Petroleum spirit did not altogether overcome the difficulty of the presence of atmospheric oxygen since by the law of partial pressures a little oxygen must be present. In the titration of highly colored liquids he had found certain sulphonated phenylrosaniline compounds very use-

ful. Fluorescein was better, since the color impression in this case depended on reflected instead of transmitted light, and was therefore more or less independent of the color of the solution.

PROF. H. R. PROCTER said that the film of petroleum spirit on the surface of the liquid excluded air almost completely, and tannin substances were not very absorbent of oxygen in the acid condition. Difficulties in the use of fluorescein as an indicator were in obtaining a standard color for comparison. He believed that by the use of one or two acid salts, such as sodium hydrogen phosphate, along with Bismarck Brown, the color with fluorescein would be a good imitation of that of the tannin liquors. He suggested the use of flattened capillary tubes. These gave a fairly wide surface. One of the tubes should be used for the standard liquid, and the other should be a pipette with a bulb very much like a penfiller which could be dipped into the liquid. The drop removed could be returned after examination. He pointed out the difference between the strength of an acid, *i.e.*, its sourness, and its concentration. Sörensen had recently investigated this with regard to enzymes, by the use of indicators, but checking his results by the determination of the hydrion concentration electrolytically. Although he had rejected this method in practice on account of its difficulties, he intended to check indicators by actual electrical measurements, which were now comparatively easy by the employment of Dr. Sand's apparatus as used by Wood and Law. Indicators on paper often gave quite a different effect from that in solution. On the paper they were probably in colloidal combination, and therefore less likely to be affected by colloidal proteid.

MR. A. SEYMOUR-JONES said that whereas the lime-water method only estimated those acids which had soluble calcium salts, the fluorescein method estimated the potential and actual hydrogen ions. Fluorescein gave higher results than lime in the proportion of about 1.1 to 1.0. Petroleum spirit was sufficient for practical purposes. Sörensen had found that Congo Red was colloidal in character, whilst fluorescein was crystalloidal, as it belonged to the eosin group.

DISCUSSION (AT NOTTINGHAM).

MR. D. J. LAW said that in dealing with the acidity of tan

liquors they were concerned with hydrogen ion concentration. The original hydrion concentration of the liquid future investigations would probably show to be related to its swelling power; on the other hand, there was the amount of alkali which had to be added until the liquid assumed approximately the hydrion concentration of pure water. This would be a measure of the capacity which the liquor would show for dissolving lime. The fact that methods for the determination of hydrion concentrations, involving the use of indicators, would always suffer from a certain lack of flexibility, more especially when dark liquids, such as tan liquors were to be investigated, would militate against their application when such problems as the relation of hydrion concentration to plumping effects were to be investigated. These considerations led Mr. J. T. Wood to suggest to Dr. Sand and himself that they should investigate the applicability of the electrometric method to the examination of tan liquors. The electrometric method, which was based on the determination of the difference of potential between the liquid under examination and a plate of platinized platinum saturated with hydrogen, was formerly more or less impracticable owing to complication of apparatus. Recently, however, the apparatus for such purposes had been so much improved by Dr. Sand for the purpose of the electro-analytical separation of metals (Trans. Faraday Soc., 1909, 5, 159) that its application was now an exceedingly simple matter. The results obtained so far, showed that for the titration of acids, such as acetic and lactic acid, added to given quantities of tan liquors, the electrometric method was easy of application and gave very satisfactory results. He hoped that the investigation referred to would shortly be completed when it would be laid before the Society.

Dr. J. Gordon Parker said in the past it had been assumed that lactic, formic, and similar acids were the panacea for all troubles, but until the effects of those acids had been thoroughly investigated by some method resting upon a scientific basis it was unwise to make such assumptions. He admired the simplicity of the electrometric process and hoped that the price of the apparatus would not be prohibitive.

Prof. H. R. Procter remarked that it was of the greatest importance to tanners to know not only the total quantity of

acid present in a liquor, but its "strength" under the actual working conditions, since upon this its effect on the tanning process mainly depended. The "strength" differed greatly in different acids, and was proportional to the concentration of free ionized hydrogen atoms actually present in the liquor, which was measured directly and with great accuracy by the electrical method, and he congratulated Messrs. Sand and Law on having shown that the method was convenient and practical in the laboratory, since Mr. Seymour-Jones and himself had been deterred from attempting to use it in practice from its apparent difficulty with the ordinary apparatus, and had tried to solve the same question by the use of colored indicators in a less perfect but much more simple way.

MR. J. T. WOOD said he had the privilege earlier in the year of reading and judging Mr. Seymour-Jones' thesis for his B.Sc. degree, on "the acidity of tan liquors," and this caused him to give attention to the subject and read Salm's paper as well as to refer to the literature of the electrometric method by Böttger and others. Had it not been for Dr. Sand's loan of his potentiometer and his help in discussing the problems presented to the tanner, probably nothing would have come of it. He considered that it was the simplicity of Dr. Sand's arrangement which rendered the electrometric method practicable. He was sure it would give the tanner much useful information as to changes taking place in the liquors.

WATER OF CRYSTALLIZATION OF MAGNESIUM, ALUMINUM AND SODIUM SULPHATES WHEN PRESENT IN LEATHER.[1]

By Dr. J. Gordon Parker and M. Paul.

Nowadays sole leathers are frequently treated with various salts, including magnesium sulphate, sodium sulphate, and aluminum sulphate. These salts are used because of their cheapness; they are non-hygroscopic and contain a large proportion of water. When their amount does not exceed 6 or 7 per cent. of the weight of the leather, no crystallization takes place on the grain, and it is quite impossible by simple examination to see if the goods are adulterated. Moreover, in the

[1] *Journal of the Society of Chemical Industry*, Nov. 30, 1910.

analyses, the percentage of ash is very low, due to the fact that dissociation takes place during the burning. Epsom salt especially is completely dissociated into magnesia, in such a way that one part of magnesia corresponds to 6.16 of $MgSO_4,7H_2O$.

These sulphates are determined in the ash, magnesium sulphate as phosphate,[1] aluminum sulphate as alumina, and sodium sulphate by estimation of sulphuric acid. The percentages which are obtained from the ash are calculated as hydrated salts. Generally, magnesium sulphate is reckoned with seven mols. of water, because it crystallizes in the air in this state.

Chemists do not agree concerning sodium and aluminum sulphates. This uncertainty sometimes causes big differences in proportion to the high percentage of water with which the salts may crystallize. For instance, the proportions of hydrated salt corresponding to one part of anhydrous salt are, according to the number of molecules of water of crystallization, as follows:—

Magnesium sulphate.—One part of anhydrous salt corresponds to 2.04 parts of $MgSO_4,7H_2O$, 1.74 parts of $MgSO_4,5H_2O$, and to 1.11 parts of $MgSO_4,H_2O$.

Sodium sulphate.—One part of anhydrous salt corresponds to 2.26 parts of $Na_2SO_4,10H_2O$, 1.63 parts of $Na_2SO_4,5H_2O$, and to 1.35 parts of $Na_2SO_4,3H_2O$.

Aluminum sulphate.—One part of anhydrous salt corresponds to 1.95 parts of $Al_2(SO_4)_3,18H_2O$, 1.63 parts of $Al_2(SO_4)_3$, $12H_2O$, and to 1.31 parts of $Al_2(SO_4)_3,6H_2O$.

The chemist knows that the method of calculation is somewhat optional, therefore this does not matter, but for the practical tanner who examines the analyses and sees only the percentages which are given to him,[2] it makes a great difference in his appreciation of the results.

This uncertainty is further increased, because the average moisture of ordinary sole leathers after some weeks of exposure to the air of a laboratory is between 16 and 18 per cent.;

[1] Levi & Manuel (Tanners' and Chemists' Handbook, p. 32), say that magnesium sulphate is found as the anhydrous salt in the ash. But when the burning to ash is done in a muffle furnace, magnesia is always found.

[2] The percentage of magnesium sulphate with 7 molecules of water calculated from the ash is always too great, because the magnesia from the water and from the lime used in the tanyard are counted in the same way.

in determining the moisture of leathers containing 3 to 4 per cent. of sulphates (calculated as anhydrous salts by heating in the air oven at 100°—105° C. for three hours) we have frequently been surprised at not finding the corresponding increase of the amount of water coming from the water of crystallization, that is to say, about 3 or 4 per cent. This might be due to the difficulty of dehydrating the salt, but by heating in a vacuum for a long time till constant weight, we have only recovered this difference for magnesium and aluminum sulphates whereas with sodium sulphate the moisture was not very much increased.

We have therefore investigated the possibility of determining and verifying the amount of water of crystallization for the three above-mentioned salts in leather. For the other non-hygroscopic heavy salts, such as barium chloride, the ratio of water to salt is very low, and therefore the question is not an important one.

Curried leathers and leathers treated with various percentages of glucose have been tried, but we unfortunately got discordant results; with fatty leathers because the oxidation of the greases and oils is too variable, and with the leathers treated with glucose because very small variations in the moisture of the air produce great differences in weight, due to the hygroscopic nature of the glucose.

Therefore we give only the method and the results for sole leathers.

The microscopic examination does not reveal very much because these salts produce some non-crystalline precipitates with the soluble matters from the leather.

The principle of the process was as follows:—We took 12 pieces of leather, 4 in. square, from the same belly portion of the hide, before rolling, to get two sufficiently homogeneous series of six pieces each; after six days the moisture of each series was determined under the same conditions, taking one piece of 1 in. by 4 in. from each sample. For the two portions the difference in moisture was about 0.02 per cent.

The remaining two portions were left together in the air and weighed every day. The daily variations were the same, and for one month the greatest difference was 0.04 per cent. (average 0.009 per cent.).

This point has been verified three times; once in operating as above, and twice with samples moistened with 25 per cent. of water.

Now, if one of the series is impregnated with a solution containing a known weight of anhydrous salt and the other one moistened with the same volume of pure water, and the two series allowed to dry in the air under the same conditions it will be possible to find out the amount of water which has been fixed by the salt. As the two portions are similar, the comparison between the weights of the two samples taken from time to time will show the relative increase of weight produced by the salt; the weight of anhydrous salt being known, the water from this salt and therefore the number of molecules of fixed water can be calculated.

This suggestion may be criticised from a theoretical point of view, but it answers sufficiently for practical purposes, because the interesting point is to see the relative increase in weight produced by a certain amount of salt.

We have made several experiments with each salt, using various proportions of anhydrous salts on the weight of the leather, varying the conditions of drying with various leathers containing different amounts of water soluble matters.

Sampling.—To allow of an easy impregnation we took porous ox hide bellies; after ordinary scouring and setting out, mineral oil was used for oiling instead of cod oil to produce a more porous grain. The drying was done at the ordinary temperature for three weeks, the experiments being carried out with samples of 3 in. square, six pieces for each group; all the pieces put together for eight days to arrive at an average moisture-content, and the weights taken every day to see the concordance of the variations.

The weights of the various groups were about 100 grms.

Impregnation with solutions of sulphates.—The salts used were pure recrystallized products. Solutions were made containing 16 per cent. of anhydrous salt at 20° C. The strength was determined by estimation of sulphuric acid for each salt, and estimation of magnesium as phosphate, and aluminum as alumina.

With these three standard solutions, three new series of solutions were made containing in 25 cc. of liquid 4 grms., 2 grms.

and 1 grm. respectively of anhydrous salt in such a way that by using 25 cc. of the solution for 100 grms. of leather, the percentages of salts were respectively 4, 2 and 1 per cent. as anhydrous salt on the weight of the leather. With more than 4 per cent. the salt crystallizes on the outside. Each group of six pieces was impregnated with the 25 cc. of the corresponding solution. When the liquid is carefully run from a burette drop by drop on the grain and on the flesh side, it is quite possible to put 25 per cent. of liquid in a porous leather without any loss. Immediately after impregnation the leather was weighed to verify that no loss had occurred.

The groups with water were moistened with 25 cc. of pure water. The drying of the various groups was done exactly in the same way. The first at ordinary temperature of the laboratory (15°—18° C.), the second in the drying room at 22°—24° C., and the third at 28°—30° C. The second and the third groups were removed from the drying room as soon as the drying was normal to prevent the alteration which accompanies a more complete drying. All the samples put together were weighed three times a week for two months.

The variations of weight were in concordance six days after the impregnation for the drying at ordinary temperature, and after ten days for the other groups. Each group compared with the corresponding one treated with water gave the relative increase of weight produced by the amount of anhydrous salt, therefore the fixed quantity of water, and the number of molecules of fixed water could be calculated.

The numbers in the following table give the average of these determinations which were in concordance at each weighing.

On examination of the table we see that magnesium sulphate has taken about seven mols. of water for the leathers which are dried at ordinary temperature. This quantity decreases to five mols. for leathers dried at high temperatures. For aluminum and sodium sulphates, the difference is smaller, depending on the temperature of drying, the amounts being 10—12 mols. of water for aluminum sulphate and three for sodium sulphate.

The results also show that the percentage of soluble matter varying between 5 and 20 per cent. of the leather does not affect the quantity of water fixed by the salt.

MOLECULES OF WATER FIXED BY

Magnesium sulphate

Percentage of anhydrous salt	Drying at 15°-18° C.	Drying at 22°-24° C.	Drying at 28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.1	5.4	3.1*
Leathers with 10 per cent. of soluble matter	7.1	6.0	5.2
Leathers with 5 per cent. of soluble matter	6.4	5.7	4.8
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.7	6.1	5.4
Leathers with 10 per cent. of soluble matter	6.5	5.3	3.3*
Leathers with 5 per cent. of soluble matter	6.8	5.0	5.1
One per cent. of the weight of the leather			
Leathers with 20 per cent. of soluble matter	6.9	6.0	5.2
Leathers with 10 per cent. of soluble matter	7.2	6.2	4.9
Leathers with 5 per cent. of soluble matter	7.0	5.1	5.2

Sodium sulphate

Percentage of anhydrous salt	Drying at 15°-18° C.	Drying at 22°-24° C.	Drying at 28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	2.3	2.6	2.9
Leathers with 10 per cent. of soluble matter	2.9	2.8	2.2
Leathers with 5 per cent. of soluble matter	2.6	2.7	3.2
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	2.7	2.2	2.5
Leathers with 10 per cent. of soluble matter	2.4	2.9	2.7
Leathers with 5 per cent. of soluble matter	3.0	2.4	2.3
One per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	3.1	2.4	2.2
Leathers with 10 per cent. of soluble matter	2.7	2.7	2.8
Leathers with 5 per cent. of soluble matter	3.2	2.6	3.1

Aluminum sulphate

Percentage of anhydrous salt	Drying at 15°-18° C.	Drying at 22°-24° C.	Drying at 28°-30° C.
Four per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	11.2	9.9	9.6
Leathers with 10 per cent. of soluble matter	11.8	10.2	10.4
Leathers with 5 per cent. of soluble matter	11.4	9.8	10.8
Two per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	11.5	10.1	10.0
Leathers with 10 per cent. of soluble matter	12.2	9.7	10.6
Leathers with 5 per cent. of soluble matter	10.1	12.3	11.3
One per cent. on the weight of the leather			
Leathers with 20 per cent. of soluble matter	12.8	10.9	10.7
Leathers with 10 per cent. of soluble matter	10.7	11.1	11.2
Leathers with 5 per cent. of soluble matter	11.0	11.2	9.8

The samples marked * show crystallization outside.

In addition we have made some determinations with 100 grms. of small pieces of leather about 1 in. square, put in basins to facilitate the impregnation with the solutions, but the results were not satisfactory, because crystallization takes place on the surface of the samples and on the bottom of the basins; the number of molecules of water was always smaller than the number given in the above table.

Finally, we have made a determination with larger pieces of leather, with three groups of samples (500 grms. each); the first group with 3.5 per cent. of anhydrous magnesium sulphate on the weight of leather, the second with 3.5 per cent. of anhydrous sodium sulphate, and the third with the same volume of water, doing the drying at ordinary temperature. The results were for magnesium sulphate, 6.8 mols. of water, and for sodium sulphate 3.1 mols.

THE SEYMOUR-JONES ANTHRAX STERILIZATION METHOD.[1]

By Alfred Seymour-Jones.

For many years the terrible scourge of anthrax has exacted an annual toll of human and animal life from this and other countries, and the disease was rendered all the more awful in that until recently it was, except in the earliest stages, incurable. Now, however, thanks to the work of Drs. Fortineau and Sclavo, it seems apparent that human beings may, to a certain extent, be saved, even when in the actual grip of this deadly malady. One very important step in the extermination of anthrax in European countries and America is the disinfection of the anthrax-infected materials which are imported into these countries without inpairing their usefulness for the various manufacturing processes which they subsequently undergo. This part of the problem the present writer claims to have solved and, as will be seen, his claim is supported by a mass of experimental work, not only by himself, but also by leading experts of the country. The process to be subsequently described will effectually disinfect, without injury, dry and wet hides and skins, wool, mohair, horsehair, and similar materials which are carriers of disease.

[1] *Leather Trades Review.*

The difficulty in solving the problem of anthrax sterilization has rested hitherto in discovering a method of sterilizing the anthrax spore when embedded in a gelatinous, aluminous or other colloid body, without injury to the material or fabric to be disinfected. The materials which act as carriers of anthrax are:—Hides and skins (especially when dry), wool, horsehair, mohair, rags, etc.

Sufficient evidence has been collected by the British Board of Agriculture and the British Home Office to warrant the supposition that animal foodstuffs, when imported, receive contagion from association with the foregoing materials, previous to importation. Assuming that this suspicion is justified, it follows that much, and probably nearly all the agricultural risks, can be eliminated, if the infected material is not placed in the neighborhood of such foodstuffs prior to shipment at foreign ports, by a thorough treatment of the infected material by means of some efficient sterilizing process at the port of shipment.

Any process which sterilizes hides and skins will naturally be applicable to their products, hair and wool, and consequently the adoption of a satisfactory method for the former should solve the difficulties in the latter and all other similar cases. At the same time the method must not interfere with any subsequent operation through which the disinfected material has to pass.

In all tropical and semi-tropical countries such as South America, India, China and Africa, hides and skins are dried either in the sun or in a shaded air current, or are plastered over with an earth salt while drying. The restoration of all such hides and skins to the green, raw, or wet state has always been a source of great difficulty and loss to the tanner, whose troubles were directly proportional to the method of curing and drying.

The method devised by the present writer overcomes in a quick and satisfactory manner the difficulty of sterilizing and restoring dry hides and skins to their former condition, and it is proposed that the whole operation should be carried out at the port of shipment before embarkation. To give full effect to the provisions of the method and to ensure that no industry is placed at a disadvantage, it would be advisable, if not necessary, that the leading Powers or Governments should agree upon a common course of action coming into operation after a given date.

The process proposed depends on the fact that an acid solu-

tion is very readily absorbed by colloidal albuminoid substances, *e. g.*, blood, gelatine, or hide, the absorption being accompanied by a peculiar swelling of the whole treated material, due to a simple absorption of considerable quantities of water according to the osmotic laws. This swelling is known to tanners as "plumping," and has been specially studied with relation to gelatine by Professor H. R. Procter.

The usual place of secretion of anthrax spores is on the surface of and immediate inside of a colloidal albuminous mass, such as a blood clot, and the outer "skin" of the spore consists of similar albuminoid matter. The difficulty up to the present has been to obtain a disinfecting solution which would penetrate firstly the dried blood clot, and secondly the hard "skin" (cell wall) of the spore. The treatment with acid solution provides a way out of this difficulty, for it causes the clot and the spore to swell, absorb water, and become very soft and tender. The acid itself has a deleterious effect on the spores, but sterilization by it alone is not sufficient. The process provides for this by treating swollen and tender material with a very dilute solution of a most powerful bactericide, but this will be dealt with later.

Many experiments have been carried out with a view to finding which of the many acids at our disposal was the most suitable for the above-mentioned swelling.

The author's experiments have shown that the acids least likely to interfere with the useful character of the infected material are the organic acids. Of these formic acid is to be preferred owing to its high ionization constant, which makes it a very strong acid, and its low molecular weight, both of which factors contribute towards rendering it the most efficient and, in the long run, the cheapest organic acid to use. It may be completely removed by washing, and is a disinfectant for all classes of fungoid growths, for so long as it is present no moulds, etc., will appear.

Its effect upon anthrax spores, when used cold, is interesting, although at present unexplainable. Animals inoculated with anthrax spores in dry blood clots, which have previously been subjected to a 24-hour treatment in a cold 5 per cent. solution of formic acid, survive from five to nine days before death ensues. Complete sterilization is not effected with formic acid solution

alone, but if the blood clots have been maintained at 90—95° F. for 24 hours in a 5 per cent. formic acid solution, then the subsequently inoculated animals survive the operation.

It would not be practicable to maintain any such temperature without a special and expensive plant to obtain it and keep it constant; therefore the employment of a powerful disinfectant is necessary when the operation has to be carried out with cold solutions. All the coal tar and similar disinfectants are impracticable for one of the following reasons:—

(*a*) They sometimes produce a tanning or tawing effect on the hide.

(*b*) They fail to penetrate the infected material.

(*c*) They adhere very strongly to the hair, wool or hide, and often communicate a strong irremovable aroma.

(*d*) In many cases they fail to sterilize.

Experiments were conducted with a considerable number of metallic salts as sterilizers and without going into the merits and demerits of each it may be stated that as a result of much work mercuric chloride ($HgCl_2$) was chosen as the most suitable bactericide. One of its great advantages lies in the fact that excellent results were obtained, even using extraordinarily dilute solutions of the salt, which were such as to render its use in the requisite concentration perfectly harmless to human beings.

A chart is given to show the rate of absorption of acid and mercuric chloride by hide; on the ordinate (perpendicular) is plotted the amount of the acid and chloride remaining in solution, while on the abscissa (horizontal) is plotted the time taken to absorb. As will be seen, the concentration of acid in the solution round the hide falls regularly and gradually, showing a perfectly uniform absorption of acid throughout the experiment. On examining the mercuric chloride curve, however, we find a different effect, for the concentration of the mercuric chloride actually increases during the first hour or so, thus showing that the water is more rapidly absorbed than the mercuric chloride contained in it. As soon as the hide becomes softened the chloride begins to penetrate, and afterwards the absorption is rapid and regular, until it becomes fairly constant, equilibrium being established. By this time the piece of dried hide is quite

soft and completely disinfected, the whole process only taking 24 hours.

Professor H. R. Procter, M. Sc., and Professor Dr. Edmund Stiasny have reported that the treatment of hides and skins by this process has no harmful effect on the leather subsequently produced, and also state that this method of treatment is most efficacious in rapidly softening dried hides. The reports are appended.

Mr. Howard Priestman, the wool and textile expert of Bradford, has reported that the process has no deleterious effect on wool, and his report is given below.

The sterilization efficacy of the method has been the subject of investigation by Dr. Constant W. Ponder, who is carrying out researches into the question of anthrax on behalf of the Leathersellers' Company. His report will, it is hoped, in due course be published by the Worshipful Company of Leathersellers.

The method is also undergoing a searching examination by Dr. F. W. Eurich, bacteriological expert to the Bradford Anthrax Investigation Board, who are interested in the wool and mohair problem, and he will, in due course, report to his Board, who will doubtless publish the results.

Below are given the details of the method of disinfection, and if carried out abroad the procedure in the case of wool and mohair requires no modification. If, however, the sterilization takes place in countries where a higher temperature can be conveniently obtained, in the latter case such a temperature, not exceeding 130° F. for wool, or 212° F. for hair, is not only permissible, but considerably accelerates the process. It is, of course, obvious that no raised temperature can be employed in the case of hides and skins

REPORT OF EXPERIMENTS ON THE CURE OF HIDES WITH FORMIC ACID AND SALT MADE AT THE REQUEST OF A. SEYMOUR JONES, ESQ.

Half of a dried China hide was soaked in a ½ per cent. solution of formic acid (the formic acid used being 40 per cent., the dilution was 1:80). After 12 hours a very considerable soaking effect was noticeable; the soaking was continued for 48 hours, when the hide appeared sufficiently soft. Now, a saturated salt solution was prepared and the hide allowed to remain in this

for another day or two, when the hide was dried. A piece of this dried hide was easily soaked back again in cold water, behaving as ordinary salted hide.

The other half of the dried China hide was treated in a similar way, the concentration of the formic acid solution being 5 per cent. This hide, after the acid and salt treatment was washed with water in the drum, then limed with a sulphide lime (10 days), unhaired, fleshed and scudded. In this state it looked very well and was sent to Penketh Tannery to be tanned for sole leather.

As far as experiments on so small a scale allow any judgment, it may be stated that the treatment of dry hides with a dilute formic acid solution and subsequently with saturated salt solution has a very good soaking effect, the hides, after being washed out from the salt, behaving in the limes like fresh salted hides would do.

Drying out after salting does not affect this behavior, as resoaking is very easily effected.

H. R. PROCTER.
EDMUND STIASNY.

Leeds University
June 27, 1910.

The China half-hide was sent, after liming, unhairing and fleshing, to the Penketh Tanning Company to be tanned along with their ordinary goods. No intimation was conveyed to them of its previous treatment.

Mr. C. E. Parker writes as follows:—

"The side that we got through you from Leeds is now finished. It weighs 20 lbs., and the leather looks all right. We do not notice any difference between our own sides and this."

It will not escape observation, that the foregoing side was treated to an acid solution, five times stronger than recommended to be employed in the process.

REPORT ON THE ABSORPTION OF $HgCl_2$ BY HIDE SUBSTANCE.

The point to be examined was the rate of absorption. To this

end 87.5 grams of dried hide were cut into small pieces about 1 inch square, and immersed in 1 liter of 0.5 per cent. formic acid + $\frac{1}{10,000}$ $HgCl_2$ solution.

The experiment was started at 11.05 A. M. and hide was not completely softened by 5.35 P. M. When examined at 9.05 A. M. next morning was quite soft:—

THE CONCENTRATION OF $HgCl_2$.

At 11.05 A. M	1	part in	10,000
At 11.35 A. M	1.1	parts in	"
At 12.05 P. M	0.97	"	"
At 12.35 P. M	0.92	"	"
At 1.05 P. M	0.88	"	"
At 2.05 P. M	0.82	"	"
At 2.35 P. M	0.70	"	"
At 3.05 P. M	0.56	"	"
At 3.35 P. M	0.37	"	"
At 4.05 P. M	0.35	"	"
At 4.35 P. M	0.34	"	"
At 5.05 P. M	0.32	"	"
At 5.35 P. M	0.31	"	"
At 9.05 A. M. next morning less than	0.10	"	"

In the earlier stages water is apparently more rapidly absorbed by the hide than $HgCl_2$. Consequently the concentration of the latter increases.

The result of the above experiment as regards the total quantities is as follows:—

Amount of $HgCl_2$ absorbed by the hide up to 9.05 A. M.

= 0.0935 grams.
= 93.5 per cent. of original amount of $HgCl_2$.
= 0.13 per cent. on the dry weight of the hide.

DUPLICATE EXPERIMENT.

97.5 grams of dry hide in one piece immersed in 1 liter of 0.5 per cent. formic acid solution and $\frac{1}{10,000}$ $HgCl_2$ solution. Experiment was started at 11.05 A. M. Hide not soft at 5.35 P. M., but quite soft at 9.05 A. M. next morning.

The course of absorption was as follows:—

THE CONCENTRATION OF $HgCl_2$.

At 11.05 A. M	1	part in	10,000
At 11.35 A. M	1.08	parts in	"
At 12.05 P. M	0.97	"	"
At 12.35 P. M	0.95	"	"
At 1.05 P. M	0.94	"	"
At 2.05 P. M	0.93	"	"
At 2.35 P. M	0.93	"	"
At 3.05 P. M	0.93	"	"
At 3.35 P. M	0.92	"	"
At 4.05 P. M	0.92	"	"
At 4.35 P. M	0.91	"	"
At 5.05 P. M	0.80	"	"
At 5.35 P. M	0.72	"	"
At 9.05 A. M. next morning	0.47	"	"

The phenomena are the same as in Experiment 1, but the absorption is slower owing to the hide being in one piece.

Amount of $HgCl_2$ absorbed = 0.0695 grams.
Amount of $HgCl_2$ absorbed = 69.5 per cent. of original $HgCl_2$.
Amount of $HgCl_2$ absorbed = 0.073 per cent. on weight of dry hide.
Temperatures of solutions = 70 degs. F.

This work was carried out under my supervision.

HENRY R. PROCTER.

September 12, 1910.

REPORT AS TO THE SOLVENT ACTION OF A 5 PER CENT. SOLUTION OF FORMIC ACID ON HIDE SUBSTANCE.

Liquor taken in which a China hide had been soaked until soft. No dissolved hide substance was detectable in this liquor by the Kjehldal process.

July 5, 1910.

This work was carried out under my supervision.

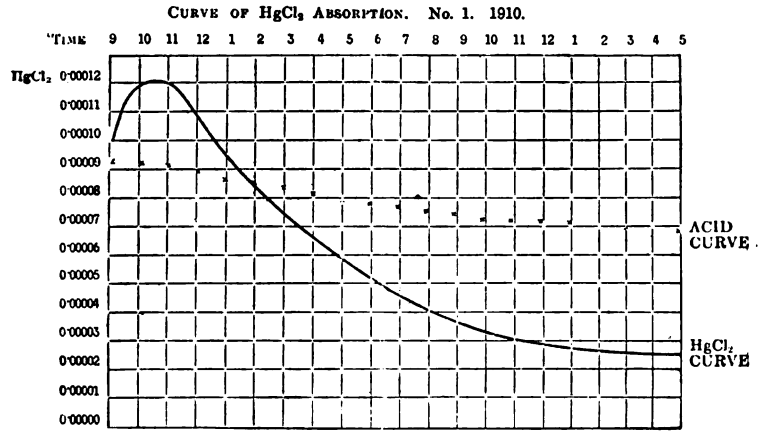
HENRY R. PROCTER.

REPORT OF THE ABSORPTION OF MERCURIC CHLORIDE (CORROSIVE SUBLIMATE) BY DRIED HIDE IN ACID SOLUTION.

Four solutions were made up, each of which contained 1 part of mercuric chloride in 10,000 of water. In addition solutions A and B were both 0.5 per cent. solutions of formic acid and solutions C and D were 1.0 per cent. solutions of formic acid. Four pieces of dried China hide were cut as far as possible into uniform sizes and shapes, and one piece immersed in each of the

four solutions respectively, the volume of each solution being 1 liter. In these the pieces of hide remained for 24 hours, the acidity of the solutions and the concentrations of $HgCl_2$ being determined every hour. The results are given below.

N.B—The initial acidity of the liquors as described was only approximately produced by rough weighing. The initial concentration of $HgCl_2$, however, was most accurately obtained.



THE "SEYMOUR-JONES" ANTHRAX STERILIZATION PROCESS APPLIED TO HIDES IN DRY STATE.

A pit of suitable dimensions is required for the immersion of the hides.

Into the pit run sufficient cold water to cover the hides contained in the pit.

The volume of water must be a known amount.

To this volume of water add 1 per cent. of formic acid of 90 per cent. strength then after plunging to mix the acid and water, add 1 part mercuric chloride to every 5,000 parts of water. The mercuric chloride should be previously dissolved by heating in water. Finally plunge the whole pit well before adding the hides.

In this pit the hides are left for 24 hours, when it will be observed that their condition is somewhat similar to that of a

Readings of $HgCl_2$ Experiment in Absorption

	No. 1 Weight of hide 110 grams		No. 2 Weight of hide 102 grams	
Time	Sol. 0.5% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration of $HgCl_2$	Sol. 0.5% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration $HgCl_2$
9.0	9.3	0.00010	9.3	0.00010
10.0	9.2	0.00012	9.2	0.00011
11.0	9.15	0.00012	9.0	0.00011
12.0	8.9	0.00010	8.9	0.00010
1.0	8.75	0.00009	8.7	0.00010
2.0	8.65	0.00008	8.6	0.00009
3.0	8.40	0.00008	8.4	0.00009
4.0	8.2	0.00007	8.35	0.00008
5.0	8.0	0.00006	8.30	0.00007
6.0	7.9	0.00005	8.15	0.00007
7.0	7.8	0.00004	8.05	0.00006
8.0	7.6	0.00004	8.05	0.00006
9.0	7.5	0.00004	8.0	0.00006
11.0	7.3	0.00003	7.75	0.00005
1.0	7.2	0.00003	7.70	0.00003
3.0	7.1	0.00003	7.6	0.00003
5.0	6.95	0.00002	7.5	0.00002

	No. 3 Weight of hide 111 grams		No. 4 Weight of hide 105 grams	
Time	Sol. 1% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration of $HgCl_2$	Sol. 1% formic acid Acidity	1 in 10,000 $HgCl_2$ Concentration $HgCl_2$
9.0	17.8	0.00010	18.6	0.00010
10.0	17.75	0.00012	18.3	0.00012
11.0	17.70	0.00011	18.15	0.00010
12.0	17.6	0.00010	17.6	0.00010
1.0	17.5	0.00009	16.8	0.00009
2.0	17.2	0.00009	15.95	0.00009
3.0	17.10	0.00008	15.7	0.00008
4.0	17.0	0.00007	15.55	0.00008
5.0	16.7	0.00006	15.4	0.00006
6.0	16.6	0.00006	15.25	0.00006
7.0	16.5	0.00005	15.0	0.00006
8.0	16.3	0.00005	14.75	0.00005
9.0	16.1	0.00005	14.6	0.00005
11.0	15.7	0.00004	14.45	0.00004
1.0	15.6	0.00003	14.25	0.00003
3.0	15.05	0.00003	14.0	0.00003
5.0	14.8	0.00002	13.8	0.00002

raw hide, only firmer. This pit completes the act of sterilization. From the sterilization pit the hides should be drawn and allowed to drain in such a manner as will permit the liquor to flow back into the pit for further use.

After draining the hides are transferred to a pit containing a saturated solution of common salt and water. In this case it is advisable to have a good layer of undissolved salt lying on bottom of pit before immersing hides. In this pit the hides need not be left more than one hour, when they should be hauled up and placed on a drainer, in order that the salt liquor may return to the salt pit for further use. Or if it is found more convenient the hides may be opened out flesh up and hand salted, then placed in pile for a few days before baling. Or they may be again dried.

After draining, the sorting or classing, weighing and bundling may be proceeded with prior to export.

THE "SEYMOUR-JONES" ANTHRAX STERILIZATION PROCESS APPLIED TO GOAT AND SHEEP SKINS IN THE DRIED CONDITION.

A pit of suitable dimensions is required for the immersion of the skins.

Into this pit run sufficient water (cold) to cover the skins contained in pit.

The volume of water must be a known amount.

To this volume of water add one-quarter to one-third of 1 per cent. of formic acid of 90 per cent. strength, then after plunging to mix the acid and water, add 1 part of mercuric chloride to every 5,000 parts of water. The mercuric chloride should be previously dissolved by heating in water. Finally plunge the whole pit thoroughly before adding skins.

In this pit the skins are left for 24 hours, when it will be observed that their condition is somewhat similar to that of a raw skin, only firmer. This pit completes the act of sterilization. From the sterilization pit the skins should be drawn and allowed to drain in such a manner as will permit the liquor to flow back into the pit for future use. As skins usually have long hair or wool, this draining may be expedited by placing boards and heavy weights on the pile to exert a pressure.

After draining the skins may be transferred to pit containing a saturated solution of common salt and water. In this case it is advisable to have a good layer of undissolved salt lying on the bottom of the pit before immersing skins. After lying in the salt solution one hour they can be hauled up and drained as in the case of the sterilization pit.

Or if it is found more convenient the skins may be opened out flesh up and the salt strewn on flesh side liberally, then allowed to remain in a pile for a day or so until salting is completed. Or they may be again dried.

They are now ready for classing, weighing, etc.

COST AND ECONOMY OF THE PROCESS.

The economical working of the Seymour-Jones process may be controlled by anyone with average intelligence. It is estimated that, buying formic acid at 5d. per lb., and mercuric chloride at 2s. 6d. per lb., the cost of the process will work out at about 3¾d. for a large hide and, of course, proportionately less for skins or wool.

As will be seen from the results of the work carried out at Leeds University, the amount of formic acid absorbed by the hide varies approximately from 20 to 25 per cent., leaving 80 to 75 per cent. still in the pit. Consequently, it is unnecessary to have a fresh bath for every lot of infected material, for if we start with a fresh solution, and after one lot of material 25 per cent. of our acid is taken up, on the second occasion the bath will only have to be strengthened to that extent, thus effecting a considerable saving.

The question of the analytical control of the mercuric chloride concentration is more complicated, and while the report and method of Professor Procter and Mr. Arnold Seymour-Jones is appended, I do not think it is at all necessary to follow it up in practice because as will be noted from the charts herewith, in the case of the hides and skins, nearly all the mercuric chloride is absorbed. It is therefore suggested that, unless there is suitable apparatus on the spot for carrying out the control as outlined in the analytical report, the pit be recharged each time with 1 part of mercuric chloride per 5,000 parts of water in the pit.

A point of interest is that the Seymour-Jones process is very efficacious in preserving hide substance. As is unfortunately only too well known to the tanner, dried hides and skins in soaking back are apt to lose a relatively large percentage of their weight owing to solution of the decomposed skin matter. By effecting a thorough sterilization and cure of the hide or skin shortly after it comes off the animal's back, the Seymour-Jones process prevents putrefaction, and if the proposals embodied in this paper be properly carried out, it cannot be doubted that the loss due to this cause will be considerably diminished.

To increase the economy the following method specially worked out for the control of this process at the University of Leeds is given below.

THE ANALYTICAL EXAMINATION OF A 1.0 PER CENT. FORMIC ACID AND A 1 IN 10,000 MERCURIC CHLORIDE SOLUTION.

I. Estimation of the Acid.—This is accomplished in the usual way by titration of an aliquot part of the solution with decinormal sodium hydroxide in the presence of phenolphthalein. Each cubic centimeter of N/10 NaOH required corresponds to 0.0046 grms. of pure formic acid.

II. Estimation of the Mercuric Chloride ($HgCl_2$).—This estimation depends on the fact that mercuric chloride in such low concentrations as we are considering, in the presence of formic acid on treatment with sulphuretted hydrogen (H_2S) gas is converted into mercuric sulphide which remains in colored colloidal solution. We have determined by experiment that the depth of color of this solution is practically directly proportional to the concentration of the original mercuric chloride. The experimental details used in the present case were therefore, as follows:—

Ten cc. of the 1 in 10,000 mercuric chloride acid solution are pipetted into a test-tube and saturated with sulphuretted hydrogen gas. The colloidal mercuric sulphide solution so produced is poured into the dipping vessel of a Schmidt and Haensch dipping colorimeter, and the stage so adjusted that the solution under observation is exactly 10 millimeters thick. If the means are at hand this color can be most accurately matched with Lovibond's standard tinted glasses (red, yellow, and blue), and

this forms a convenient permanent standard. As a rule, however, it is quite sufficient to use the color produced in a 1-centimeter cell by a solution of 1 in 10,000 $HgCl_2$ + 1.0 per cent. formic acid freshly precipitated with sulphuretted hydrogen gas.

The 1-centimeter cell of this standard color is placed on the matching platform, and into a clean, dry dipping vessel are pipetted 10 cc. of the acid $HgCl_2$ solution of unknown concentration previously saturated with H_2S. By manipulation of the dipping stage we then proceed to determine the depth of this solution which will match the standard color. This is accomplished by varying the depth of the liquid examined until a uniform field is obtained in the telescope. Let us suppose that the depth so found is x millimeters, then

$$\frac{\text{The concentration of standard}}{\text{The concentration of the unknown}} = \frac{10}{x}.$$

Knowing the concentration of the standard and the value of x, we can calculate the value of the unknown. We may thus determine the concentration of any formic acid mercuric chloride solution between 1 part in 10,000 and 1 part in 100,000 with very reasonable accuracy.

We have only used this method of estimation of mercuric chloride in the presence of formic acid, but experiments are now proceeding to determine if it is possible to perform it in the presence of other acids. We have found by extended tests that an observer being given a solution of mercuric chloride and formic acid, the concentration of which was unknown to him but known to others, can estimate very exactly the concentration of that solution by this method.

Although in our experiments the colorimeter used was a Schmidt and Haensch, a Dubosc or any other form of dipping colorimeter may be used instead.

(Signed) HENRY R. PROCTER.
ARNOLD SEYMOUR-JONES

Re INVESTIGATIONS FOR MR. A. SEYMOUR-JONES.

I have now completed all the laboratory investigations which are possible in regard to the effect of formic acid upon wool. Anything more complete would need the active co-operation

of some spinner or comber who would be willing to experiment on a large scale.

Formic acid is now in common use in the trade, and is considered so much the best acid for certain dyeing purposes that its high price does not prevent its use.

To make sure of my ground I began by steeping fine clean Botany wool in 90 per cent. formic acid for 12 hours. This treatment made no alteration in the condition or prominence of the scales or serrations, or on the nature of the fiber when seen under a microscope giving 200 magnification.

I have steeped limed slipe in 90 per cent. formic acid for 12 hours without discovering any effect on the serrations of the fibers, although the "handle" of the wool was greatly improved by the removal of the lime and lime combination.

I have tried steeping both the above qualities in 20 per cent. solution and 5 per cent. solution of formic acid, transferring them to saturated salt solutions after four hours' or more immersion. None of these experiments have any effect on the scales or serrations of the fibers.

See micro-photographs herewith.

Magnification 226 times.

To discover whether either the acid or the salt had any effect on the strength or softness of the fiber I prepared 24 hanks, each composed of 40 wraps, 1½ yds. in circumference, 2/18 fine Botany yarn, and I append tables of breaking strains:—

SAMPLES.

	1 Four hours acid 20%. 45 min. salt	2 Four hours acid 5%. 45 min. salt	3 Forty-five minutes salt	4 Not treated
	..	62½	..	..
	..	63½	61½	62½
	62½	65	65	62½
	64½	64	63½	62½
	61½	61½	62½	61½
Total	187½	317½	252½	249
Aver.	62½	63½	63⅛	62¼

No. 1 was steeped four hours in 20 per cent. formic acid and 45 minutes in saturated solution of common salt.

No. 2 was steeped as directed—four hours in 5 per cent. formic acid and 45 minutes in saturated solution of common salt.

No. 3 was steeped 45 minutes in saturated solution of common salt.

No. 4 was not treated in any way.

All the hanks treated are apparently stronger than those not treated.

This slight variation of less than 2 per cent. is doubtless due to slight variation in the yarn itself. Such variations are always present, and it may be taken that the treatment does not affect either the strength or the handle of the yarn.

Yours,

March 18, 1910. HOWARD PRIESTMAN.

I have just completed another series of tests as to the effect of 5 per cent. formic acid and saturated salt solution at 40 to 50° C.

I can detect no alteration in the microscopic structure, and I doubt if steeping alone in the solutions would have any effect whatever.

In order to keep the temperature regular I had to move the yarns very frequently, and to this is doubtless due the irregularity of the tests, because it would disturb the arrangement of the threads composing the various hanks.

As things are there is only a reduction of 1½ per cent. in the average strength, and I do not think that this small reduction would have any appreciable effect on the class of wool which is usually associated with anthrax.

I am, yours truly,

April 14, 1910. HOWARD PRIESTMAN.

Report on four hanks, each containing 40 wraps or 80 threads, 2/18 fine Botany yarn, all steeped four hours in 5 per cent. formic acid at 105 to 108° F., and for half an hour in saturated solution of salt at the same temperature:—

1st hank	58½ lbs.
2d hank	56½ "
3d hank	65½ "
4th hank	64 "
	4)244½ "
Average strength	61⅛ "

This is a reduction of 1½ per cent. on the untreated yarn.

April 14, 1910. H. P.

ABSTRACTS.

The Mouldiness of Leathers. From *"Les Laines et Cuirs"* through *"Le Cuir,"* 1910 (3), No. 23, pp. 649 and 651.—The first condition for avoiding the mouldiness of leather is to keep the walls, floor and pillars very clean, whether it is during the drying or in the store houses. The filthiness which often exists there is the principal cause of the growth of mould. In many tanneries mould comes from old rinsing vats These vats should never be more than three feet in depth so that they can be easily cleaned. Too long a use also causes a thick growth of mould in them.

To avoid mould in store-rooms the best method is to entirely empty them from time to time, and fumigate them with sulphur. If this cannot be done, the floor may be sprinkled with very dilute hydrofluoric acid. In this case great care must be exercised because this acid is very corrosive and its fumes easily attack the respiratory organs.

Certain persons recommend formaline for the same purpose, but it does not appear that this would be as efficacious. A 5/100 per cent. solution of sublimate is certainly better for destroying mould germs in posts and the rods of the dryers, etc.; but being rather unstable, the substance does not hinder the development of germs for long. A 2 per cent. solution of fluoride of sodium which can also be used on leather itself is very much better. One should always specify, in procuring this substance that the pure and entirely soluble salt is desired, for it is often adulterated with fluoride of silicon which does not possess the same antiseptic properties.

The mouldiness of leather may often come from casks containing the oil with which it is treated. This is prevented by heating the oil before using and allowing it to cool again. A little salicylic acid added to the oil also destroys mould germs.

The Treatment of Mouldy Leathers. From *"Laines et Cuirs"* through *"Le Cuir,"* 1910, (3), No. 22, pp. 610 and 611.—When a leather merchant perceives that some of his goods are mouldy, alarmed by this discovery, he generally makes the great mistake of wishing to get rid of the mould as quickly as possible by rubbing or brushing. But this mould is damp and sticky, so that by such an operation exactly the opposite result is obtained from that hoped for. Instead of disappearing, the mould is fixed still more strongly on the leather in being pressed on the surface with rags used for rubbing or with the brush, thus becoming thin and more visible than before. If mould is to be removed from leather, it is necessary first to take the leather from the place where it became mouldy and to dry it. This drying may be done in the open air if the weather permits or in a warm place in case of rain. The cause of mould is removed in this way and also the mould itself is made easily removable. In fact when mould is dried, a brush or small broom will take it off without leaving any very marked traces on the surface of the leather. For thick leather the operation may also be

facilitated by spreading on the surface very dry bran, which the brush removes together with the mould. The bran cleans the pores of the leather and besides it leaves in the small holes in the surface, traces of the meal, which help greatly in giving a certain gloss to the leather which too deep a mould would have tarnished considerably. It is very important that the bran in question should be used perfectly dry, and that it should never be used more than once.

The leather from the surface of which mould has been taken is then vigorously rubbed with a suitable rag. If the leather is black it is again rubbed with a rag soaked in bone oil. For chestnut leather the oil is replaced by soapy blacking. This rubbing restores the shade of the leather and gives it the luster which it had lost. Very rarely a new application of dye is made.

It is unnecessary to mention that leather cleared of mould is very often exposed to the same conditions which caused the mould. People seem to believe that the mould proceeds from the leather alone, and that the first cleaning guarantees it against further accident of the kind. Mould germs always exist in places where leather is. Therefore most particular care should be taken with leather which has once been mouldy, and it should be separated as far as possible from that which might injure it anew. If possible this leather should be placed in a very dry place. When this is not possible, and if it must be stored in the same room, this should at least be aired and cleaned, and subjected to frequent airing whenever good weather permits. It is also well to coat the walls and floor of the room with an antiseptic and to repeat the operation from time to time.

Finally, preparations should not be used for restoring luster to cleaned leathers, which themselves contain mould germs, and which afford excellent nourishment for microbes. Preparations consisting of blood albumin, glue, etc., are of this kind. These substances favor the development of germs which attack the leather. They should therefore be used only with moderation and after sterilization.

Bookbinding Leather; its Nature, Decay and Prevention of Same. DR. LOUBIER. *Zentralblatt f. Bibliothekwesen*, 1910, pp. 322-49.—This paper by the custodian of the library of the Kunstgewerbe Museum in Berlin is based upon the reports of the special committee on bookbinding leather of the London Society of Arts 1901-5 supplemented by his own experiences. Systematic inquiry has shown that early bindings are durable, but that there has been a falling off since 1830 and those made since 1860 have shown the least endurance. The "red decay," whereby the leather becomes burnt, red and brittle is the most striking; in the form prevalent since 1860 the leather actually rots to a powder. The decay is independent of the amount of use and is most marked in well lighted and heated rooms. Since the ancient leathers have withstood, exposed to the same conditions, the essential cause must lie in the manufacture of the leather itself.

The leathers used in bookbinding are: (1) Goat leather (morocco)

for superior bindings, manufactured in Europe, Africa and the East; the foreign leathers are native tanned and dyed in Europe. This leather is used both with natural grain and grain pressed. (2) Calf leather, smooth, without grain, vegetable tanned, plain and dyed. (3) Sheep leather; in Germany, "bock" leather means the East Indian sheep; split leather is generally sheep. (4) Pig skin leather, natural color or dyed yellow brown. (5) Seal skin leather, with fine natural grain or coarse, artificial grain. (6) Cow skin leather, little used.

With regard to the nature of the tannage, it has been found that the pyrogallol tans, especially sumac and gall-nuts, have proved the best. Oak is not injurious, but the red color produced is unsuited for dyeing. The so-called Niger leather from Guinea is said to be tanned by the natives with a species of gall-nut. The catechol tannins, such as quebracho, have shown themselves injurious, containing acids which attack the leather. The East Indian or "Persian" morocco and sheep skins have proved the least durable of all bindings, showing red decay in a year.

In the dyeing of leather, formerly only vegetable dyes were used. Since 1870 the coal tar dyes have been employed; the frequent use of sulphuric acid to intensify the color has greatly shortened the life of much binding. Another source of this injurious ingredient in leather is its use as a pickle. As for the dyes themselves, experiment has shown that many coal tar dyes give just as durable, light fast hues as the vegetable colors; care need only be given to avoid strong acids and harmful mordants. Dr. Lamb examined 1,500 samples of leathers dyed with coal tar colors and found red, blue and black the most durable towards light. The author exposed red brown Niger leather to direct light for 6 weeks and found the color held very well.

With respect to currying, the leather is often too much degreased by the acids used in tanning and dyeing. In spite of the greasing given in currying, the bindings often become too dry in the heated libraries. An attempt has been made to remedy this by oiling the bindings with vaseline or degras.

Artificially grained calf and sheep leathers are unsuited for bindings, the durability being lowered by the hot pressing used in the manufacture. Split leather is also too weak. Sheep is the softest and loosest of all binding leathers, but is more durable than bookbinders generally admit; it should not be shaved too thin and must be tanned and dyed without acids. Pig skin is strong but suited only for heavy volumes and it easily soils. The new Russian leather has little endurance although it has been highly rated. A discussion follows of the details in the mechanical work of binding and its best practice. Lastly the author treats of the best conditions for preserving bindings; hot air, vapor from gas lights, direct sunlight are all injurious. A plea is made for official inspection of binding leather and the requirement of guarantees from the manufacturer.

W. J. K.

Fundamental Rules of Practice, (continued). L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, 217-9, 369-71.—A further advantage of extraction in closed vessels is in the possibility of transferring the liquors by pressure instead of pumping, this method being cheaper, better and quicker. The pressure may be applied by direct steam or compressed air. Although it has been previously shown that extraction under pressure decomposes some tannin, this evil need not be feared on merely subjecting the *surface* of the liquor to steam pressure to drive over the liquor. This can be easily verified by thus driving over cold liquor and it will be found that this remains cool up to the last portions which finally consist of a little warm condensed water. The spent bark becomes a little warmed and on this account it is better to use compressed air which is cheaper. The disadvantage of pumping hot liquors as is necessary in open extractors is that the hot liquor evaporates in the rarefied chamber of the pump and the exhaustion must be further increased; if too hot it cannot be pumped at all, until cooled off. Further, the bark is not so fully freed of liquor by pumping but contains 6-10 per cent. more water than when pressure transmission is used. Also the surplus or dead liquor below the perforated bottom of the extractor is greater in open vats and therefore the degree of the following extraction is proportionally lessened. The author found that on entire removal of the residual liquor from an open vat, the bark was 0.2 per cent. better extracted. Another advantage of extraction in closed vessels is the production of a lighter colored liquor; although apparently dark, on dilution to the same strength as the vat liquors, it is lighter. The author concludes from his own extensive experience that for the same space, closed extractors perform twice as well as open leaches.

In computing the loss of tannin in spent bark from the analysis, it is erroneous to reckon as is often done, the direct percentage of tannin found as loss in the original material. If for instance a pine bark yields up 20 per cent. of its total weight on extraction, and the spent bark be found to contain 2.5 per cent. tannin, this correctly computes to only 2 per cent. loss as based on original substance. It is further incorrect to reckon the tannin left in the bark as lost on the theoretical ground that it is all available for tannage. The author has earlier pointed out in the Report of the Freiberg Tanning School for 1903-4 that in the weak solutions used in tannin analysis substances are present and are estimated as tannin which would separate in the strong liquors of the tannery and remain useless. To properly judge whether a bark is sufficiently extracted, the spent material is examined and regard paid to its nature and the behavior of the liquor. If the last decoction which at the most shows 0.5 B., on standing and cooling gives a copious sediment and if the liquor by further warming and extraction of the same bark cannot be further enriched, then the practical limit is reached. The tannin content of this spent bark may serve as a standard and regular examinations of spent bark will be of great use in plant control. For greater accuracy hydrometers graduated to

1/100° B. are used with the last liquors. To ensure no loss, the tannin content of the spent bark may be let reach 0.3-0.5 per cent. less than found in the above experiment, if conditions permit. Eitner showed in 1907 (abstr. this JOURNAL, II, 370) that in the analyses of fresh pine bark substances are extracted and rated as tannin which in practical extraction remain insoluble and although higher temperatures yield more extract, the proportion of sediment on cooling increases. It is not correct therefore to compute all the tannin left in the bark as loss nor all that is extracted as gain. W. J. K.

A Sensitive Reaction of Glue. E. SCHMIDT. *Chemiker-Ztg.*, [34] 839. —If to an aqueous solution of glue the ordinary acidified ammonium molybdate (phosphoric acid reagent) be added, a white precipitate is formed. Neutral molybdate does not give the reaction, this first appearing on addition of a few drops of dilute nitric acid, this is the preferable method in using the reaction, which is very delicate and characteristic. The precipitate and supernatant liquid become pale bluish green after standing. The method is well suited to test the materials used in dressing leather; concentrated solutions of gum arabic, linseed, and white of egg were found to give only a slight cloudiness which is easily distinguished from the glue reaction with practice. The author hopes to employ the method for gravimetric determination and is experimenting in this direction. W. J. K.

PATENTS.

Apparatus for Evaporating Solutions. U. S. Patent No. 980,108. SAMUEL MORRIS LILLIE, Philadelphia, Pa.

An essential feature of the method consists in passing the gases of combustion from the fire through a vertical flue, down which the liquid to be evaporated is sprayed.

Vacuum Drying Apparatus. U. S. Patent No. 980,444. OLIVER S. SLEEPER, Buffalo, N. Y.

Cylinder Grinder for Leather-Shaving Machines. U. S. Patent No. 980,561. OSCAR REIRSON, Peabody, Mass.

Process of Making Leather-Board. U. S. Patent No. 981,591. ALBERT L. CLAPP, Braintree, Mass.

Belt-Stretcher. U. S. Patent No. 979,599. FREDERICK THOMAS, London England.

Clarifying Extracts Containing Tannin. U. S. Patent No. 979,656. HERMANN DAMKOHLER AND HUGO SCHWINDT, Bremen, Germany.

The process consists in adding to the extract barium meta-aluminate and precipitating the resulting color-lake by means of a water-soluble sulphate.

Apparatus for the Sterilization of Water and Other Liquids. U. S. Patent No. 979,999. CASMIR STANISLAUS PIESTRAK, Paris, France.

The method employes air, which has been ozonized by passing through an annular space between two electrodes carrying a suitable electric current.

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ELECTIONS.

ACTIVE.

Max F. Woltz, Salem, Virginia.

TESTS FOR ESTIMATING THE PURITY OF COMMERCIAL CHESTNUT OAK BARK EXTRACTS.

By Fritz H. Small.

The purpose of this article is to describe briefly certain tests which have been used by the writer and his assistants in the laboratory of the Graton & Knight Mfg. Co. for estimating the

purity of commercial chestnut oak bark extracts. The tests are not original with the writer save in the manner of use. The figures are original and may prove of assistance to any one who is at work on the problem stated above.

While some rather skilful counterfeits of a chestnut oak bark extract have been made by mixing various foreign and native tanning materials, the usual chestnut oak bark extract in the domestic market is pure except for a possible admixture of chestnut wood extract or of extract from other oak barks than chestnut. The oak barks sometimes used are red, Spanish, water, and rarely black. The investigation of the extract to determine which, if any, of these latter materials are present will usually show whether a more complex mixture is being studied.

It may be stated at the outset that the writer was much disappointed in his study of this problem to find as his investigations progressed that there is as much variation among different specimens of genuine chestnut oak bark as among different specimens of genuine Newfoundland cod livers. Because of this variation it seems improbable that an exact determination of the amount of chestnut oak bark tannin in a mixed extract of even so simple a composition as a mixture of chestnut oak bark and chestnut wood extracts can be attained,—much more improbable if the mixture is more complex. On the other hand while the variations in individual samples of chestnut oak bark are considerable, the average pure chestnut oak bark extract of commerce runs through a rather small range of values and if fairly consistent in its reactions and constants. It must be understood, therefore, that the results given below are for average samples, and that while these are the results to be expected, individual specimens may show quite other.

To be able to make satisfactory comparisons by qualitative tests it is essential that the tests be made under as nearly as possible the same conditions. The procedures described are those which the writer has found best. In all cases analysis solutions of as nearly as practicable 0.4 gms. tannin to 100 cc. were used. Inasmuch as the qualitative reactions are apt to be altered by the age and condition of the solution tested, it is desirable always

to work with a fresh analytical solution. Following are some of the qualitative tests which the writer has found helpful:—

Sulphuric Acid Test[1]:—Put three drops of solution in a test-tube; run in down the side 1 cc. of concentrated sulphuric acid; shake gradually until a uniform color is obtained; note color. Dilute with 3 cc. of water; note color and precipitate.

Ferric Ammonium Alum Test[2]:—Dilute ⅔ cc. of solution to 10 cc. and add one drop of a 1 per cent. solution of ferric ammonium alum,—test-tube. Note color and formation of precipitate.

Ammonium Acetate Test[3]:—Add concentrated acetic acid to concentrated ammonia till slightly acid. To 10 cc. of solution in a test-tube add 5 cc. of the ammonium acetate solution obtained above, and let stand one hour; note formation of precipitate. Boil and note precipitate.

Lime Water Test[4]:—To 10 cc. of solution in a test-tube add 5 cc. of lime water; shake and allow to stand undisturbed for twenty-four hours; note color of precipitate, and color of clear top solution by both reflected (fluorescence) and transmitted light.

	C. O. bark	Red oak	Black oak	Spanish oak	Water oak	Chestnut wood
H_2SO_4 con.....	crimson	crimson	reddish yellow	brown	brown	yellow
dil.	pink	pink	yellow	brown	yellow brown	yellow brown
$Fe_2(NH_4)_2(SO_4)_4$ ·	green	green	green	blue	blue	blue
$(NH_4)C_2H_3O_2$ cold	pr.	pr.	pr.	pr.	pr.	pr.
boil	clears up	clears up	clears up	remains in part	remains in part	much remains
CaO_2H_2	crimson	crimson	crimson	straw	straw	green

These tests will serve to show the probable purity of the extract and give an idea of the nature of the foreign materials present.

To estimate the probable extent of the impurities the writer

[1] Procter, L. I. L. B., Chap. VIII.
[2] Procter, L. I. L. B., Chap. VIII.
[3] Communicated to writer in a letter by A. W. Hoppenstedt.
[4] Procter, L. I. L. B., Chap. VIII.

has found the formaldehyde-hydrochloric acid method[1] of Stiasny most helpful. Stiasny has shown that the reaction does not separate quantitatively the pyrogallol and catechol tannins. In the writer's experience, however, the method can be so used as to give a constant weight of precipitate from a given solution. When so used moreover it will be found that if two solutions be mixed, the precipitate-weight of the mixture will be that calculated from the precipitate-weights of the components. After some months of experimenting the following procedure was settled upon as yielding the sharpest differentiation of materials and most consistent results.

Prepare a 2 per cent. solution of formaldehyde and a ½ per cent. solution of hydrochloric acid. Mix these in equal volumes (1-1) immediately before use.

Prepare a solution of the extract to be tested as for analysis, making it to contain as nearly as practicable 0.4 gms. tannin to 100 cc. Filter this solution as for a soluble-solids determination by the official method and obtain 160 cc. or more of clear soluble-solids filtrate.

To 50 cc. of the clear soluble-solids filtrate in a crystallizing dish add 50 cc. of the mixed formaldehyde-hydrochloric acid solution. To 100 cc. of clear soluble-solids filtrate in a 250 cc. graduated flask add 100 cc. of the mixed formaldehyde-hydrochloric acid solution. Cover the crystallizing dish with a watch-glass to prevent evaporation and place both it and the flask on adjacent openings of a steam bath. Heat with a good flow of steam for 2½ hours; remove; allow the flask to cool one hour in the air, then cool with water at approximately 20° C to 20° C and make up to the mark. Filter this solution as for a soluble-solids filtration by the official method, discarding the 75 cc. of liquor used for digestion, and collecting for use only when the filtrate comes clear.

Pipette 125 cc. of the clear filtrate into a crystallizing dish and evaporate both it and the solution in the other crystallizing dish, to which 25 cc. of water has been added, to dryness on a steam bath. (Because of hydrochloric acid fumes the combined evaporator and dryer must not be used for this evapora-

[1] *Der Gerber*, 1905, p. 186; *Collegium*, 1908, p. 419.

tion.) Transfer to the combined evaporator and dryer and dry for 16 hours; put in desiccators, cool, and weigh. These weights should be corrected for any variation from 0.4 gm. tannin to 100 cc. in the strength of the original solution.

A series of tests of various mixtures of wood and bark liquors by this method gave results as follows:—

	Wt. of total	Wt. of filtrate	Precip.-wt. found	Precip.-wt. calculated
Bark No. 1	0.3553	0.2010	0.1543	..
Wood	0.2731	0.2581	0.0150	..
1 bark No. 1, 3 wood	0.2946	0.2435	0.0511	0.0499
2 bark No. 1, 2 wood	0.3140	0.2286	0.0854	0.0847
3 bark No. 1, 1 wood	0.3339	0.2166	0.1173	0.1195
Bark No. 2	0.3255	0.1559	0.1696	..
1 bark No. 2, 2 wood	0.2871	0.2203	0.0668	0.0666
3 bark No. 2, 1 wood	0.3138	0.1798	0.1340	0.1310

The average precipitate-weight of the usual chestnut wood extract by this method is not far from 130. Results from various samples of chestnut wood extract are as follows:—122, 118, 124, 135, 141, 138, 146, 150. The average precipitate-weight of chestnut oak bark extract is above 1,600. A great many tests of chestnut oak bark extracts and of chestnut oak barks have been made in this laboratory and a succession of values from the note books may be recorded here:—1878, 1610, 1840, 1866, 1678, 1709, 1818, 1725, 1889, 1757, 1623, 1543, 1553, 1615, 1640, 1644, 1658, 1690, 1760, 1660, 1826, 1717, 1652, 1604, 1630, 1777, 1741, 1737, 1520, 1661, 1684, 1673, 1753, 1733, 1688.

Opportunity has been found in this laboratory up to the present to test comparatively few specimens of other oak barks than chestnut. A test of a series of samples of red, Spanish and water oak barks furnished the writer by Mr. G. A. Kerr, and of black oak bark furnished the writer by Mr. H. C. Reed gave results as follows:—

	Analysis			Wt. of	Wt. of	Precip.
Kind	Sol. sol.	Non-tan.	Tannin	total	filtrate	weight
Red	11.09	4.28	6.81	0.3298	0.1661	0.1637
Black	14.24	5.68	8.56	0.3409	0.1516	0.1893
Spanish	14.32	7.78	6.54	0.4316	0.2864	0.1452
Water	7.70	4.43	3.27	0.4773	0.3665	0.1108

It will be noticed that while the results of the tests made by this method on different samples of chestnut oak bark and chest-

nut oak bark extract show a considerable variation, none of the precipitate-weights found are below 1,500. Owing to the fact that this variation exists in samples of undoubted genuineness, the impossibility of establishing a standard precipitate-weight for chestnut oak bark is evident. Inasmuch, however, as the results of the many tests of chestnut oak barks and chestnut oak bark extracts made in this laboratory during the past year have discovered no genuine chestnut oak bark extract which gave a precipitate-weight below 1,500,—it may be stated with very small likelihood of error that any extract tested by this method which shows a precipitate-weight of less than 1,500 is not a pure chestnut oak bark extract. In the same way in estimating the percentage composition of mixtures of chestnut oak bark and of chestnut wood extracts, if 1,500 be assumed for the precipitate-weight of chestnut oak bark and 130 for the precipitate-weight of wood, and the percentage composition of the mixture be calculated from these values and from the precipitate-weight of the mixture as found, it is certain with little chance of error that the calculated percentage gives the extract credit for all the chestnut oak bark extract likely to be present.

It is manifestly impossible in an article of this sort to explain in detail all the applications of the method. While its usefulness for testing the purity of chestnut oak bark extract has been suggested in this article, the principle and method are of much wider application and it only needs the establishing of a series of values for different materials to enable one to estimate more accurately than by any other method known to the writer the percentage composition of a mixture, the components of which are known, or otherwise, to assist him in the determination of the nature of the components in an unknown mixture.

THE USE OF CASEIN IN DETERMINING TANNIN.

M. Nierenstein.

(*Chemiker Zeitung*, No. 4, 1911, p. 31.)

In the year 1903, at the suggestion of Dr. T. Körner, at that time an instructor in the German Tanning School in Freiberg, Saxony, I experimented on the use of casein as an agent for

detannization in the analysis of tanning materials. Since that time, through my own work and that of E. Drabble, D. Spence, H. E. Roaf,[1] T. A. Webster and L. R. Thompson I am convinced of the trustworthiness of this method for the estimation of tannin in barks and fruits. On the whole we have carried out from 750 to 800 analyses. The values so obtained were from 1 to 1.5 per cent. higher than those by the hide-powder method.

Our method is not adapted to the analysis of tanning extracts, because the decolorized extracts often contain aluminum oxide, which the casein dissolves, thus causing the figures for the non-tannins to come out too high.

Recently I had occasion to discuss with Prof. Dr. E. Knecht the analysis of tannins in the dyeing industry, and mentioned among others this method also, which was as yet unpublished. The possible importance of the method for the textile industry induces me now for the first time to make it public.

We employed for the analyses Kahlbaum's casein, carefully freed from fat by extraction with ether, according to Hammarsten, 100 cc. of the tan-liquor were shaken for 10 minutes with 6 gr. of casein, and then treated with 3 more grams of casein and filtered. Then we proceeded as in the hide-powder method. The following are test analyses performed on Schering's pure levigated tannin.

5 g. tannin dissolved in 500 cc. water gave for 50 cc.

I.		II.	
Total solids..	0.4982 g.	Total solids..	0.4986
Non-tans	0.0014 g.	Non-tans	0.0010
Tannin	0.4968 g. = 99.36%	Tannin	0.4976 = 99.52%

5 g. tannin and 5 g. gallic acid in 1000 cc. water; 50 cc. gave

I.		II.	
Total solids..	0.4988 g.	Total solids..	0.4998
Non-tans	0.2496 g.	Non-tans	0.2478
Tannin	0.2496 g. = 49.8%	Tannin	0.2520 = 50.4%

5 g. tannin and 5 g. glucose in water; 50 cc. gave

Total solids..	0.4994
Non-tans	0.2476
Tannin.....	0.2518 = 50.36%

[1] Dr. H. E. Roaf made the interesting observation that casein which has been acted on by tannin does not give the Millon reaction. This observation tends to support my hypothesis that tannage is accompanied by chemical processes.

I have already[1] reported on a series of quantitative estimations of sugar in tanning solutions which had been detannized by means of casein, so that I omit further sample analyses. From the instances cited it is evident that casein absorbs tannin quantitatively, while it does not take up gallic acid nor glucose, which so often accompany the tannins.

THE EMPLOYMENT OF THE ELECTROMETRIC METHOD FOR THE ESTIMATION OF THE ACIDITY OF TAN LIQUORS.[2]

PART I.

By Henry J. S. Sand, PH.D., D.SC., and Douglas J. Law, B.SC., F.I.C.

The determination of the acidity of tan-liquors is a matter which is at the present time undergoing a considerable amount of discussion. This is due not only to the difficulty of finding indicators which give a plain color-change in the dark liquids to be titrated, but more still, to the uncertainty which has prevailed in the minds of tanners as to an exact definition of the terms acid, alkaline, and neutral. We may say that apart from the ionic theory, no attempt ever has been made to fix these ideas in an objective manner. It is a commonplace that different indicators will turn at entirely different points when such weak acids as occur in tan-liquors are present, and also that the degree of acidity on which a property such as swelling power depends cannot be simply expressed by stating the equivalent concentration of the acid. As is well known, the ionic theory affirms that degree of acidity depends on the concentration of hydrogen ions, a strongly acid solution being one in which the hydrion concentration is great, an alkaline solution, one in which it is extraordinarily minute, and if we wish to adopt absolutely pure water as our standard of neutrality, a neutral solution is one in which the hydrion concentration is approximately 10^{-7} normal. The ionic theory also furnishes us with a direct means of estimating hydrion concentration, and this means consists in

[1] M. Nierenstein, *Chem. Zeitung*, 1909, p. 15.

[2] *Journal of Society of Chemical Industry*, Jan. 16, 1911.

measuring the difference of potential between that liquid and a hydrogen electrode. Other methods for the same purpose must obviously be as numerous as are the functions of hydrogen-ion concentration, but more particularly for the determination of small hydrion concentrations, the electrometric method is the most direct, and has in most cases served to standardize the others. Of the subsidiary methods that of indicators is by far the most important, and owing to the researches of Friedenthal (Zeits. Elektrochem. 1904, **10**, 113; *ibid.* 1908, **14**, 125); Salessky (Zeits. Elektrochem. 1904, **10**, 204); Fels (Zeits. Elektrochem. 1904, **10**, 208); Salm (Zeits. Elektrochem. 1904, **10**, 344. Zeits. Phys. Chem. 1907, **57**, 471); Sörensen (Sur la mésure et l'importance de la concentration des ions hydrogène dans les reactions enzymatiques. Comptes Rendes Laboratoire de Carlsberg, 1909, **8**, 1); and others, we now possess a whole range of indicators which have been standardized in such a manner that it is possible to select one or more, to indicate almost any arbitrarily fixed hydrogen ion concentration. For the investigation of tan liquors, however, only a small fraction of these is available owing to the deep color of the solutions to be titrated; and the turning points of this fraction do not necessarily correspond to a hydrion concentration which is of importance to the tanner. The electrometric method, on the other hand, allows any arbitrarily fixed hydrion concentration to be determined, and it was this consideration which led Mr. J. T. Wood to suggest to us the desirability of testing the electrometric method, more especially in order to examine its practicability for determining the original hydrion concentration of a tan liquor and also the amount of alkali which must be added until a hydrion concentration corresponding to the turning point of some well recognized indicator such as particularly phenolphthalein, is reached. There is reason to believe that the former is an essential factor on which the swelling power of the liquor depends, and that the latter will be connected with its capacity for dissolving lime (see table 2). The present results are of a preliminary nature, and are given with a view to show the general practicability of the method, and in response to repeated requests that we should publish a complete and coherent account of the form in which

the electrometric process is employed by us. This method of titrating acids and alkalies was first put forward by Böttger (Zeits. Phys. Chem., 1897, 24, 253) working in Ostwald's laboratory in 1897, and may be said to depend on the fact that when metals and also hydrogen absorbed by platinum black, are brought in contact with solutions which contain these same substances in the ionised condition, a potential difference is established which depends, not only on the nature of the substances in contact, but also, on the concentration of the ions in solution. In the form in which the method was described by Böttger, it could however hardly be employed in the titration of the weak acids occurring in tan-liquors. It is generally believed that the complication of apparatus required for carrying out estimations of this sort is so great as to render the method unsuitable for practical purposes. We have found however, that when the auxiliary electrode and a potentiometer-box devised by one of us for the purpose of the separation of metals by graded potential (Sand. Trans. Faraday Soc., 1909, 5, 159; Trans. Chem. Soc., 1907, 91, 373, and 1908, 93, 1572) are employed, the method becomes easy and certain of application, and all the apparatus may be set up in a few minutes.[1]

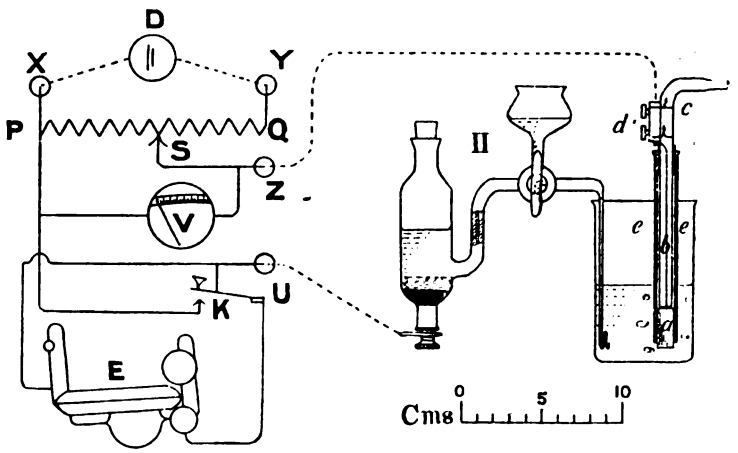
Apart from the beaker containing the liquid to be examined and a burette for delivering alkali into it, the apparatus consists of the hydrogen electrode and the auxiliary electrode, both dipping into the liquid; and the potentiometer box for measuring the difference of potential between them.

The accompanying figure shows the hydrogen electrode I. and the auxiliary electrode II., drawn to scale, on the right, whereas the electrical apparatus is explained diagrammatically on the left.

We are at present engaged in examining various forms of hydrogen electrode in order to find which is the most suitable for our purpose. The one shown in the figure has been improvised for the experiments recorded here, and we therefore describe it, but do not on this account wish to put it forward as the best form available. It will be seen that it consists essential-

[1] The apparatus was made partly by Universitätsmechaniker Fritz Köhler, of Leipzig, and partly by Messrs. Griffin, of London.

ly of a thin platinum plate, *a*, which is fastened to a long thin platinum wire, *b*. The latter is fitted inside the glass tube, *c* and is sealed through it near the top, and then ends in the terminal, *d*. The plate, *a*, is surrounded to within about 2 mm. from the bottom by the glass tube, *e*, which is fitted to *c* by a piece of rubber. The hydrogen escapes through the liquid at the bottom. The whole apparatus is suspended by means of a piece of string from a ring fitted on the burette-stand in such a manner that it may be employed for stirring the liquid, but cannot come in contact with the bottom of the beaker. The



platinum plate, *a*, is coated with platinum black by the Lummer Kurlbaum method, *i.e.*, by making it the cathode in a 3 per cent. solution of platinum chloride containing one-fortieth per cent. lead acetate, the current being regulated so as to produce a moderately vigorous evolution of hydrogen. A single coating has lasted for more than fifty titrations. Hydrogen obtained by the action of hydrochloric acid on zinc and purified by means of alkaline permanganate solution enters at the tube, *c*, and escapes at the bottom. The initial saturation of the platinum black requires a passage of the gas for 25 to 30 minutes. When once saturated, however, the transference of the electrode from one liquid to another occasions no loss in saturation greater than

can be remedied by allowing the hydrogen to pass for about one minute before proceeding with the titration.

The auxiliary electrode-vessel, II., will require little further explanation. For our purposes in which an accuracy of about one centivolt is sufficient, we believe that the normal calomel electrode is the most suitable. This electrode was made up according to the directions given by Ostwald-Luther's Handbuch[1] and not exposed unnecessarily to light. The left limb of the capillary connection is filled from the funnel with normal potassium chloride solution, whereas the other limb contains a 3.5 normal solution of the same substance. It is known that the diffusion-potential between this solution and the other solutions of small concentration is always small. In those cases in which Bjerrum (Zeits. Phys. Chem., 1905, **53**, 428), succeeded in determining such diffusion potentials, they did not exceed one centivolt. During use, the tap of the electrode, which must be maintained free from grease, is kept closed, the layer of liquid held by capillary attraction around the barrel forming the connection.

One of the most important points in every method of titration is what may be called the end-reaction. In the present case we have to decide which potential-difference between the calomel and the hydrogen electrode is to be taken as an index that the titration is complete. If the object of the titration be to estimate the number of equivalents of acid present, then this potential-difference can only be determined if it is known which is the acid present and what is the concentration of the sodium salt resulting from the titration.[2]

We have not gone into this matter fully as yet, and it is by no means certain that an end-reaction resulting from considerations

[1] Some pure mercury is poured into the electrode vessel. On this a layer of about 1 cm. in height is poured of a paste made by shaking up mercury very thoroughly with calomel in a normal potassium chloride solution, pouring off the supernatant liquid and repeating the operation several times. Finally the vessel is charged with a normal solution of potassium chloride, which has been thoroughly saturated with mercurous chloride by shaking up with the above paste.—For a discussion of the sources of error in this electrode see Coggeshall. *Zeit. Phys. Chem.*, 1895, 17, 63.

[2] For a discussion of this matter see Salm und Friedenthal, *Zeit. Elektrochem.*, 1907, 13, 125.

of this kind would be of special importance to the tanner. In the meantime we have adopted the value 0.69 volt as our end-voltage. This number was obtained primarily by running a $N/10$ soda solution into a $N/10$ acetic acid solution containing phenolphthalein until the first indication of pink was observed. At the dilution of this experiment the change of color very nearly corresponds to the point at which the base has been added in a quantity equivalent to the acid originally present. The value 0.69 volt also corresponds very nearly to a hydrion concentration equal to that of pure water as is shown by the following considerations.

Taking the potential difference between a normal calomel electrode and a hydrogen electrode placed in contact with hydrions of normal concentration to have the value given by Wilsmore (Zeits. Phys. Chem., 1900, **35**, 302) of 0.283 volt, then Nernst's formula leads to the corresponding P. D. (π) for a hydrion concentration C. at 17° of

$$\pi = \left(0.283 + 0.0575 \log \frac{1}{C}\right) \text{ volt} \ldots \ldots \ldots \ldots (1)$$

For a hydrion concentration C. of 10^{-7}, corresponding approximately to pure water, this leads to $\pi = 0.283 + 0.403 = 0.69$ volt. Similarly, by the employment of a new method, Lorenz and Mohn (Zeit. Phys. Chem., 1907, **60**, 422), arrived at the value 0.75 volt for the potential difference between a $N/10$ calomel electrode and a hydrogen electrode placed in an accurately neutral liquid. This would correspond to a voltage between 0.69 and 0.70 if a N calomel electrode had been employed. Our results thus lead to the conclusion that phenolphthalein begins to change color at a hydrion concentration of 10^{-7} normal. This value agrees with that given by Salessky (Zeit. Elektrochem, 1904, **10**, 204) but is greater than that of Friedenthal (*ibid.* p. 117) and Salm (Zeit. Phys. Chem., 1906, **57**, 471).

The potentiometer-box already referred to is employed for measuring the potential-difference between the calomel and the hydrogen electrode. The principle of the method of measurement consists in connecting the two ends, P and Q, of a sliding rheostat to the terminals of a dry cell, D, and balancing the potential-difference to be measured against the potential-differ-

ence between one end, P, and the slider, S, by means of a special form of enclosed capillary electrometer, E. The value of this potential-difference is read directly on a delicate voltmeter, V. The connections, which are found ready-made in the box, have been drawn out, whereas those to be made by the operator are shown by dotted lines. The steps to be taken by the latter consist first in taking off the capillary electrometer and manipulating it in such a manner that on returning it into position the capillary may be partly filled with a thread of mercury and partly with the acid. The terminals, X and Y, marked battery + and —,are connected to a dry cell, and the terminals, Z andU, marked cathode and auxiliary respectively, to the hydrogen and the calomel electrode. Very careful insulation of the connection between the terminal marked auxiliary and the calomel-electrode is necessary. The hydrogen is passed through the hydrogen electrode until a constant P. D. between it and the calomel electrode is obtained. This P. D. is measured by moving the slider up and down until no movement of the mercury in the capillary electrometer is observed on depressing the key K marked electrometer. In carrying out this operation care must be taken not to touch any bare terminals or wires with the hand, as false earth connections may otherwise be introduced. The key should be depressed long enough to allow the mercury to move; we have had occasion to observe that many operators have an exaggerated idea of the liability the instrument might show to become polarized. The initial P. D. is then read directly on the voltmeter on the scale ranging from 0 to 1.5 volt.[1] As already stated, this measures the original hydrion concentration of the liquid which there is reason to believe bears some relation to its swelling power. Alkali is then run in until, after equilibrium has been established, the voltmeter shows 0.69 volt, when the liquid is assumed to have been neutralized. When a hydrogen electrode is employed which has been saturated before the beginning of

[1] NOTE.—The potentiometer-box as used for purposes of electro-analysis contains in addition to the apparatus and terminals shown in the diagram, a terminal and a tapping key, both marked anode. When the latter is depressed the voltmeter reads directly the difference of potential between the terminals "anode" and "cathode" on a second scale ranging from 0 to 6 volts.

the experiment, a titration usually occupies about three minutes. The initial reading of the voltmeter during the titration of the tan-liquors which we have examined was usually found to be about 0.54 volt, which, according to equation (1), corresponds to the value;

$$x = \log \frac{1}{C} = \frac{1}{0.0575}(0.54 - 0.283) = 4.5.$$

Following the example of Sorensen (*loc. cit.*) we may call x the exponent of the hydrogen-ion concentration and may conveniently employ it to measure the smallness of the acidic action of our solution.

The readings of the voltmeter may be checked from time to time by means of a Clark or Weston cell connected to the terminals, cathode and auxiliary. If the volt-meter has been fitted in a hermetically sealed case, and mounted on rubber, there is little reason to apprehend that its readings will become untrustworthy. The instrument employed by us has been in use for about two years without showing any error.

The method was checked by first titrating a tan-liquor electrometrically with $N/10$ alkali and then adding known quantities of $N/10$ acetic, lactic, or butyric acid to the neutralized liquids and titrating again. The acids had been standardized previously against $N/10$ soda by means of phenolphthalein. The following are typical results (table 1).

TABLE I.

Acid : Acetic		Lactic		Butyric	
Cc. added	Cc. found	Cc. added	Cc. found	Cc. added	Cc. found
5	4.9	5	5.0	9.9	9.85
10	9.9, 10.0, 10.05	10	9.90, 9.95, 9.90	14.85	14.75
15	15.1	15	15.08, 15.05	..	..

Table 2 gives a comparison between the acidity of various liquids determined electrometrically on the one hand and by Procter's lime-water method on the other.

TABLE II.

Cc. N/10 Alkali Required to Neutralize 10 cc. of the Liquors.

No.	1	2	3	4	5	6	7
Electrometric	7.0	9.1	10.0	10.6	10.3	10.45	10.65
Lime-water	5.88	8.24	8.75	9.4	9.03	9.40	9.26

We hope shortly to be able to make definite proposals as to the

most suitable form of hydrogen electrode and to be in a position to discuss more fully the information which may be derived from the different potentiometer readings, more particularly in its bearing upon questions affecting the tanning of leather. We trust, however, that the preceding account may be of use to anyone wishing to employ the method in the meantime and may prove, that when carried out with the means at present at our disposal, the method is both simple in application and certain in its results.

A NEW METHOD OF ESTIMATING CHROMIUM.[1]

During the last decade chrome tannage has satisfactorily developed in England. This is due to the researches of Professor Procter, who, in the year 1897, published freely and without patent, or payment, a new method of producing single-bath chrome liquor by the reduction of bichromate with sugar or glucose, and in 1898 a second for the use of chrome alum. We have now about 10 different kinds of "one-bath" chrome liquor in the market, made on the same principles. For the sake of economy, as well as for the satisfactory tannage, analytical control of the various processes now in vogue is absolutely necessary. In one-bath chrome liquor what is usually required is the concentration and basicity of the solution, *i.e.*, the strength in chromium and the amount of the acid radical combined with it. Chromium in the liquor can be estimated in several ways, either by gravimetric or by the volumetric methods; but the former is elaborate and long, and is likely to tax the patience of the experimenters. Of the volumetric methods two are most commonly employed according to the nature of a liquor. These are the "peroxide method," using sodium peroxide as an oxidizing agent, and the "fusion method" whereby the dry residue of chrome liquor is oxidized with the fusion mixture, consisting of sodium carbonate and magnesium oxide in equal proportions. The "fusion method" is comparatively much slower and is more suited to the estimation of chromium in leather. The peroxide method is quicker, no doubt, but not without some difficulty. Sodium peroxide is dangerous and requires careful manipulation. When

[1] *The Leather Trades Review.*

the reagent is added to the liquor a large amount of oxygen is evolved, causing a brisk effervescence; so that, unless the beaker is quickly covered, there is always liability of a certain loss by spurting. Besides, special precaution and constant watching are necessary when the mixture is heated to destroy the excess of peroxide. The writer, in course of his investigations on "two-bath" chrome tannage, while oxidizing with alkaline bromine sodium tetra-thionate in a solution containing the sulphates and the chlorides of chromium (the products of the second bath) discovered the formation of yellow chromate. This led him to think of employing alkaline bromine instead of peroxide. After repeated experiments on one-bath chrome liquor he found the following method as satisfactory as any other, and at the same time free from much trouble:—

Prepare the reagent by addition of bromine water in slight excess in a saturated solution of caustic potash. A liter of this reagent is quite sufficient for 40 different experiments. A quantity of liquor to contain 0.3 to 0.5 gms. of chromium is measured into a rather large beaker and diluted (if necessary) to 100 cc. with distilled water. To this add solution of KOH, which is kept as a laboratory reagent, till the precipitate re-dissolves. Then 25 cc. of the reagent are added to it, and the beaker is placed on the steam-bath to warm. Ten to 15 minutes warming is enough for complete oxidation. Leave the beaker for another 15 minutes on the bath to drive off the excess of bromine, which is much facilitated by the addition of dilute HCl. If the used liquor is to be analyzed destroy the organic matter contained therein by boiling it with 5 cc. of strong HNO_3 before adding the reagents. Sufficient HCl is added to the chromate solution for the complete liberation of the bichromic acid, from which chromium is estimated in the usual way by means of $\frac{N}{10}Na_2S_2O_3$, and starch in presence of 10 per cent. solution of potassium iodide. The reactions may be represented by the following equations:—

$$Cr_2(SO4)_3 + 6KOH = 2Cr(OH)_3 + 3K_2SO4.$$
$$Cr(OH)_3 + 3KOH = Cr(OK)_3 + 3H_2O.$$
$$2Cr(OK)_3 + 4KOH + 3Br_2 = 2K_2CrO_4 + 6KBr + 3H_2O.$$

The results of four experiments along with those found by some standard methods, are given in the following table in terms of the quantity of $\frac{N}{10}Na_2S_2O_3$ required in each case.

For 25 cc. of the different solution	1	2	3	4
Using Na_2O_2.....	17.5 cc.	15.85 cc.	19.6 cc.	14.35 cc.
Using Alkaline Br ...	17.6 cc.	15.8 cc.	19.6 cc.	14.3 cc.

THE ECONOMIC POSSIBILITIES OF THE MANGROVE SWAMPS OF THE PHILIPPINES.[1]

By Raymond F. Bacon and Vicente Q. Gana.

In the United States, and in other countries where large amounts of leather are manufactured, the forests yielding native tanning materials have been so far exhausted that these nations must look to other countries for their source of supply. At the present time very large quantities of tan barks and cutch are imported into the United States from Borneo, Dutch East Africa, Brazil and other tropical countries, and the use of mangrove tanning materials is constantly increasing. The most abundant source of tanning substances in the Philippines is the mangrove swamps of the Islands. At the present time there is no mangrove bark exported from the Philippines, and as yet the area of these swamps is not known. They occur as narrow fringes along the coast or in considerable areas at the mouths of large rivers, especially at the head of bays. Some limited areas have been mapped and measured by the Forestry Bureau. These are as follows:

(1) Island of Mindoro, about 10,000 hectares, which will yield approximately 50,000 tons of bark.

(2) The east coast of the Zamboanga Peninsula, Mindanao, contains about 9,000 hectares of mangrove swamp; this will yield at least 90,000 tons of bark, found on a coast line about 45 miles in length. In the same region, on the other side of the Gulf of Subuguay, there are probably 9,000 hectares more which will also yield at least 10 tons per hectare. With the exception of a number of areas of 1,000 hectares or less, no fur-

[1] Condensed from the *Philippine Journal of Science*, Vol. IV, No. 3.

ther regions have been examined carefully. The above statement gives a very small proportion of the total area of the mangrove swamps. It is believed that the swamps of Mindanao alone will yield enough bark to furnish a continuous supply to a very large cutch factory.

The tan barks of Mindanao average from 23 to 25 per cent. of tannin, and these are the best that have thus far been examined from the Islands. Such bark could not be profitably shipped to the United States to compete with the East African barks carrying 50 per cent. of tannin. A careful analysis of conditions shows that the only method of handling the tan barks commercially is by means of an extract factory at the source of supply and it appears that such a factory could be operated very profitably with free trade between the Philippines and the United States

All the species of mangrove trees of the eastern tropics, which are used commercially for tanning purposes, are also found in the Philippines. These are:

Rhizophora mucronata Lam.
R. conjugata L.
Bruguiera gymnorhiza Lam.
B. eriopetala W. & A.
B. parviflora W. & A.
B. caryophylloides Blume.
Ceriops tagal (*Perr.*) C. B. Robinson.

There are three large cutch factories in Borneo using tan barks from the same species of mangrove as those found in the Philippines.

Tables of analyses made on mangrove tan barks are given below. It will be noted that the barks from Mindanao run very much higher in tannin than those from Mindoro, and it has often been observed that, as the equator is approached, the tannin percentage increases. The analyses below were made by the methods of the International Leather Chemists Association, using the American "shake modification." As our machine does not give very violent shaking and as we have used unchromed hide powder, it is possible that our results may be as much as 2 per cent. low. We are now taking measures to standardize our

analyses with those made by a recognized leather chemist and in a subsequent communication will report several hundred analyses of mangrove tan barks from the southern islands, so that perfectly reliable data will be at hand for possible investors in this field.

TABLE I.—ANALYSIS OF BARKS FROM PORT BANGA, ZAMBOANGA.

Forestry Bureau No.	Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bark			
					Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
9,356	2,056	Tabique	*Xylocarpus obovatus* A. Juss	14.9	69.7	30.3	8.6	21.7
9,357	2,057	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.4	65.2	34.8	11.6	23.2
9,358	2,058	Bacauan	*Rhizophora mucronata* Lam	14.4	61.7	38.3	12.4	25.9
9,359	2,059	Pototan	*Bruguiera parviflora* W. & A.	13.9	84.1	15.9	7.1	8.8
9,360	2,060	Pototan	*Bruguiera gymnorrhiza* Lam	16.1	63.0	36.96	9.8	27.2
..	..	Tabique	*Xylocarpus obovatus* A. Juss	14.2	67.6	32.4	7.7	24.7

These barks were collected on Jan. 1908 by Dr. H. R. Whitford and W. I. Hutchinson from Port Banga, Zamboanga. They are rather large quills with thick, harsh, dirty brown scales on the outer surface. Tabique gave a very dark, red infusion; tangal a somewhat light red infusion; bacauan gave an intense red infusion. Pototan (*Bruguiera parviflora*) is a fibrous bark difficult to grind; it gave a red infusion. Pototan (*Bruguiera gymnorrhiza*) gave the same grind; it gave a red infusion. Pototan (*Bruguiera gymnorrhiza*) gave the same colored infusion as the previous one.

The barks were collected by Mr. M. L. Merritt in Mindoro in March, 1908. Bacauan bark is brittle and is very easily ground. It has a dirty brown scale of variable thickness which is very easily removed from the true or inner bark.

Analyses were made on both entire and inner bark of each variety. In every case inner bark showed a higher percentage of tannin than when entire bark was assayed.

TABLE II.—Analysis of Barks from Mindoro.

Forestry Bureau No.	Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bath: Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
9,779	1,911	Bacauan	*Rhizophora conjugata* L.	13.2	67.4	32.6	12.0	20.6
9,780	1,912	Bacauan	*Rhizophora conjugata* L.	14.4	66.6	33.4	10.7	22.7
9,781	1,913	Hangalay	*Bruguiera parviflora* W. & A.	14.0	77.4	22.4	9.6	12.8
9,782	1,914	Pototan	*Bruguiera gymnorrhiza* Lam	13.9	60.2	39.8	11.6	28.2
[1]9,783	1,915	Bacauan	*Rhizophora mucronata* Lam	13.2	64.3	35.7	14.1	21.6
9,795	1,921	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	11.8	69.1	30.9	9.7	21.2
9,816	1,922	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.3	72.5	27.5	10.5	17.0
9,851	1,984	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	12.7	71.5	28.5	8.0	20.5
[1]9,780	1,912	Bacauan	*Rhizophora conjugata* L.	13.5	64.8	35.2	10.8	24.4
..	1,912½	Bacauan	*Rhizophora conjugata* L.	14.1	67.1	32.9	10.0	22.9
..	[1]1,913½	Hangalay	*Bruguiera parviflora* W. & A.	14.8	75.5	24.5	9.6	14.9
..	1,913¾	Hangalay	*Bruguiera parviflora* W. & A.	12.9	82.1	17.9	8.3	9.6
..	1,914½	Pototan	*Bruguiera gymnorrhiza* Lam	13.9	63.4	36.6	12.6	24.0
..	[1]1,915½	Bacauan	*Rhizophora mucronata* Lam	13.4	67.1	32.9	15.1	17.8

Bacauan numbered 1,912 contained approximately 10 per cent. outer scale.

Bacauan infusions were red, but varied in intensity.

The Hangalay barks are reddish-brown in color with rough, dark brown scales.

The inner bark of Hangalay is fibrous and the ground bark was very irritating to the mucous membranes of the nose and throat when inhaled. They also gave red infusions.

[1] Analysis of inner bark.

Barks of Pototan and Tangal also possess rough, brownish scales.

The infusions were somewhat lighter than those of Bacauan.

TABLE III.—ANALYSIS OF BARKS FROM PORT BANGA, ZAMBOANGA.

Field No.	Common name	Scientific name	Moisture (per cent.)	In parts per 100 of water-free bark: Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
11,534	Bacauan	*Rhizophora conjugata* Lam	13.4	68.7	31.3	13.3	18.0
11,535	Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	11.9	58.6	41.4	19.1	22.3
11,536	Pototan	*Bruguiera gymnorrhiza* Lam	13.5	62.0	38.0	13.5	24.5
11,537	Lañgaray	*Bruguiera parviflora* W.& A.	13.8	80.4	19.6	8.0	11.6

This table shows results of analysis made on another lot of barks from Port Banga, Zamboanga, collected by H. N. Whitford on December, 1908.

TABLE IV.—ANALYSIS OF MANGROVE BARKS FROM SARAWAK, BORNEO.

Common name	Scientific name	Moisture (per cent)	Insolubility (per cent.)	Total extract (per cent.)	Non-tannin (per cent.)	Tannin (per cent.)
Gayong	*Rhizophora mucronata* Lam	14.4	70.1	29.9	9.4	20.5
Bakô	*Rhizophora conjugata* Lam	14.7	58.3	41.7	9.6	32.0
Putut	*Bruguiera gymnorrhiza* Lam	15.5	64.3	35.7	9.0	26.7
Tumu	*Bruguiera eriopetala* W. & A.	16.1	64.0	36.0	8.8	27.2
Tangal	*Ceriops tagal* (Perr.) C. B. Robinson	13.8	63.8	36.2	6.9	29.3

Analysis was made of some samples of mangrove bark brought from Sarawak, Borneo by Dr. Foxworthy of the botanical division of this Bureau. These barks are used by cutch factories and among the species in Borneo probably yield the highest amount of tannin.

ABSTRACTS.

Enzymatic Studies.[1] S. P. L. SORENSEN. *Comptes rendus des Travaux du Laboratoire de Carlsberg,* Vol. 8, No. 1.—1. *Acidity: Concentration of hydrogen ions.*—The rate at which molecules are split up in enzymatic reactions depends, among other things, on the acidity or alka-

[1] The paper of which this abstract embraces somewhat less than one-third, is that referred to in Procter and Jones' paper in the Feb. JOURNAL, and in Law and Sand's in the present number. The rest of the paper will appear in subsequent numbers.

linity of the medium in which the change is going on. The degree of acidity or alkalinity in such cases is commonly calculated and reported on the basis of the total amount of base or acid added in titrating, no account being taken of the degree of dissociation of the acid or base employed, nor of the power of the solution in question to fix acids or bases.

Present-day ideas on the nature of solutions, based on the theory of electrolytic dissociation put forth by Arrhenius, ought to find application in this case. For example, when pepsic digestion takes place in N/10 hydrochloric acid, the dissociation of the HCl being incomplete, the "real" acidity, rationally called the concentration of the hydrogen ions or hydrion concentration, is a little less than the stated normality, (0.1). It is necessary, further, to take account of the salts, phosphates or others, which the solution may contain, and which may react with the hydrochloric acid, as well as other substances capable of influencing the concentration of the hydrogen ions. In the case of certain proteids which are being split up by enzymes, a part of the acid is fixed by the substance itself. Suppose two solutions one of which contains 1 gram of proteid in 100 cc. N/10 HCl and the other 5 grams of the same proteid in the same quantity of N/10 HCl. It is evident that if the proteid is one which combines with HCl, the quantity of really free acid is less in the solution containing the more proteid, although in the ordinary mode of statement both have the same acidity, since both will take the same number of cc. when titrated with N/10 NaOH. The hydrion concentration of the two solutions may be very different.

What has been said in the case of pepsic digestion in regard to degree of acidity and hydrion concentration applies to all enzymatic reactions. Pepsic digestion is chosen as a characteristic example because this reaction works better in the presence of so strong a concentration of hydrogen ions and because it is easier to observe its details, which are besides pretty well known in their main features.

Similar modes of observation may be used in the case of those enzymatic reactions which take place best in a medium which is only feebly acid, or is neutral or alkaline.

2. *Magnitude of the concentration of hydrogen ions. Index of hydrion concentration.*—Designating by C_H^+, C_{OH}^- and C_{H_2O} the concentration respectively of hydrogen ions, of hydroxyl ions and of water in an aqueous solution, we shall have by the law of mass action $\frac{C_H^+ \times C_{OH}^-}{C_{H_2O}} =$ a constant. Since in a dilute solution C_{H_2O} may be considered invariable, it follows that $C_H^+ \times C_{OH}^- =$ a constant. This constant is called the dissociation constant of water. Its commonly accepted value at 18° C. is 0.64×10^{-14}. A series of experiments made in the Carlsberg laboratory gave as a mean value 0.72×10^{-14}, or, to state

it differently, $10^{-14.14}$. It is easily seen that this quantity permits the calculation of the hydrion concentration of an aqueous solution when the concentration of hydroxyl ions in it is known, and vice versa. A solution which has been found to be N/100 with respect to hydrogen ions is said to have a hydrion concentration of 10^{-2}, and a solution which is N/100 with respect to hydroxyl ions will have a hydrion concentration of $10^{-12.14}$, since $10^{-2} \times 10^{-12.14} = 10^{-14.14}$. By this notation, water perfectly pure, and solutions perfectly neutral, having equal numbers of hydrogen and hydroxyl ions, show a hydrion concentration of $10^{-7.07}$, ($10^{-7.07} \times 10^{-7.07} = 10^{-14.14}$). Thus the degree of concentration of the hydrogen ions is expressed as the normality of the solution in terms of hydrogen ions, a factor which is stated in the form of a negative power of 10. The numerical value of the exponent is designated by p_H^+ and is called the index, or exponent of hydrogen ions. In the examples cited above, p_H^+ has the respective values, 2, 12, 14 and 7.07.

3. *Influence of hydrion concentration compared with that of temperature*: *Curves of hydrion concentration.*—In enzymatic reactions, hydrion concentration plays a part quite analogous to that of temperature. The "curve of temperature" of an enzyme is generally understood to mean the curve obtained by taking for ordinates the quantities of matter split up in a unit of time, and for abscissas the temperatures at which the experiments have been carried out. Such a curve shows that for each enzyme there is a definite temperature, the optimum temperature, at which the splitting up takes place most rapidly.

In the neighborhood of the optimum temperature, in what may be called the optimum zone of temperature, division takes place at a speed almost equal to that observed at the optimum temperature itself. On both sides of this zone, the speed falls off, commonly most rapidly on the side toward increasing temperatures, so that if the temperature be high enough or low enough, the substance suffers very little splitting up. The sharp fall of the curve as the temperature rises above the optimum zone indicates that under these conditions the enzyme is destroyed. Thus the curve of temperatures ought to be considered as the difference of two curves, that is to say, between the "real curve of temperature," which rises as the temperature rises, and the curve of destruction of the enzyme. The latter shows very small[1] ordinates at low temperatures, as far as the optimum, and then rapidly rises with in-

[1] Such a comparison is not possible unless we adopt the same unit for the ordinates of both curves. The ordinates of the curve of destruction of the enzyme should show the difference between the quantity of matter which would be split up if the enzyme experienced no destruction, and the quantity which actually suffered molecular division under the conditions of the experiment.

crease of temperature, quickly becoming almost parallel to the axis of ordinates.[1]

The curve of hydrogen ions of an enzyme has for ordinates the quantities of matter split up in unit time under the given experimental conditions, and for abscissas, the exponents of hydrogen ions of the liquors experimented upon.

Experiments have begun in the Carlsberg laboratory, in the attempt to determine whether the analogy which exists between the influence of temperature and that of hydrion concentration goes further, so that, for example, the drop of the two branches of the curve may be due to a milder action of the enzyme with the ionic concentrations corresponding to that branch, while the descent of the other branch is owing to an increasing destruction of the enzyme with ionic concentrations corresponding to this latter branch; or whether as is possible, the descent of both branches of the curve may be attributed to the latter cause.

In studying enzymatic reactions, it is quite as important to know the hydrion concentration with which one works, as to be aware of the other agents,—temperature for instance—which exercise an influence on the speed of the reaction.

Before explaining the methods used in measuring hydrion concentrations, the author explains why he has used in constructing the curves the exponent of the hydrion concentration, and not the hydrion concentration itself. In all enzymatic splitting up of substances, the single exception being pepsic digestion, the actual content in hydrogen ions is extremely small. For example, in the breaking up of cane-sugar by the agency of invertase an action which proceeds best in a slightly acid medium, the ionic concentration being that most favorable to the reaction, the total content of hydrogen ions in 100 cc. of the solution is less than in a single drop of N/10 HCl. In other words, if to a solution of pure cane-sugar be added invertase, freed[2] as far as possible by dialysis or other means from substances capable of fixing acids or bases, the addition of a single drop of N/10 caustic soda to 100 cc. of the solution immediately changes its character. Having been slightly acid, it becomes feebly alkaline, and the inversion entirely ceases.

For all enzymatic reactions thus far examined, the modifications of the speed with which the reaction proceeds depend, not on the absolute magnitude, but on the relative magnitude of the ionic concentration. It follows that in studies of this kind it is not convenient to calculate

[1] See for example, Th. Madsen and S. Walbum: Recherches sur l'affaiblissement de la présure (*Festskrift Tillgnad Olof Hammarsten* 1906, Afh. No. 10), and L. W. Famulener and Thorvald Madsen: Die Abschwächung der Antigene durch Erwärmung, (Bioch., *Zeitschrift*, 11, 186 (1908).

[2] It is impossible to prepare a solution of invertase completely free from substances which fix acids or bases, but on the other hand, it is not difficult to obtain an enzymatic solution sufficiently pure for the presence of minute quantities of alkali, (such, for instance, as those furnished by glass,) to make themselves distinctly felt.

with the absolute values of the hydrion concentration, but with their logarithms, that is to say, with the before mentioned "indices of the ions." Expressed in this manner, a change in ionic concentration from 10^{-5} to 10^{-4} signifies a change equal to that produced by a modification from 10^{-2} to 10^{-1}. Also, by this method it is possible to represent graphically the influence of hydrion concentration, that is to say, by means of curves of concentration of the hydrogen ions. This would hardly be possible if the unit of abscissas were any absolute quantity of hydrogen ions, for example that corresponding to an ionic concentration of 10^{-7}. In this case, solutions having concentrations of 10^{-6} and 10^{-5} on the one hand and 10^{-8} and 10^{-9} on the other would be represented by abscissas of 10 and 100 for the first two, and 0.1 and 0.01 for the last two; and if graphic representation should embrace a still greater range of ionic concentration, the difficulties would be insurmountable.

The question arises whether these considerations of convenience correspond to a real cause: that is to say, whether the hydrion concentration enters, not with its absolute value, but with the logarithm of this value, into the equation which expresses the relation which exists between the speed of the reaction and the ionic concentration of the medium. To answer this question would necessitate a much larger number of experiments than have thus far been made.

4. *Methods of determining hydrion concentration.*—Solutions of the kind concerned in enzymatic splitting contain almost always a more or less important proportion of incompletely dissociated bodies, such as feeble acids or feeble bases, and of substances liable to be hydrolyzed, such as phosphates, or compounds which have been formed by proteids or the products of their splitting up, uniting with acids or bases. All these things are concerned in determining the content of hydrogen ions and of hydroxyl ions in the solution, and the product of these last two contents ought to be constant. If the equilibrium is disturbed, say by the introduction of a small quantity of a base, and therefore of hydroxyl ions, the re-establishment of equilibrium in the solution demands the disappearance of a certain number of hydroxyl ions. This is what takes place when, for example, the hydrolysis of the salts of feeble acids present is checked, or when the hydroxyl and hydrogen ions unite to form water, which, in its turn, results in a new formation of hydrogen ions (either by the further dissociation of weak acids, or further hydrolysis of the salts of weak bases). It is clear therefore that the addition of bases or acids to such a solution not only causes the neutralization of an equivalent portion of acid or base, but brings about at the same time phenomena of dissociation and hydrolysis, the extent of which depends on the nature and quantity of the substances which enter into play, but whose quantitative results ordinarily entirely escape estimate.

Suppose one has to do with a solution of a proteid substance in hydrochloric pepsin. In titrating by means of an appropriate indicator,

one may estimate the proportion of acid in the solution beyond the quantity necessary to give to the mixture the hydrion concentration corresponding to the turning point of the indicator. Nevertheless, the result of the titration does not permit us to draw any conclusion in regard to the hydrion concentration of the solution titrated, for only a part of the acid titrated was in the free state; the rest has been separated little by little in the course of the titration.

The hydrion concentration ought not to be measured by any method which involves in the course of the operation a modification of that concentration, which is the case with many methods based on volumetric estimation of acidity or alkalinity.

H. Dreser[1] has pointed out a method for the estimation of free hydrochloric acid in the gastric juice which is affected by the sources of error mentioned above. After treatment of the gastric juice with solid oxalate or chromate of barium, he estimates the quantity of barium entering into solution. At the same time he determines the quantity of barium which dissolves under the same conditions when the gastric juice is replaced by hydrochloric acid diluted to so high a degree that titrated with Congo red it shows the same content of "free" hydrochloric acid as the gastric juice. From the mean of the quantities of barium found, Dreser calculates the "avidity" of the gastric juice. He himself remarks that the usual volumetric methods should not be used in the determination of hydrion concentration, not perceiving that the method which he recommends permits similar sources of error, since pure dilute hydrochloric acid is not in every respect comparable to the gastric juice. The latter contains a certain proportion of fixed hydrochloric acid, depending among other things upon the quantity of nitrogenous bodies present in the juice, and this acid may be partially liberated by shaking with the insoluble barium salt. Also, determinations made with the same liquid by means of oxalate and chromate of barium have given divergent values for the "avidity."

Another group of methods, also somewhat numerous, takes advantage of the catalytic power which the solution presents in reactions the speed of which is proportional to the concentration of hydrogen or hydroxyl ions in the medium.

The oldest of these methods is that based on the inversion of cane-sugar. This method is based on the researches of W. Ostwald,[2] and was worked out at his suggestion by F. Albin Hoffman.[3] As is well known, treatment with acids causes cane-sugar to undergo inversion, the speed of which in the case of acids sufficiently dilute, has more recently been discovered by W. Palmaer[4] to be proportional to the hydrion concentration. If now we compare the speed with which a

[1] *Beitr. zur Chem. Physiol. und Pathol.*, **8**, 285 (1906).
[2] *Journ. f. prakt. Chemie*, N. F. **29**, 385 (1884).
[3] *Centralbl. f. klin. Medicin*. **10**, 793 (1889).
[4] *Zeitschr. physik. Chemie*, **22**, 492 (1897).

solution of cane-sugar undergoes inversion when treated with the solution to be examined, with the speed of inversion of the same sugar solution when it has been treated with a solution of hydrochloric acid of a suitable degree of dilution (whose hydrion concentration may be easily calculated), we may compute the hydrion concentration of the solution in question by a simple proportion, since the speeds of inversion are proportional to the hydrion concentrations. Since the solution examined (*e.g.* a sample of gastric juice) may sometimes contain inversive enzymes, or optically active bodies whose rotation may be modified by heat, it is necessary to take account of these possible secondary reactions by means of suitable control experiments.

Shortly afterward, F. A. Hoffman published another similar method, also based on the researches of W. Ostwald.[1] Methyl acetate, when introduced into aqueous solution, splits up into acetic acid and methyl alcohol. This reaction is accelerated by catalysis on the addition of acid, and here again the speed of saponification is proportional to the hydrion concentration. The presence of hydroxyl ions also tends to increase the speed of decomposition of ethereal salts. In the same manner by measuring the saponifying action exerted by similar solutions of ethyl acetate. J. Shields[2] has estimated the content of hydroxyl ions in the solutions of salts of feeble acids.

Another method of the same kind is that pointed out by K. Koelichen[3] for measuring the concentration of hydroxyl ions. This author has shown that the transformation of diacetonyl alcohol into acetone:

$$CH_3.CO.CH_2C(OH)(CH_3)_2 = 2CH_3.CO.CH_3$$

takes place spontaneously and with a considerable increase of volume, so that it may be measured by the amount of expansion. The splitting up is favored by the presence of hydroxyl ions, and the speeds are proportional to the concentration of these ions.

Finally, G. Bredig and W. Fraenkel[4] have recently worked out a beautiful method for the determination of hydrion concentration by using as the basis of their process the splitting up, described by Th. Curtius,[5] of diazoacetic ether in the presence of a dilute acid, with the evolution of free nitrogen:

$$N_2.CH.COOC_2H_5 + H_2O = N_2 + CH_2OH.COOC_2H_5.$$

The quantity of nitrogen released is easily measured, and the reac-

[1] W. Ostwald, *Journ. f prakt. Chemie*, N. F. **28**, 449 (1883). J. Walker, *Zeitschr. physik. Chemie*, **4**, 322 (1899); F. A. Hoffman, Verh. des X intern. medic. Congresses, Berlin, 1890, Abth. V. p. 201.

[2] *Zeitschr. physik. Chemie*, **12**, 167 (1893).

[3] *Ibid.*, **33**, 129 (1900); compare also W. Will and G. Bredig: Umwandlung von Hyoscyamin in Atropin durch Basen. Ber. der deutschen chem. Ges. **21**, 2777 (1888).

[4] *Zeitschr. f. Electrochemie*, **11**, 525 (1905); *Zeitschr. physik. Chemie*, **60**, 202 (1907); compare also Bror. Holmberg, *Ibid.*, **62**, 726 (1908).

[5] *Jour. f. prakt. Chemie*, N. F., **38**, 396 (1888).

tion is purely monomolecular. The speed of the reaction is proportional to the hydrion concentration and the catalytic action is considerable, so that quite feeble concentrations can be measured.

In the case of the methyl acetate method, the increase of hydrion concentration due to the acetic acid formed in the reaction is of very little importance, since that acid dissociates but little. The methods which have been described are not on the whole very satisfactory, because they do not work well except in the case of relatively strong concentrations, which practically limits them to a single case of enzymatic reaction, that of pepsic digestion.

The measurement of hydrion concentration ought to be made at a temperature as near as possible to that which it is proposed to employ in the enzymatic reaction itself which is to be investigated.

In the application of any of these methods, as for example the inversion of cane-sugar by acetate of methyl or diacetonyl alcohol, it is necessary to take account of what is conveniently called "the effect of neutral salts,"[1] as well as of the fact not less important that even if the method is applied easily to solutions of simple composition, it may sometimes be entirely inapplicable in the case of highly complex mixtures such as are generally involved in enzymatic reactions. G. Bredig and P. F. Ripley[2] have shown that the diazoacetic ether method fails if the medium contains even the slightest trace of chlorine or SO_4 ions, for in this case accessory reactions occur at the same time that the hydrion concentration undergoes a modification. For example,

$$N_2CH.COOC_2H_5 + HCl = N_2 + CH_2Cl.COOC_2H_5.$$

In attempting to determine the content of hydroxyl ions in the blood by the diacetonyl alcohol method described by Koelichen, Taav. Laitinen[3] has obtained a value whose order of magnitude is quite different from that ordinarily found.

The second group of methods are not of general application, and if one of them should be employed in a particular case, it should be rigorously checked.

Two other methods are known by which the concentration of hydrogen or hydroxyl ions in a solution may be determined. These are the measurement by means of the gas electrode and the method of indicators, called also respectively, the electrometric and colorimetric methods.

These are the two methods which have been used in the enzymatic researches at the Carlsberg laboratory. They supplement each other. The electrometric is the more exact, but is much more complicated, while the colorimetric method, although less precise, is very simple in execution. The author has recognized the need of a simple method of

[1] Arrhenius, *Zeitschr. physik. Chemie*, 1, 110 (1887); 4, 237 (1889); 31, 197.

[2] *Berichte d. d. chem. Ges.*, 40, 4015 (1907); see also W. Fraenkel: *Zeitschr. physik. Chemie*, 60, 202 (1907).

[3] *Festskrift tillegnad Olof Hammarsten*, 1906, Afh. Nò. IX.

determining hydrion concentration, and has made extensive researches in regard to the applicability of various indicators. The electrometric method has also been employed, and a comparison of the two has been made.

Electrometric Method.—When a platinum plate covered with platinum black is placed in an aqueous solution acid, neutral, or alkaline, and when this plate is saturated with hydrogen, there will be a difference of potential between the solution and the immersed platinum, the magnitude of the difference depending on the hydrion concentration of the solution. The hydrion concentration may therefore be determined by measuring this difference of potential.[1]

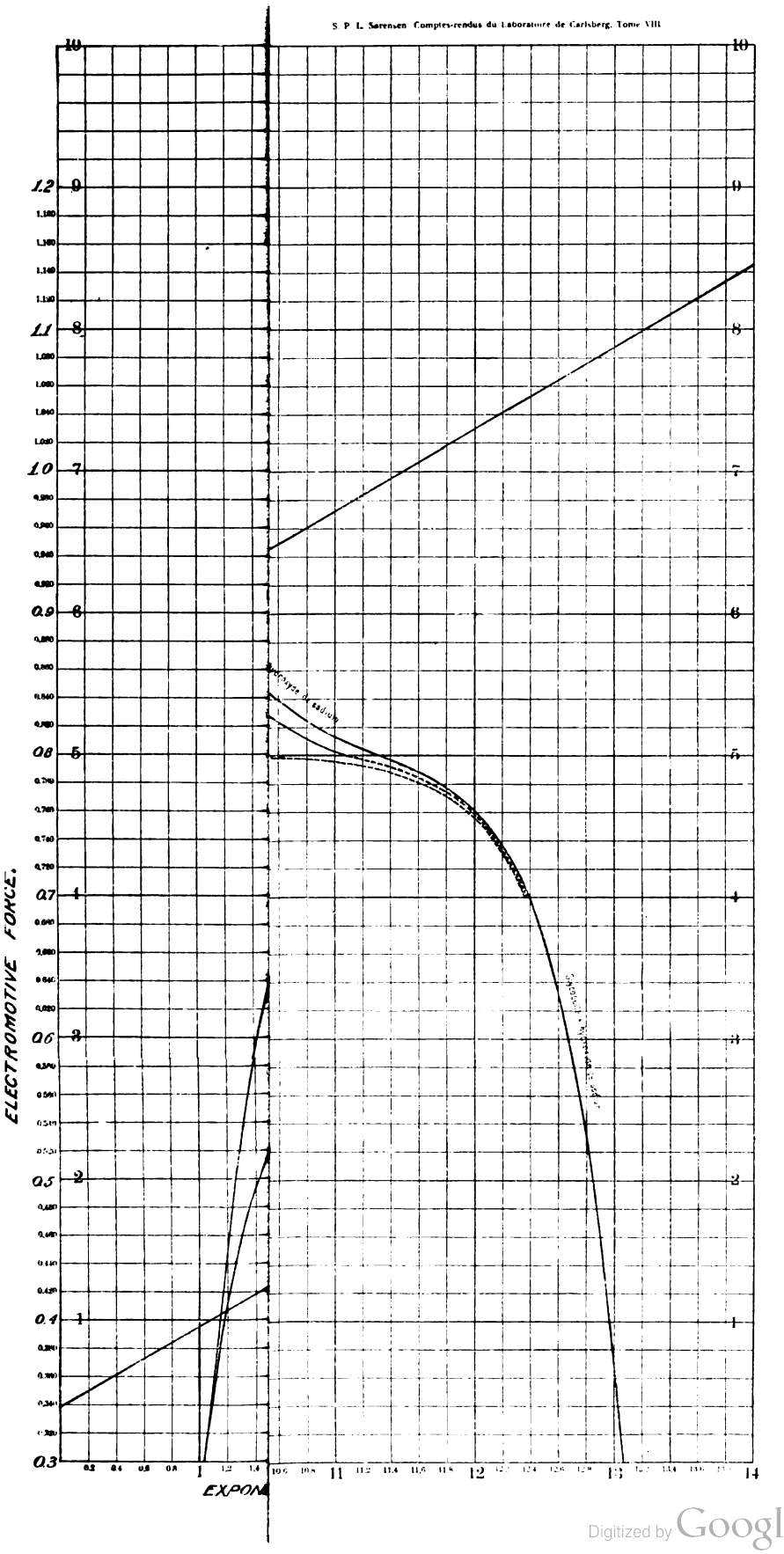
Colorimetric Method.—The end point of a titration shows that the hydrion concentration of the solution tested has or has not reached, or has even passed, a certain intensity, different for the different indicators, and which shows the ionic concentration at the turning point of the indicator considered. Thus by the color which a solution takes when an indicator is added, one can decide whether this solution has a hydrion concentration higher or lower than that which corresponds to the turning point of the indicator.

It is this simple principle which forms the basis of the method of indicators, or the colorimetric method. The principle has been known a long time, but it was not until the remarkable researches of Friedenthal and Salm[2] that the scattered materials were examined and in part completed, so that they have established a complete series of indicators presenting turning points at the most diverse hydrion concentrations. It is therefore to these two scientists that the honor is due for working out the first colorimetric method for the determination of hydrion concentration. Their results, however, are not applicable to enzymatic research without additional investigation, since a method which works with comparatively simple substances may fail when tried with the very complex substances which so often take part in enzymatic reactions. It is necessary to investigate the applicability of each indicator to the case of each solution. A hundred different indicators have thus been examined, the work covering a period of several years. Publication was long postponed in order to test the value of the method.

If something more than a purely qualitative appreciation is needed it will be possible to judge of the intensity on the shade of a color only by comparing it with similar intensities or shades. The task which first presented itself was to prepare solutions suitable to serve as standards, which mixed together in convenient proportions, permit

[1] W. Nernst, *Zeitschr. physik. Chemie*, 4, 129 (1889).

[2] H. Friedenthal, *Zeitschrift für Electrochemie*, 10, 113 (1904: Ed. Salm, *Ibid.*, 10, 341 (1904); 12, 99 (1906); Ed. Salm and H. Friedenthal, *Ibid.*, 13, 125 (1907); Ed. Salm, *Zeitschr. physik. Chemie*, 57, 471 (1906), 63, 83 (1908); compare also W. Salesky, *Zeitschr. f. Electrochemie*, 10, 204, (1904), and Bruno Fels, *Ibid.*, 10, 208 (1904).



one to obtain liquors for comparison possessing hydrion concentrations established exactly in advance in each particular case. It was necessary that these standard solutions should be easy to prepare, and moreover, that they should present a constitution such that the liquors of comparison obtained from them should always have (practically speaking) the same hydrion concentration, even if the standard solutions had stood months at a time, for example in a glass flask of alkaline reaction. In this process were used a number of simple substances guaranteed pure, furnished by C. A. F. Kahlbaum, in Berlin. After dissolving them in boiled water, they are preserved in Woulff bottles provided with a burette and the usual arrangement which allows the liquor to be taken out without admitting carbonic acid from the air. By mixing these liquids in convenient proportions, liquors of comparison may be procured possessing a hydrion concentration of from about 10^{-1} to 10^{-13}.

Next comes the question of which indicators are most suitable, which presents much greater difficulties. Most indicators in fact are apt to combine with natural proteid substances, and there are some which unite even with the products of more or less advanced decomposition of proteids. As a result, even if the combinations are not always indicated by a visible deposit, the indicator does not change color at all in most cases and hence becomes useless. This is the reason, as has been said, that it was necessary to prove the excellence of each particular indicator, and to determine the degree of precision which it will give.

For this it was necessary to prepare a large number of different mixtures, principally of proteid substances and of their products of decomposition. The real hydrion concentration of these mixtures had been determined by an electrometric measure which thus served as a fundamental method. There are some indicators (*e. g., p.* nitrophenol and phenolphthalein) which possess a very extensive usefulness, while there are also some which are found entirely useless after the products of the splitting of proteids even rather well demolished come into play. Congo red, used so much in physiology, comes under the latter category.

We have already noted above that in enzymatic reactions where neither the material nor its products of decomposition are capable of fixing acids on bases (*e. g.* in the inversion of cane-sugar by invertase) it may often be difficult to keep the hydrion concentration constant because the alkaline ingredients coming from the glass, or in other cases the carbonic acid of the air may exercise a marked influence. In this case it is suitable to fix the amount of ionic concentration by adding a buffer ("tampon"). We mean by this a suitable mixture of salts which have no appreciable influence on the speed of the enzymatic reaction, but which keep the hydrion concentration constant in the course of the experiment. In order to do this it is necessary that the buffer be so constituted that a contribu-

tion of small portions of acid or base cannot sensibly influence the hydrion concentration. Nature herself makes use of such buffers consisting ordinarily of a mixture of phosphates sometimes also of a mixture of carbonates or even of proteids and their products of decomposition. The mixtures of standard solutions mentioned above and used in the colorimetric method, make good buffers.

As has been indicated above, there is no doubt that the question of hydrion concentration extends beyond the limits of enzymology, properly speaking. The amount of ionic concentration is certainly an element which must be reckoned with all the processes of biology.

Granting that in this study it may often be important to keep the experimental conditions including the hydrion concentration as constant as possible, it will not be difficult to cite cases where the addition of an appropriate buffer might be very useful. The liquors used as nourishing mediums for microörganisms are an example. The growth of the organisms often causes a modification of the hydrion concentration of the medium, unless the latter contains a sufficient quantity of substances capable of fixing acids or bases, that is, a suitable buffer.

A. *Electrometric Measurements.—a.* Methods of measurement. For all the measurements of this kind a similar experimental arrangement was used. The cell whose electromotive force was measured consisted of one calomel electrode plunged in a N/10 solution of chloride of potassium and one hydrogen electrode (a platinum plate coated with platinum black) immersed in the solution to be examined which served as an electrolytic liquor. The potential of diffusion between the two solutions was eliminated by the method indicated by N. Bjerrum[1] to wit, the interposition between the two electrolytic solutions of either a 3.5 normal solution of chloride of potash or a 1.75 normal solution of the same salt after which the correction was made by the addition of the difference between the two potentials found.

R. Abegg and A. C. Cumming[2] have proposed to replace the chloride of potassium by ammonium nitrate, whose ions have likewise practically the same speed of displacement, but whose solubility in water is much greater than that of chloride of potash. Without doubt a strong solution of ammonium nitrate could ordinarily be used for the examination of acid liquors, and it would allow the potential of diffusion to be completely eliminated, and thus avoid the correction which is in any case more or less uncertain. The nitrate, however, cannot be used with alkaline liquids, and the Bjerrum process has the advantage of being applicable to either acid or alkaline liquids.

The apparatus used was of exactly the same kind as that described in the work of N. Bjerrum quoted above. In general the operative process indicated by N. Bjerrum was followed.

Coated platinum as well as calomel electrodes were prepared exactly in the manner indicated in the "Physiko-chemische Messungen" by

[1] *Zeitschr. physik. Chemie*, 53, 428 (1905).

[2] *Zeitschr. für Electrochemie*, 13, 17 (1907).

Ostwald-Luther (1902). The measurements were taken according to the compensation method of Poggendorff, by the aid of a Lippmann electrometer furnished with an oval capillary, and large enough to be used to zero. The measuring wire which was a meter long and was divided into millimeters, was carefully corrected by means of measurements made in the physical laboratory of the Carlsberg polytechnical school by Mr. Thorkelsson and Mr. Hansen. The normal element used was a Weston cell whose electromotive force at 18° C. was 1.0191 volts.

The hydrogen used was prepared from a 10 per cent. solution of potash by the aid of iron electrodes. After having washed the hydrogen first twice with an alkaline solution of pyrogallol, then in pure water, it was passed through a cylindrical glass containing pure cotton, from whence it was introduced into the vessel enclosing the electrode, after having been washed with a little of the solution to be examined.

The measurements were made in a room whose temperature was kept as nearly as possible at 18° C., the normal temperature of all the experiments (it rarely deviated half a degree). The barometric reading underwent great changes (from 722 to 794 mm.) during the long space of time which these experiments lasted, and consequently all the measurements have been reduced to a pressure of 760 mm.

b. Determination of π_o.

Let us designate by π_p the electromotive force of a cell composed of one calomel electrode plunged in a N/10 solution of chloride of potassium and an electrode of hydrogenized platinum placed in an electrolytic liquor whose hydrion concentration expressed with a normal hydrion solution as unity is C_p ($= 10^{-p}$). If then we designate by π_q and C_q ($= 10^{-q}$) the corresponding quantities of a similar cell, we shall have

$$\pi_p - \pi_q = K \log \frac{C_q}{C_p}. \qquad (I)$$

where K may be supposed, with a sufficient approximation, equal to $0.0577 + 0.0002\ (t° - 18°)$.[2]

If by experiment, we determine π_p for an electrolytic liquid, say hydrochloric acid conveniently dilute, whose hydrion concentration C_p may be calculated by means of the normality of the acid (A_p) and its degree of dissociation (α); and if in equation (I) above, the values of π_p and C_p are substituted, this equation will contain no other unknowns but π_q and C_q, so that π_q may be calculated for some value of C_q and *vice versa*. In designating by π_o the electromotive force of a cell of the kind used here, and where

[1] W. Ostwald, Lehrbuch der Allgemeinen Chemie, Zweite Aufl. Band 2, Teil 1, p. 895 (1893); F. I. Small, *Zeitschr. physik. Chemie*, 14, 582 (1894).

[2] W. Nernst, *Zeitschr. physik. Chemie.*, 4, 129 (1889); *Zeitschr. f. Elektrochemie*, 10, 630 (1904).

the electrolytic liquid surrounding the hydrogen electrode is normal with respect to the hydrogen ions ($C_o\ 10^{-o} = 1$) we shall have

$$\pi_o = \pi_p - 0.0577 \log \frac{C_o}{C_p} = \pi_p - 0.0577 \log \frac{1}{C_p}. \qquad (II)$$

In table 1 which follows are collected a considerable number of measurements made by means of hydrochloric acid of different concentrations, for the purpose of determining the value of π_o.

The first column of the table represents the composition of the solutions examined, while the concentration of the hydrochloric acid varies greatly (from N/10 to N/200) the concentration of the total chlorine is kept constant, viz., equal to N/10 with the exception of one experiment. Following Arrhenius[1] a like degree of dissociation (a) of the hydrochloric acid is assumed in all the solutions. Assuming the figure found by Kohlrausch[2] for the molecular conductivity of N/10 hydrochloric acid at 18° C. (351) and supposing the molecular conductivity at an infinite dilution equal to 383 and we shall have $a = 0.9165$. In the exceptional experiment on N/100 hydrochloric acid without the addition of sodium chloride we shall have $a = 0.9661$.

In the second column is the hydrion concentration of the solution (C.) a figure obtained simply by multiplying the degree of dissociation by the normality of the acid. The third column gives the value of the product $0.0577 \times \log \frac{1}{C}$.

In the fourth and fifth columns of the table are entered the electromotive forces with the substitution respectively of 1.75 normal and 3.5 normal solutions of chloride of potash, and the sixth column contains the value of π corrected by means of these two values. Finally the last column contains the value of π_o calculated by means of equation (II) indicated above.

It is indicated in the table by transverse spaces that the measurements may be arranged in four series of experiments, the first of which was executed some three years ago by the author, while the three others were made at different times by Mr. S. Palitzsch.

The mean value of π_o taken from all the measurements is 0.3377, and the deviation from this mean is in only one case greater than one millivolt; generally it is much less. The differences between these experiments are of the same order of magnitude as those in the measurements made by N. Bjerrum,[3] but the mean here given (0.3377) is higher by one millivolt than that found by Bjerrum (0.3367), and moreover it agrees excellently with that found by Bjerrum in his experi-

[1] *Zeitschr. physik. Chemie.*, 31, 204 (1899).

[2] F. Kohlrausch and L. Holborn, *Das Leit vermögen der Elektrolyte*, 1898, p. 160.

[3] See *Zeitschr. physik. Chemie*, 53, 432 (1905). Mém. de l'Acad. Roy. de Danemark. [7], Sect. d. Sc. t., IV, 15. Studier over basiske Kromiforbindelser, p. 38 (1908).

TABLE I.—Electromotive Force π_0 of a Cell Composed of One Calomel Electrode Plunged into a N/10 Solution of Chloride of Potash, and One Hydrogenized Platinum Electrode Placed in a Solution Normal with Respect to Hydrogen Ions at 18° C.

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times \alpha)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π corrected	$\pi_0 = \pi(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4066	0.4020	0.3974	0.3375
0.1 n	0.0916_5	0.0599	0.4082	0.4029	0.3976	0.3377
0.05 n + NaCl 0.5 n.....	0.0458_3	0.0773	0.4219	0.4184	0.4149	0.3376
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4415	0.4401	0.43°7	0.3385
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4569	0.4560	0.4551	0.3375
0.005 n + NaCl 0.095 n.....	0.00458_3	0.1350	0.4733	0.4733	0.4733	0.3383
0.01 n (without NaCl).....	0.00966_1	0.1163	0.4599	0.4571	0.4543	0.3380
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4402	0.4392	0.4382	0.3380
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4390	0.4382	0.4374	0.3372
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4576	0.4568	0.4560	0.3384
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4569	0.4563	0.4557	0.3381
0.005 n + NaCl 0.095 n.....	0.00458_3	0.1350	0.4733	0.4733	0.4733	0.3383
0.005 n + NaCl 0.95 n.....	0.00458_3	0.1350	0.4726	0.4726	0.4726	0.3376

TABLE I.—ELECTROMOTIVE FORCE π_o OF A CELL COMPOSED OF ONE CALOMEL ELECTRODE, PLUNGED INTO A N/10 SOLUTION OF CHLORIDE OF POTASH, AND ONE HYDROGENIZED PLATINUM ELECTRODE PLACED IN A SOLUTION NORMAL WITH RESPECT TO HYDROGEN IONS AT 18° C.—(*Continued*).

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times \alpha)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π_o corrected	$\pi_o = \pi(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4070	0.4022	0.3974	0.3375
0.1 n	0.0916_5	0.0599	0.4064	0.4015	0.3966	0.3367
0.1 n	0.0916_5	0.0599	0.4065	0.4017	0.3969	0.3370
0.1 n	0.0916_5	0.0599	0.4063	0.4015	0.3967	0.3368
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4167	0.4134	0.4101	0.3374
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4170	0.4134	0.4098	0.3371
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4252	0.4227	0.4202	0.3374
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4251	0.4225	0.4199	0.3371
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4405	0.4390	0.4375	0.3373
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4404	0.4389	0.4374	0.3372
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4566	0.4555	0.4544	0.3368
0.01 n + NaCl 0.09 n.....	0.00916_5	0.1176	0.4560	0.4553	0.4546	0.3370

TABLE I.—ELECTROMOTIVE FORCE π_0 OF A CELL COMPOSED OF ONE CALOMEL ELECTRODE PLUNGED INTO A N/10 SOLUTION OF CHLORIDE OF POTASH, AND ONE HYDROGENIZED PLATINUM ELECTRODE PLACED IN A SOLUTION NORMAL WITH RESPECT TO HYDROGEN IONS AT 18° C.—(*Continued*).

Composition of the solutions examined	Hydrion concentration $C_H^+ (= A \times a)$	$0.0577 \times \log \frac{1}{C_H^+}$	π 1.75 normal solution of potassium chloride	π 3.5 normal solution of potassium chloride	π corrected	$\pi_0 = \pi(\text{cor.}) + 0.0577 \times \log \frac{1}{C_H^+}$
Acid hydrochloric 0.1 n	0.0916_5	0.0599	0.4082	0.4032	0.3982	0.3383
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4187	0.4148	0.4109	0.3382
0.06 n + NaCl 0.04 n.....	0.0549_9	0.0727	0.4187	0.4146	0.4105	0.3378
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4267	0.4241	0.4215	0.3387
0.04 n + NaCl 0.06 n.....	0.0366_6	0.0828	0.4273	0.4243	0.4213	0.3385
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4418	0.4402	0.4386	0.3384
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4419	0.4403	0.4387	0.3385
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4420	0.4406	0.4392	0.3390
0.02 n + NaCl 0.08 n.....	0.0183_3	0.1002	0.4410	0.4393	0.4376	0.3374
						Mean, 0.3377

ments using Planck's formula for the elimination of the potential of diffusion.

If the hydrogen electrode is as it should be, it is easy in measuring solutions such as those under discussion, to obtain constant results. Measurements of the same solution usually differ by only a few tenths of a millivolt. Slightly greater variations occur in the table, and the factors which might influence the exactness of the result are next discussed.

The solutions examined had all been prepared with such care that they presented no differences of composition electrically measurable. Ordinarily more than one calomel electrode was used, and in the rare cases where one electrode gave results differing by more than two or three-tenths of a millivolt from the values obtained (in otherwise similar conditions) from the other calomel electrodes, the defective electrode was thrown away. Thus there was slight probability of errors.

With the hydrogen electrodes the case is not the same. Two hydrogen electrodes do not always act exactly alike, and it may even happen, although rarely, that a perfect electrode may suddenly give false results. It is therefore necessary to pay continual attention to the hydrogen electrodes, and to take care to verify their normality. As a control we measured at intervals some mixtures taken from the solutions described below, for example, a mixture composed of eight volumes of the solution of glycocoll and two volumes of N/10 hydrochloric acid. These mixtures were chosen so that their composition excluded the possibility that a slight impurity, perhaps from alkaline ingredients coming from the glass might influence the result of measurement. Mixtures were chosen for which no corrections were necessary, in order to avoid possible errors due to inaccurate corrections. An effective control is thus obtained, so that electrodes of abnormal action may be rejected. On the whole, the probable limit of error is perhaps less than ½ a millivolt.

The method of eliminating the potential of diffusion by means of a correction also introduces a source of error which must be taken into account. On the other hand the table does not show the least indication of a relation between the size of the correction and the value of π_o. It is proved that the magnitude of the correction diminishes nearly proportionately to the hydrion concentration in solutions in which one may consider the concentration of chlorine ions as constant.

Composition of solutions	0.1 N. HCl	0.06 N. HCl 0.04 N. NaCl	0.05 N. HCl 0.05 N. NaCl	0.04 N. HCl 0.06 N. NaCl	0.02 N. HCl 0.08 N. NaCl	0.01 N. HCl 0.09 N. NaCl	0.005 N. HCl 0.095 N. NaCl
Mean value of the correction in millivolts..	4.9	3.7	3.5	2.7	1.4	0.8	0.0

Thus there is scarcely room to believe that the correction can have had the effect of disturbing in one way or the other the mean of the mean values of π_o. In considering how the corrections for the undividual experiments differ from the mean values of the correction indicated above, it will be seen that the error connected with a determination as a result of the correction could not be calculated to less than half a millivolt.

In measurements of this kind it is necessary to insulate as completely as possible all the articles used. In the course of these experiments certain difficulties were encountered due without doubt to defective insulation, and they were only conquered by placing, by the advice of Professor Prytz, each piece of measuring apparatus on a block of paraffine on the one hand, and then by passing the hydrogen through two tubes containing chloride of calcium and connected by a glass tube, in its passage from the electrolytic gas generating apparatus the vessel enclosing the electrode. This arrangement prevented the formation on the inside of the latter tube of a layer of moisture conducting electricity. Formerly it sometimes happened that when the short circuit ceased or a new one was introduced the capillary electrometer showed the existence of a difference of tension more or less strong, even when the electrometer was not connected in any circuit. With these precautionary measures no measurable movement of the mercury column was observed when the circuit was broken.

Substituting the value of π_o in equation (II), we have:

$$\pi_p = 0.3377 + 0.0577 \log \frac{1}{C_p}. \qquad \text{(III)}$$

In all the cases discussed here C_p (which means the normality of the solution with respect to hydrogen ions, or in other words the number of gram-ions of hydrogen per liter) is smaller than 1 and can be placed equal to 10^{-p}, where for the number p, the author proposes the name "index of hydrogen ions" and the designation of p_H^+. The index of hydrogen ions $\left(p_H^+\right)$ of a solution means therefore the logarithm of the reciprocal of the normality of the solution relative to the hydrogen ions.[1]

By introducing in formula (III) above the value $10^{-p_H^+}$ for C_p, we shall have

$$\pi = 0.3377 + 0.0577 \times p_H^+. \qquad \text{(IV)}$$

$$p_H^+ = \frac{\pi - 0.3377}{0.0577}. \qquad \text{(V)}$$

[1] As it is not usual to have solutions stronger than normal with respect to hydrogen ions, the above definition of the index of hydrogen ions has been chosen, which therefore will generally be a positive number. It will only be negative when the solution is stronger than normal.

It will be seen that by means of these last two equations one can calculate π when the hydrion concentration is given and thus the index of hydrogen ions and *vice versa*. Besides it is clear that the relation between π and p_H^+ may be expressed graphically by a straight line, which, when the values of π are ordinates and those of p_H^+ abcissas, will cut the axis of ordinates at the point 0.3377 and whose direction is entirely determined by the factor 0.0577. By changing the value π_o (0.3377) this line would be displaced in the system of coördinates, but the direction would not change. On the contrary the latter will vary with temperature, seeing that the factor 0.0577 is valid only at 18° C.

On the main chart of curves will be found this "line" designated as the *line of exponents.* The significance of this line is that by means of it we can, without any calculation graphically convert a value measured in π into the corresponding value of p_H^+, and inversely.

C. DETERMINATION OF THE DISSOCIATION CONSTANT OF WATER.

As has already been said in the introduction, it is usually easiest to calculate with the hydrion concentration because it is more susceptible of direct and exact determination than is the concentration of hydroxyl ions. There are many cases where it is easier to determine the hydroxyl ion content of an alkaline liquid; it therefore becomes very important to know exactly the constant of dissociation of water, a quantity which has very often been determined in entirely different ways, with results fairly concordant. A new determination of this has been made by the aid of the gas electrode.

The principle of the process is as follows:—by electrometric measurements by the method described above the hydrion concentration was determined in some solutions conveniently diluted with sodium hydroxide. The degree of dissociation of these solutions was known and consequently also the hydroxyl ion concentration. By multiplying the measured hydrion concentration by the calculated hydroxyl ion concentration the constant of dissociation of water was determined.

A test was made to determine whether the correction (which was of different magnitude in solutions of different concentrations) introduced a source of noticeable error. It appears from what follows that it does not, and this result indicates that even in the case of liquids rather strongly alkaline, it is safe to use the method of correction proposed by Bjerrum. The experiments in question are recorded in Table 2.

In the first column of this table is indicated the composition of the solutions examined. It appears that the concentration of the sodium hydroxide underwent great variations (from N/10 to N/100) while the whole content of sodium was the same (N/10) in all the experiments. For this reason the calculations are made for the same degree of dissociation (α) for the sodium hydroxide in all the experiments.

TABLE II.—Dissociation Constant of Water at 18° C.

Composition of solutions	Concentration of hydroxyl ions	π, 1.75 normal solution KCl	π, 3.5 normal solution KCl	π corrected	Hydrion concentration calculated from mean of π corrected $\left(C_H^+ = 10^{-p}\right)$	Constant of dissociation of water: $10^{-(p+q)}$	Constant of dissociation of water: $k \times 10^{-14}$
	q				p	$p+q$	k
0.1 n NaOH	1.075	1.0849	1.0871	1.0893	13.026	14.101	0.793
0.1 n NaOH	1.075	1.0861	1.0880	1.0899	13.036	14.111	0.774
0.1 n NaOH	1.075	1.0873	1.0892	1.0911	13.057	14.132	0.738
0.1 n NaOH	1.075	1.0876	1.0895	1.0914	13.062	14.137	0.729
0.1 n NaOH	1.075	1.0852	1.0871	1.0890	13.021	14.096	0.802
0.1 n NaOH	1.075	1.0848	1.0867	1.0886	13.014	14.089	0.815
0.05 n NaOH + 0.05 n NaCl	1.376	1.0700	1.0713	1.0726	12.736	14.112	0.773
0.05 n NaOH + 0.05 n NaCl	1.376	1.0699	1.0708	1.0717	12.721	14.097	0.800
0.02 n NaOH + 0.08 n NaCl	1.775	1.0480	1.0488	1.0496	12.338	14.113	0.771
0.02 n NaOH + 0.08 n NaCl	1.775	1.0478	1.0487	1.0496	12.338	14.113	0.771
0.01 n NaOH + 0.09 n NaCl	2.075	1.0315	1.0315	1.0315	12.024	14.099	0.796
0.01 n NaOH + 0.09 n NaCl	2.075	1.0316	1.0316	1.0316	12.026	14.101	0.793
0.01 n NaOH	1.075	1.0890	1.0910	1.0930	13.090	14.165	0.684
0.01 n NaOH	1.075	1.0885	1.0902	1.0919	13.071	14.146	0.715
0.01 n NaOH	1.075	1.0884	1.0900	1.0916	13.066	14.141	0.723
0.06 n NaOH + 0.04 n NaCl	1.297	1.0767	1.0780	1.0793	12.853	14.150	0.708
0.06 n NaOH + 0.04 n NaCl	1.297	1.0772	1.0786	1.0800	12.865	14.162	0.689
0.04 n NaOH + 0.06 n NaCl	1.474	1.0673	1.0683	1.0693	12.679	14.153	0.703

TABLE II.—DISSOCIATION CONSTANT OF WATER AT 18° C.—(*Continued*).

Compositions of solutions	Concentration of hydroxyl ions	π, 1.75 normal solutions KCl	π, 3.5 normal solution KCl	π corrected	Hydrion concentration calculated from mean of π corrected	Constant of dissociation of water	
					$\left(C_{\frac{+}{H}}=10^{-p}\right)$	$10^{-(p+q)}$	$k\times10^{-14}$
	q				p	$p+q$	k
0.04 n NaOH + 0.06 n NaCl	1.474	1.0675	1.0685	1.0695	12.683	14.157	0.697
0.02 n NaOH + 0.08 n NaCl	1.775	1.0509	1.0514	1.0519	12.378	14.153	0.703
0.02 n NaOH + 0.08 n NaCl	1.775	1.0508	1.0514	1.0520	12.379	14.154	0.701
0.01 n NaOH + 0.09 n NaCl	2.075	1.0345	1.0345	1.0345	12.076	14.151	0.706
0.01 n NaOH + 0.09 n NaCl	2.075	1.0343	1.0343	1.0343	12.073	14.148	0.711
0.1 n NaOH	1.075	1.0887	1.0902	1.0917	13.067	14.142	0.721
0.1 n NaOH	1.075	1.0880	1.0901	1.0922	13.076	14.151	0.706
0.1 n NaOH	1.075	1.0873	1.0889	1.0905	13.047	14.122	0.755
0.1 n NaOH	1.075	1.0872	1.0895	1.0918	13.069	14.144	0.718
0.1 n NaOH	1.075	1.0877	1.0902	1.0927	13.085	14.160	0.692
0.06 n NaOH + 0.04 n NaCl	1.297	1.0759	1.0771	1.0783	12.835	14.132	0.738
0.06 n NaOH + 0.04 n NaCl	1.297	1.0763	1.0778	1.0793	12.853	14.150	0.708
0.06 n NaOH + 0.04 n NaCl	1.297	1.0762	1.0778	1.0794	12.854	14.151	0.706
0.04 n NaOH + 0.06 n NaCl	1.475	1.0668	1.0679	1.0690	12.674	14.148	0.711
0.04 n NaOH + 0.06 n NaCl	1.475	1.0673	1.0683	1.0693	12.679	14.153	0.703
0.02 n NaOH + 0.08 n NaCl	1.775	1.0507	1.0512	1.0517	12.374	14.149	0.710
0.02 n NaOH + 0.08 n NaCl	1.775	1.0507	1.0514	1.0521	12.381	14.156	0.698

Accepting the figures of Kohlrausch[1] for the molecular conductivity of a N/10 solution of sodium hydroxide (183), and making the molecular conductivity at an infinite dilution equal to 217.6 (the sum of the speeds of displacement of the two ions 43.6 + 174.[2] We shall have $a = 0.841$.

In the second column is found the concentration of hydroxyl ions calculated by means of the degree of dissociation and the content of sodium hydroxide. The third and fourth columns indicate the electromotive force measured by interposing one after the other two solutions 1.75 normal and 3.5 normal, of chloride of potassium. The fifth column contains the value of π corrected according to equation V above.

The last two columns give the product of the hydrion and hydroxyl ion concentrations of the measured solutions, the product expressed either by a negative fractional power of 10 or by a factor multiplied by 10^{-14}.

The transverse spaces indicate that the measurements were made in three series at different times on different materials, and each time with freshly prepared solutions. The value of the constant of dissociation of water has been found higher in the first series than in the two others, the mean of k in the three series of experiments being 0.78_6, 0.70_4 and 0.71_4. The first series was done before, the other two after the adoption of the precautionary measures mentioned above, so that it is reasonable to have more confidence in the values found latest. In the calculation of the total mean double importance has been given to the values of the second and third series. The mean value, calculated in this way, of the dissociation constant of water at 18° is

$$0.72 \times 10^{-14} = 10^{-14.14}.$$

Consequently, in pure water and in really neutral solutions the concentration of hydrogen and of hydroxyl ions will be $0.85 \times 10^{-7} = 10^{-7.07}$.

It will be observed that the variations from the mean are greater in Table 2 than in Table 1, sometimes exceeding 2 millivolts. Under normal conditions such errors rarely occur.

It appears from Table 2 that the correction does not introduce an appreciable error, for the constant k in the last column does not vary with the correction. As will appear from the small table below, the correction diminishes with the concentration of the sodium hydroxide.

Composition of solutions	0.1 Normal NaOH	0.06 N. NaOH 0.04 N. NaCl	0.05 N. NaOH 0.05 N. NaCl	0.04 N. NaOH 0.06 N. NaCl	0.02 N. NaOH 0.08 N. NaCl	0.01 N. NaOH 0.09 N. NaCl
Mean value of the correction in millivolts..	1.9	1.4	1.1	1.0	0.7	0.0

[1] F. Kohlrausch and L. Holborn, *Das Leit vermögen der Elektrolyte*, 1898, p. 160.

[2] F. Kohlrausch, *Lehrbuch der praktischen Physik*, (1901) p. 596.

For comparison, the more important determinations of the constant of dissociation of water are here briefly described. The coefficient of temperature is so great that in order to reduce to 18° C. the values obtained at 25° C., it is necessary to subtract about 24 per cent.[1]

First. By means of the gaseous chain between normal acid and normal base, W. Ostwald[2] found a difference of potential of about 0.7 volt, from which W. Nernst[3] deduces the constant of dissociation of water at 18° C $= 0.64 \times 10^{-14}$.

Second. From the experiments of Shield on the hydrolysis of sodium acetate, S. Arrhenius[4] derives the value 1.27×10^{-14} for 25°. Reduced to 18° this gives 0.73×10^{-14}.

Third. At the suggestion of van't Hoff, J. J. A. Wijs[5] has observed the speed of saponification of methyl acetate in pure water, and gets the value 1.44×10^{-14}, at 24.8° C., or 0.83×10^{-14} at 18° C.

Fourth. In determining the conductivity of water purified with every possible care, F. Kohlrausch and Ad. Heydweiller[6] have found that 1 liter of water contains at 18° C., $0.8 \times$ —[7] grams of hydrogen ions, and at 25° C., 1.05×10^{-7} gram. From this the constant of dissociation of water is calculated as follows:

$$\left(\frac{0.8}{1.008} \times 10^{-7}\right)^2 = 0.63 \times 10^{-14} \text{ at } 18°$$

and

$$\left(\frac{1.05}{1.008} \times 10^{-7}\right)^2 = 1.09 \times 10^{-14} \text{ at } 25°.$$

Fifth. At 25° to 26° C., R. Lowenherz[7] has measured the electromotive force of a cell composed of two hydrogen electrodes, one immersed in N/10 or N/100 hydrochloric acid, and the other in N/10 or N/100 sodium hydroxide. The intermediate liquid was an equimolecular solution of lithium chloride, and the potentials of diffusion were calculated according to Planck. The principle of this method was therefore exactly the same as that which forms the basis of Sorensen's experiments. Eight experiments[8] on N/10 hydrochloric acid and N/10 sodium hydroxide gave Lowenherz 1.187×10^{-7} and six experiments[9] with the same substances in N/100 solution gave 1.075×10^{-7}. The mean of these two values gives for the constant of dissociation of water at 25° to 26° C., 1.28×10^{-14}, or about 0.74×10^{-14} at 18° C.

[1] Kohlrausch and Heydweiller, *Wied. Ann.*, 53, 234 (1894).

[2] *Zeitschr. physik. Chemie*, 11, 521 (1893).

[3] *Zeitschr. physik. Chemie*, 14, 155 (1894).

[4] *Zeitschr. physik. Chemie*, 11, 827 (1893).

[5] *Zeitschr. physik. Chemie*, 11, 492 (1893); compare also J. J. van Laar, *Ibid*, 13, 736 (1893).

[6] *Wied. Ann.*, 53, 209 (1894).

[7] *Zeitschr. physik. Chemie*, 20, 283 (1896).

[8] The greatest deviation from the mean was 3.1 millivolts.

[9] The greatest deviation from the mean was 3.8 millivolts.

Sixth. More recently C. W. Kanolt[1] in examining the hydrolysis of the ammonium salt of diketotetrahydrothiazole, has found for the constant of dissociation of water at 25°, 0.82×10^{-14} and at 18°, 0.46×10^{-14}.

Seventh. H. Lunden,[2] in measuring the hydrolysis of the trimethylpyridine salt of *p*-nitrophenol has obtained at 15° C. the value 0.46×10^{-14}, and at 25° C., 1.05×10^{-14}. These correspond to about 0.61×10^{-14} at 18° C.

D. STANDARD SOLUTIONS AND THEIR MEASUREMENT BY THE ELECTROMETRIC METHOD; TABLE OF PRINCIPAL CURVES.

The standard solutions used in the colorimetric method and mentioned in the introduction are as follows:—

TABLE III.—GLYCOCOLL MIXTURES.

Composition of the mixture	Electromotive force π	Index of ions of hydrogen P_H^+
10.0 cc. glycocoll	about 0.6900	about 6.106
9.9 cc. glycocoll + 0.1 cc. HCl	0.5922	4.411
9.75 cc. glycocoll + 0.25 cc. HCl	0.5680	3.991
9.5 cc. glycocoll + 0.5 cc. HCl	0.5500	3.679
9.0 cc. glycocoll + 1.0 cc. HCl	0.5305	3.341
8.0 cc. glycocoll + 2.0 cc. HCl	0.5063	2.922
7.0 cc. glycocoll + 3.0 cc. HCl	0.4881	2.607
6.0 cc. glycocoll + 4.0 cc. HCl	0.4692	2.279
5.0 cc. glycocoll + 5.0 cc. HCl	0.4492	1.932
4.0 cc. glycocoll + 6.0 cc. HCl	0.4326	1.645
3.0 cc. glycocoll + 7.0 cc. HCl	0.4196	1.419
2.0 cc. glycocoll + 8.0 cc. HCl	0.4099	1.251
1.0 cc. glycocoll + 9.0 cc. HCl	0.4038	1.146
0.0 cc. glycocoll + 10.0 cc. HCl	0.3976	1.038
10.0 cc. glycocoll	about 0.6900	about 6.106
9.9 cc. glycocoll + 0.1 cc. NaOH	0.7883	7.809
9.75 cc. glycocoll + 0.25 cc. NaOH	0.8130	8.237
9.5 cc. glycocoll + 0.5 cc. NaOH	0.8325	8.575
9.0 cc. glycocoll + 1.0 cc. NaOH	0.8529	8.929
8.0 cc. glycocoll + 2.0 cc. NaOH	0.8780	9.364
7.0 cc. glycocoll + 3.0 cc. NaOH	0.8982	9.714
6.0 cc. glycocoll + 4.0 cc. NaOH	0.9228	10.140
5.5 cc. glycocoll + 4.5 cc. NaOH	0.9425	10.482
5.1 cc. glycocoll + 4.9 cc. NaOH	0.9763	11.067
5.0 cc. glycocoll + 5.0 cc. NaOH	0.9900	11.305
4.9 cc. glycocoll + 5.1 cc. NaOH	1.0050	11.565
4.5 cc. glycocoll + 5.5 cc. NaOH	1.0356	12.095
4.0 cc. glycocoll + 6.0 cc. NaOH	1.0531	12.399
3.0 cc. glycocoll + 7.0 cc. NaOH	1.0690	12.674
2.0 cc. glycocoll + 8.0 cc. NaOH	1.0795	12.856
1.0 cc. glycocoll + 9.0 cc. NaOH	1.0862	12.972
0.0 cc. glycocoll + 10.0 cc. NaOH	1.0916	13.066

[1] *Journ. Amer. Chem. Soc.* **29**, 1402 (1907).
[2] *Meddelanden fron Veteuskapsacademiens Nobelinstitut*, **1**, 8 (1907).

1. N/10 hydrochloric acid (sometimes referred to simply as "HCl").

2. N/10 sodium hydroxide, (called "NaOH").

3. A N/10 solution of glycocoll to which NaCl has been added containing per liter 7.505 gr. glycocoll and 5.85 grams pure sodium chloride. (solution called "glycocoll").

4. A 1/15 molecular solution of primary potassium phosphate, 9.078 grams KH_2PO_4 per liter, (called "phosphate prim.").

Fifth. A 1/15 molecular solution of secondary sodium phosphate, 11.876 grams Na_2HPO_4 per liter, (called "phosphate sec.").

Sixth. A 1/10 molecular solution of secondary citrate of sodium, prepared by dissolving 21.008 grams of citric acid hydrate in 200 cc. of a normal solution of sodium hydroxide, and completing with water to 1 liter, (solution called "citrate").

TABLE IV.—MIXTURES OF PHOSPHATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. phos. sec.	0.8167	8.362
9.9 cc. phos sec. + 0.1 cc. phos. prim.	0.8092	8.171
9.75 cc. phos. sec. + 0.25 cc. phos. prim.	0.8015	8.038
9.5 cc. phos. sec. + 0.5 cc. phos. prim.	0.7914	7.863
9.0 cc. phos. sec. + 1.0 cc. phos. prim.	0.7790	7.648
8.0 cc. phos. sec. + 2.0 cc. phos. prim.	0.7616	7.347
7.0 cc. phos. sec. + 3.0 cc. phos. prim.	0.7500	7.146
6.0 cc. phos. sec. + 4.0 cc. phos. prim.	0.7402	6.976
5.0 cc. phos. sec. + 5.0 cc. phos. prim.	0.7308	6.813
4.0 cc. phos. sec. + 6.0 cc. phos. prim.	0.7210	6.643
3.0 cc. phos. sec. + 7.0 cc. phos. prim.	0.7109	6.468
2.0 cc. phos. sec. + 8.0 cc. phos. prim.	0.6977	6.239
0.1 cc. phos. sec. + 9.0 cc. phos. prim.	0.6787	5.910
0.5 cc. phos. sec. + 9.5 cc. phos. prim.	0.6608	5.600
0.25 cc. phos. sec. + 9.75 cc. phos. prim.	0.6438	5.305
0.1 cc. phos. sec. + 9.9 cc. phos. prim.	0.6248	4.976
0.0 cc. phos. sec. + 10.0 cc. phos. prim.	0.5990	4.529

Seventh. An alkaline solution of boric acid, prepared by dissolving 1/5 gram-molecule of boric acid (12.404 grams) in 100 cc. of N/1 sodium hydroxide and diluting to 1 liter, (solution called "borate").

These solutions were made with distilled water which had been boiled in timed copper vessels to free it from CO_2. The graduated flasks used, as well as the bottles in which the solutions were preserved were first of all filled with air free from CO_2.

(Here follow further precautions used in preparing the solutions and in testing the purity of the materials.)

In suitable mixtures of these standard solutions, the hydrion concentration was measured electrometrically as described above. Results are given in Tables 3 to 6. The first column gives the composition of 10

cc. of the mixture. The second column gives the observed electromotive force, (π), of an element consisting of a calomel electrode immersed in N/10 KCl and a hydrogen electrode with the solution to be examined as the electrolytic liquid. The third column gives the value of the index of hydrogen ions (p_H^+) calculated from the electromotive force by equation, $p_H^+ = \frac{\pi - 0.3377}{0.0577}$.

The values given for π are the means of two or more frequently of a number of measurements made at different times, with different elec-

TABLE V.—MIXTURES OF CITRATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. of citrate	0.6238	4.958
9.5 cc. of citrate + 0.5 cc. HCl	0.6197	4.887
9.0 cc. of citrate + 1.0 cc. HCl	0.6164	4.830
8.0 cc. of citrate + 2.0 cc. HCl	0.6061	4.652
7.0 cc. of citrate + 3.0 cc. HCl	0.5943	4.447
6.0 cc. of citrate + 4.0 cc. HCl	0.5776	4.158
5.5 cc. of citrate + 4.5 cc. HCl	0.5655	3.948
5.0 cc. of citrate + 5.0 cc. HCl	0.5507	3.692
4.75 cc. of citrate + 5.25 cc. HCl	0.5413	3.529
4.5 cc. of citrate + 5.5 cc. HCl	0.5318	3.364
4.0 cc. of citrate + 6.0 cc. HCl	0.5092	2.972
3.33 cc. of citrate + 6.67 cc. HCl	0.4689	2.274
3.0 cc. of citrate + 7.0 cc. HCl	0.4488	1.925
2.0 cc. of citrate + 8.0 cc. HCl	0.4195	1.418
1.0 cc. of citrate + 9.0 cc. HCl	0.4054	1.173
0.0 cc. of citrate + 10.0 cc. HCl	0.3976	1.038
10.0 cc. of citrate	0.6238	4.958
9.5 cc. of citrate + 0.5 cc. NaOH	0.6275	5.023
9.0 cc. of citrate + 1.0 cc. NaOH	0.6325	5.109
8.0 cc. of citrate + 2.0 cc. NaOH	0.6443	5.314
7.0 cc. of citrate + 3.0 cc. NaOH	0.6590	5.568
6.0 cc. of citrate + 4.0 cc. NaOH	0.6821	5.969
5.5 cc. of citrate + 4.5 cc. NaOH	0.7030	6.331
5.25 cc. of citrate + 4.75 cc. NaOH	0.7230	6.678
5.0 cc. of citrate + 5.0 cc. NaOH	0.8600 0.9200	9.052 10.092
4.5 cc. of citrate + 5.5 cc. NaOH	1.0343	12.073
4.0 cc. of citrate + 6.0 cc. NaOH	1.0511	12.364

trodes and other solutions. The mixture eight parts glycocoll and two parts HCl was thus measured many times for the sake of testing the

condition of the electrodes. As giving an idea of the agreement obtained, the set of 18 determinations is given:—

0.5064 0.5065 0.5049 0.5067 0.5063 0.5063 0.5064 0.5067 0.5057
0.5067 0.5070 0.5068 0.5064 0.5064 0.5065 0.5056 0.5052 0.5052

mean 0.5063.

The deviation from the mean is seldom greater than a millivolt, and generally much less. The author therefore believes that values of π given are within 0.001 volt of the true values.

TABLE VI.—MIXTURES OF BORATES.

Composition of mixture	Electromotive force π	Index of hydrogen ions P_H^+
10.0 cc. borate.	0.8709	9.241
9.5 cc. borate + 0.5 cc. HCl	0.8667	9.168
9.0 cc. borate + 1.0 cc. HCl	0.8620	9.087
8.5 cc. borate + 1.5 cc. HCl	0.8574	9.007
8.0 cc. borate + 2.0 cc. HCl	0.8517	8.908
7.5 cc. borate + 2.5 cc. HCl	0.8454	8.799
7.0 cc. borate + 3.0 cc. HCl	0.8384	8.678
6.5 cc. borate + 3.5 cc. HCl	0.8285	8.506
6.0 cc. borate + 4.0 cc. HCl	0.8160	8.289
5.75 cc. borate + 4.25 cc. HCl	0.8072	8.137
5.5 cc. borate + 4.5 cc. HCl	0.7958	7.939
5.25 cc. borate + 4.75 cc. HCl	0.7774	7.621
5.0 cc. borate + 5.0 cc. HCl	0.7155	6.548
4.75 cc. borate + 5.25 cc. HCl	0.4745	2.371
10.0 cc. borate	0.8709	9.241
9.0 cc. borate + 1.0 cc. NaOH	0.8778	9.360
8.0 cc. borate + 2.0 cc. NaOH	0.8860	9.503
7.0 cc. borate + 3.0 cc. NaOH	0.8960	9.676
6.0 cc. borate + 4.0 cc. NaOH	0.9132	9.974
5.0 cc. borate + 5.0 cc. NaOH	0.9768	11.076
4.0 cc. borate + 6.0 cc. NaOH	1.0518	12.376

It will be noted that in measuring the more acid and more alkaline of the solutions it has been necessary to make corrections, whose magnitude and algebraic sign agrees perfectly with what has been said before on the subject (pages 145 and 149). In these cases it is the corrected values of π which are found in the tables.

Chart of Principal Curves.—The curves called on the chart "glycocoll + hydrochloric acid," etc., have for abscissas the values of the exponent of the hydrogen ions p_H^+, shown in the last column of Tables III-VI, and for ordinates the content of the mixture in glycocoll, citrate, borate and secondary phosphate respectively.

Further, the chart contains the line of the exponents of hydrogen ions which, as has been said, permits one to determine graphically the value of p_H^+ corresponding to a π measure, and inversely.

By the aid of the curves the values of π and p_H^+ may be found for all mixtures of the standard solutions, in question, even those not given in the tables. Suppose, for example, we wish to find these values for the mixture 8.6 cc. of glycocoll + 1.4 cc. HCl. Find the ordinate 8.6 and follow the horizontal line 8.6 to its point of intersection with the curve glycocoll and hydrochloric acid. The abscissa of this point is 3.15, a number which therefore represents p_H^+ of the mixture.

Values of π for intermediate proportions of mixtures were taken from the chart, and afterward π was measured electrometrically for these same mixtures, the values thus found differing by less than 1 millivolt.

The close agreement between values of p_H^+ deduced from the curves and those for the same mixtures electrometrically determined supports the belief of the author that the values of π given in the tables are not subject to an error of more than 1 millivolt. The dotted parts of the curves are those which are not available for determining values of π or p_H^+. Since a change in the ordinate of a curve corresponds to a change in the composition of a mixture, and a change in the abscissa denotes a change in the hydrion concentration, it is evident that where the curve is nearly or quite parallel to the axis of abscissas, it could not be used, because a very minute change in the composition of the mixture corresponds to a great or even very great change in the ionic concentration.

Solutions of glycocoll which had been kept for some months did not show constant values for π. This fact the author attributes to minute impurities in the solution. The same behavior was observed on the part of those solutions containing small proportions of NaOH and HCl mixed with glycocoll. For this reason the curve of glycocoll and HCl is dotted from 10 cc. glycocoll to 9.5 cc. glycocoll and 0.5 cc. HCl, and that for glycocoll and NaOH from 10 cc. glycocoll to 9.75 cc. glycocoll and 25 cc. NaOH. For similar reasons parts of the other curves are dotted. The primary phosphate for instance gave the same value of π after nine months, while in the case of the secondary phosphate the value of π had decreased in the same time 8 millivolts.

(To be continued.)

Chrome Tannage. E. GIUSIANA. *Collegium*, No. 444, p. 33, 1911.—The author prefers in general the one-bath method on account of its greater economy and the greater certainty of results. For leathers where a soft texture and finish are desired, the two-bath process has decided advantages, however, because the sulphur deposited in the leather by the decomposition of the hyposulphite of soda of the reducing bath tends to make the finished leather smooth and supple. The maximum quantity of sulphur found was 0.7 per cent.

The author thinks that there is no essential difference in the result in the one-bath and two-bath processes, from a chemical point of view. The essential feature, he says, is the fixation of oxide of chrome on the hide-fiber by the dissociation of easily broken up basic salts of chrome by catalytic action on the part of the hide in contact with the chrome salt. He remarks that this dissociation may be seen in the case of very basic salts simply by diluting the chrome solution with water. The maximum quantity of Cr_2O_3 fixed by the hide is 6 per cent.

The author states that the chrome salt employed to the best advantage in one-bath tannage is chrome alum, rendered basic with solvay soda. In order to prepare a bibasic chrome salt, equimolecular quantities of alum and soda are taken:—

$$K_2Cr_2(SO_4)^4 + Na_2CO_3 + H_2O = K_2SO_4 + Na_2SO_4 + Cr_2(SO_4)^2(OH)^2 + CO_2.$$

If two molecules of soda are used for each molecule of alum, a tetrabasic salt is produced.—

$$K_2Cr_2(SO_4)^4 + 2Na_2CO_3 + 2H_2O = K_2SO_4 + 2Na_2SO_4 + Cr_2(SO_4)(OH)^4 + 2CO_2.$$

The latter solution tans better, but the author prefers to start the tannage with a less basic salt and add more soda a little at a time as the process goes on, stating that this method gives a finer, firmer grain.

The bichromate of sodium and sodium chrome alum possess an advantage because it is easier to wash the sodium salts out of the leather. The author prefers in making chrome liquors from sodium bichromate to make a stock liquor of 28 to 30° Bé. He does not employ sulphurous acid, but an organic reducing agent, preferring glycerine to sugar. The action of the glycerine is very violent, and the chemical reaction very complex, glyceric and tartronic acids and formaldehyde being among the products.

The analysis of a basic liquor thus prepared, at 30.6° Bé, was, water 71.1 per cent., $Na_2Cr_2O_7$ 12.16, H_2SO_4 14.69, NaCl 0.13, organic matter 1.91.

The basicity of the liquor varies according to the quantity of sulphuric acid used in the reaction.

A table is given showing quantities of soda required to convert various quantities of chrome alum into basic liquors of varying degrees of basicity. One lime of the table gives the proportions for all, 1 kg. of crystallized chrome alum corresponding to 294.5 grams of potassium bichromate or to 152.5 grams of Cr_2O_3, requires 50 grams of dry Na_2CO_3 to convert it into the monobasic salt, 100 for the dibasic, 150 for the tribasic and 200 for the tetrabasic. A second table shows the quantities of pure sulphuric acid and glycerine required to convert various quantities of potassium bichromate into basic salts. Here again one line gives proportions for all. 1 kg. of crystallized chrome alum containing 393 grams H_2SO_4 corresponds to 294.3 grams of $K_2Cr_2O_7$. To reduce this to the tetrabasic salt requires 207 grams of

sulphuric acid; to the tribasic, 254 grams to the dibasic, 299.5 grams and to the monobasic 347.5 grams, the quantity of glycerine at 28° Bé in each case being 98 grams.

Chrome Tanning. From *Le Marché des Cuirs,* 1911, (33), No. 1, pp. 1-2.—The following experiments have been made on the drums for the first and second baths, with sheepskins passed through a bran bate. There are several modifications in the process of chrome tanning in two baths. In the first place, the first bath may be made of bichromate, of salt and hydrochloric or some other acid, or alum may even be added. The second bath may be made of hyposulphite of soda, of salt and hydrochloric acid, or some other acid. Sulphites may also be used for the second bath. To simplify matters but two cases will here be considered. First case:—A bichromate bath without alum and a reduction bath of hyposulphite of soda. Second case:—A bichromate bath containing alum and the same reduction bath as above. The acid used is hydrochloric at 21° Baumé. *First Case.* The bichromate bath was made with bichromate of potassium, salt and hydrochloric acid. This liquid was kept as fresh as possible in order not to shrivel the skins. The skins were turned three hours in this first bath and were taken out over night. The second bath was used twice, first very dilute and of short duration, and then normal, the acid being diluted to five or six times its volume with water and added at the axis of the drum during the process. In this last bath the skins were examined at very short intervals after the addition of the acid to keep track of the process of the change in color.

After the first hyposulphite bath, the skins were of an old gold color and dripped strangely; that is the least pressure made the yellow solution due to the bichromate, run out, since only the surface of the skin had undergone a slight change. The second hyposulphite bath was first set up with the whole quantity of hyposulphite and salt, and one-sixth of the acid. The remainder of the acid was added one-sixth at a time every five minutes.

Five minutes after the addition of the third sixth of the acid (½ of the whole amount) the skins were of a greenish color, still verging on yellow.

Five minutes after the addition of the fourth sixth (*i.e.* 2/3 of the acid and 20 minutes of drumming) the skins had become putty color with still a faint trace of yellow.

Five minutes after the addition of all the acid the skins were green, that is completely changed, and the liquid obtained by pressure contained no trace of yellow. When a skin was cut, the inside, naturally was yellow. After 2½ hours of drumming (three hours in all) the hides were taken out on a rack. At this time a cut in the thick neck pieces still showed a tiny yellow gray line. This trace had disappeared after 24 hours on the rack. The tanning was finished.

Second Case. The bichromate bath was made up with bichromate

of potassium, salt, alum and hydrochloric acid. The skins were turned in this bath three hours and taken out over night.

For the second bath two hyposulphite baths with the same proportions of acid added in the same way were used. In this case the color change is much more rapid than in the first case, which is due no doubt to the sulphuric acid contained in the alum settled on the skins. After the first hyposulphite bath, the skins were already of a greenish yellow color. In the second hyposulphite bath the change of the surface of the skin was complete when the bath contained half the whole quantity of acid. This indicates that by this process the loss of chrome is less to be feared. As in the preceding process the tanning is completed on a rack.

Extraction of Tanning Materials. J. R. BLOCKLEY. LEATHER, II, 21, Jan. 12, 1911.—The object in leaching is to get the tannin from the material with the use of as little water as possible. In order to get all the tannin, much water must be used and the solution obtained would be too weak for use. The tannin is extracted by diffusion from the cells of the bark or wood through the cell wall into the surrounding liquor, and it is only when the liquor is weaker than the solution in the cells that tannin passes into the liquor from the cells. The same principle holds in the relations between the liquor and the hide, so that a hide will only tan in a liquor stronger than the infusion of tannin already in the hide. The writer summarizes his conclusions thus:—

1. It is impossible to extract materials well in one extraction.
2. It is unwise to bring strong liquor in contact with nearly spent material.
3. Water must be used only on nearly spent material.
4. Hides should not be kept long in a liquor of the same strength and should not be put from a stronger liquor into a weaker one.

Substitute for Platinum Triangles. R. C. BENNER. *Jour. Amer. Chem. Soc.*, 33, 189, Feb., 1911.—The writer has tested an alloy of chromium and nickel called nichrome for making wire triangles to support crucibles. He finds the nichrome triangles very resistant to heat and corrosion. The cost is about the same as that of pipe-stem triangles. They may be obtained from H. C. Stoelting & Co., Chicago.

Mangrove Bark Industry for Australia. From Vice-Consul H. D. Baker, Sydney, through *Shoe and Leather Reporter*.—It is said that the supply of black mangrove trees in Northern Australia is practically unlimited. A company has been organized to market the tanning materials in the form of solid extract. Some of the trees furnish logs 50 feet long and more than a ton of bark has been taken from a single tree The bark yields from 45 to 54 per cent. of its weight in solid extract An analysis of the bark made in Sydney gave tannin 38.2 per cent., non-tan 8.1 per cent., water 9.8 per cent.

Mangrove furnishes a tanning material easily soluble, cheap, and

satisfactory in every respect except that it gives a red color to the leather. This difficulty can be overcome as has been shown by experiments at the Sydney Technical College.

Method of Estimating the Acidity of One Bath Chrome Liquors. MORRIS BATESON, in LEATHER, 2, 263, Dec., 1910.—The addition of ammonia to a one-bath chrome liquor precipitates the chromium as hydroxide, the acid combining with the ammonia. The addition of formaldehyde forms hexamethylene tetramine and liberates the acid, which may then be titrated with N/2 caustic soda, using phenolphthalein as indicator.

The following procedure has been found convenient: to 50 cc. of the liquor (containing from 0.5 to 1.0 per cent. Cr_2O_3) ammonia is added until phenolphthalein is reddened. The sample is then made up to 100 cc., shaken and filtered. The filtrate should be pink from the phenolphthalein. To 50 cc. of the filtrate 10 cc. of 40 per cent. neutral formaldehyde is added, and titrated with N/2 caustic soda. Each cc. of soda = 0.024 gram SO_4 or 0.01775 gram Cl.

A table of results is given in which new chrome liquors show results almost the same as those obtained by titrating the boiling chrome liquor direct with N/2 NaOH. The method does not work well on old liquors, as the formaldehyde acts on dissolved hide substance to form acids.

The Dyeing of Chrome Leather. HUGO KUHL. *Ledertech. Rundschau,* 1910, pp. 394-5.—The practical problem for solution was to make a hard, parchment like split leather soft and elastic and to dye it. A successful method was worked out as follows: The excess of chromium salt was leached out with water at ordinary temperature and the leather was then soaked 2 hours in dilute HCl (1 liter 42 per cent HCl in 100 liters water) and afterward treated 3-4 hours in a concentrated soap dyeing bath, which may be used continuously on renewal each time with a little soap. The ordinary soaps used in the tannery were employed and it was found that castor oil and whale oil soaps containing excess of fat could be used. The dyed leather was fixed in 5 per cent. solution of sodium thiosulphate which is re-strengthened from time to time. With acid violet and fast blue (Badische Fabrik) a soft strong leather in bright colors was obtained, fast to soap and washing.

In another process the chrome leather first treated as above was further treated in a conc. soap bath 3-4 hours at 65° best in washing or dyeing drum. The leather then went direct into the dye-bath which contained 5 per cent. sodium thiosulphate; the dyeing was complete in 24 hours at ordinary temperatures. This gave a handsome bright leather, but not so soft as by the first process.

This process according to the author, is founded on the fact that oxidation plays an important part in tanning. Modern investigations

justify to some extent the theory of Knapp that tanning is a form of dyeing. Here the tanning agents are the soap (chamoisage) and the dyestuff. On the basis of these researches, the affinity of coal-tar dyes for leather would seem not to be so slight as stated by Lamb.

W. J. K.

Colloids; Studies on Organic——. S. LEVITES. *Z. Chem. Ind. Kolloide,* through J. S. C. J., 1910, **8**, 4-8.—Glutin is insoluble in cold water but dissolves tolerably easily in solutions of iodides and thiocyanates. Casein, which is insoluble in warm water, yields a stable opalescent solution. which can be readily filtered, when it is triturated with saline solutions (potassium iodide, sodium thiocyanate, sodium phosphate, potassium nitrate) and the mixture warmed. The casein is precipitated from the solution on addition of acid. Gliadin does not behave in an analogous manner. Glutin and casein are both insoluble in pyridine, but in aqueous pyridine the solubility increases with the pyridine content up to a maximum for the mixture, $C_5H_5N + 2H_2O$. The casein solutions are precipitated by addition of more pyridine or by strongly diluting with water, but the glutin solutions are unaffected by such treatment. The solutions in aqueous pyridine are very viscous. Glutin and Witte peptone are readily soluble in formamide, giving transparent, very viscous solutions, which are unaffected by dilution with water; the glutin shows no tendency to gelatinize even in concentrated solutions. Casein dissolves only in traces, and gliadin is quite insoluble in formamide. The precipitation of proteins by tannin is a more sensitive reaction than the biuret reaction, glutin can be detected at a dilution of 1 : 15,000, egg albumin at 1 : 800, and Witte peptone at 1 : 5000. In a series of tests in which pieces of gelatine were swollen in water then placed in contact with tannic acid solution, it was found that more tannic acid was adsorbed the longer the gelatine was previously soaked in water. Gelatine which had not been soaked adsorbed very little tannic acid. Considerably more tannic acid was adsorbed in presence of an electrolyte. By using a sufficient excess of tannic acid, gelatine can be quantitatively precipitated; the precipitation is favored by hydrogen ions, but hydroxyl ions act injuriously. The tripeptide, leucyl-glycyl-glycine, in 3 per cent. aqueous solution, is not precipitated even by a considerable excess of alcohol, but is precipitated immediately on addition of 1/40 vol. of ether.

Leather Rendement and Examination. W. APPELIUS AND L. MANSTETTEN. *Ledertechn. Rundschau,* 1910, pp. 385-6, 393-4, 401-3.—In this work are reported the conclusions from many analyses of vegetable tanned leather.

In leather analysis, the nitrogen content is of especial value: from this the degree of tannage may be computed. Dry hide substance of the hide of cattle or horse contains 17.84 per cent. N, or 1 part N = 5.62 hide substance. The addition of the N-free tannin to the hide therefore lowers the ratio of N and the lower the percentage of N, the

better the tannage. The following analysis of a North German sole leather is a type:

	Per cent.		
Water	18.0	Leather substance:	
Minerals	0.6	Fixed tannin	32.4
Fat	0.4	Hide subst	39.7
Solub. organ. matter	9.3		
Leather subst	71.7		71.7
		Per cent. N in leather	7.0
	100.0	Rendement number	254.4
		Tannage number	82.4

In this, according to von Schroeder's methods, the rendement and tannyl numbers represent the amounts of air dried leather and tannin respectively to 100 parts of hide substance. Von Schroeder also reckoned the approximate rendement based upon green or white weight, assuming that 125 parts green hide or 100 parts white hide = 28 to 31 parts dry hide substance. The authors, however, maintain that reliable valuation of the yield cannot be derived from the rendement and tannage numbers alone since the yield does not wholly depend upon the tannage. The principal additional elements which affect the rendement are: (1) Correctly stated green weight; (2) Location of the hide sample; the greater the surface of the hide in proportion to the weight, the greater the proportional loss in offal and hair as shown by the following yields out of the same lot of leathers of uniform tannage:

Thickness below 3.5 mm.		Thickness, 3.5-4.5 mm.	
Lbs. crude wt.	Per cent. yield	Lbs. crude wt.	Per cent. yield
50-59	56.9	60-69	54.1
60-69	52.0	70-79	53.2
70-79	50.7	80-89	51.9
		90-99	48.9

(3) The preliminary treatment of the hide, especially in fixing the white weight, of which the rendement may be 72-75 per cent. with the more shrunken sulphided hides, 82-85 per cent. with the more swollen limed hides. (4) Variations in the sticking.

None of these are taken account of in the analysis, hence it is not correct to refer it to the green or white weight. Von Schroeder's ratios were derived by investigation of the same hide from the green state to finished leather but in the tannery or laboratory this in general cannot be done and the computation of even the approximate rendement according to von Schroeder's rules is irrational. This is demonstrated by the following table giving the results obtained by the author with 6 pit tanned vache leathers of uniform tannage:

	(1)	(2)	(3)	(4)	(5)	(6)
Green weight, lbs.	70	70	76	72	64	72
Soft weight, lbs.	76	72	77	78	64	72
White weight, lbs.	59	63	64	63	53	60
Leather weight, lbs.	34	35.5	36	37	30	32
Leather rendm., %, factory....	48.6	50.7	47.4	51.4	45.6	44.4
Leather rendm., %, analysis..	61.1	64.2	63.2	63.7	64.4	65.5
Leather rendm., %, difference	12.5	13.5	15.8	12.3	18.8	21.1
Thickness leather, mm.	3.5	4.5	4	4	3.5	3.5

Further, in the practice of the Freiberg Tanning School, 50 different lots of hides were compared; the rendement limits were 45.7 and 59.3 per cent. of green weight according to the quality, all the same tannage, averaging each lot; individual hides showed differences of 23 per cent. By analysis the limits in rendement were 61.1 and 65.6 per cent. showing practically uniform tannage considering the approximate character of the analysis and the uncertainty of sampling. The analysis therefore does not distinguish these leathers or properly return the factory rendement.

It is extraordinarily difficult to sample fairly for analysis The various parts of the hide give different rendement figures, the butts the lower and the sides the highest; the looser hide taking up the most tannin, gives highest rendement and the hide of finer texture, the lowest. In actual manufacture, the reverse is the case; the loose hide gives the lowest rendement because as wet hide it holds much more water and contains less hide proportionately; this counts in the determination of the green weight and still more with the white weight. The relations existing in actual practice were illustrated by the following experiments. Various hides after liming were cropped and the relative weights of butts and offal determined. After tannage in pits the ratio of the leathers was likewise determined.

	Per cent. pelt of green wt.	Pelt		Leather	
		Butts	Offal	Butts	Offal
Cow 2	84.5	41.1	58.9	45.1	54.9
Ox 4	84.4	40.0	60.0	49.1	50.9
Bull 6	83.5	36.5	63.5	45.2	54.8

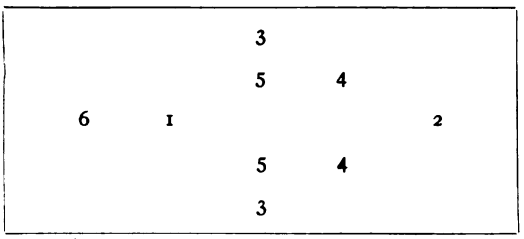
The table shows decidedly that more leather is obtained from the pelt of the butts than the waste whereas by the analyses less leather was always obtained.

It is almost impossible to secure an average sample. In the tannery, one is limited to a single hide which may accidentally greatly vary as shown in the following table of yields from large lots of dealer's hides published in the Freiberg Tanning School Report for 1905-6.

	Crude weight	Soft weight		White weight	
	Lbs.	Lbs.	Per. ct.	Lbs.	Per ct.
Best lot (15 hides)	1,092	1,047	95.9	875	80.1
Poorest lot (15 hides)	978	882	90.2	741	75.8

The analyses reported in the tables A, B, C below show the great

variations in yield according to the parts of hide taken. These were



located as follows: (1) back (near rump), (2) neck, (3) belly, (4) neck-base, (5) mid-bend, (6) root of tail. Table A shows that

TABLE A.—PIT TANNED LEATHER.

	1 Back	2 Neck	3 Belly	4 Neck-base	5 Mid-bend	6 Tail
First Layaway:						
Cow						
Rendement number	253.5	260.4	278.2	252.6	262.1	259.8
Tannage number	83.5	87.5	92.3	83.7	85.7	87.1
Organic solubles	8.3	8.7	11.4	8.0	10.2	8.5
Fixed tannin	33.0	33.6	36.0	33.2	32.4	32.8
Ox						
Rendement number	269.2	273.2	292.4	268.1	274.5	264.5
Tannage number	95.0	95.2	103.4	90.7	95.1	89.3
Organic solubles	8.2	8.9	10.8	9.4	9.0	8.8
Fixed tannin	35.3	34.8	35.4	33.9	34.6	36.2
Bull						
Rendement number	250.0	260.8	289.2	267.4	269.2	262.1
Tannage number	78.2	85.0	101.6	91.4	89.0	86.4
Organic solubles	9.2	9.6	10.6	8.9	10.3	9.5
Fixed tannin	31.3	32.6	35.2	34.2	33.1	35.0
Second Layaway:						
Cow						
Rendement number	261.8	283.0	292.5	279.6	281.3	279.8
Tannage number	85.6	93.3	97.7	94.0	96.1	101.1
Organic solubles	9.7	12.2	13.2	11.2	10.8	9.0
Fixed tannin	32.7	32.8	34.0	33.4	34.2	33.8
Ox						
Rendement number	277.8	278.2	283.4	274.3	271.4	262.1
Tannage number	96.9	99.3	92.3	91.7	87.9	87.1
Organic solubles	9.6	8.9	12.6	10.7	11.3	9.3
Fixed tannin	34.1	35.7	32.6	33.4	32.4	33.2
Bull						
Rendement number	258.7	279.8	283.4	274.3	271.4	262.1
Tannage number	88.0	90.9	92.3	91.7	87.9	87.1
Organic solubles	8.0	12.0	12.6	10.7	11.3	9.3
Fixed tannin	34.0	32.5	32.6	33.4	32.4	33.2

the rendement and tannage numbers are least in the back and confirm Paessler's prescript for taking the neck as best average. The middle piece (5) between the belly and the back is also seen to give average values. These are recommended, however, only in case but *one* sample may be taken.

TABLE B.

	Pit tannage					Drum tannage		
	Cow 1	Cow 2	She-calf	Ox	Bull	Cow	Ox	Bull
Rendement number	277.5	270.9	264.4	269.4	273.0	261.3	256.9	256.6
Tannage number	99.2	96.2	94.4	92.2	96.6	97.8	96.2	95.4
Organic solubles	8.8	8.2	7.0	9.4	8.8	5.0	4.1	4.3
Fixed tannin	35.7	35.5	35.7	33.9	35.0	37.3	37.9	37.3

In Table B (here condensed to averages from head, neck and belly) are compared pit tanned and drum tanned leather. The solubles in the last (which was to be sure very thoroughly washed) are the lowest throughout, but the fixed tannin highest which is probably due to the leather coming quicker into concentrated liquors in the drum

TABLE C.—PIT TANNED VACHE LEATHER.

Handlers	1	2	3	4	5	6	7
Rendement number	256.0	251.7	356.8	258.9	256.0	256.8	244.5
Tannage number	85.3	85.1	85.5	86.5	86.4	83.5	82.0
Organic solubles	7.9	7.1	8.3	8.5	7.7	8.9	5.9
Fixed tannin	33.4	33.7	33.3	33.5	33.7	32.5	33.9
"Versenk"							
Rendement number	256.9	258.3	259.9	256.7	257.5	263.5	254.5
Tannage number	82.0	81.6	84.2	82.8	83.1	90.7	80.9
Organic solubles	9.7	10.1	9.6	9.3	9.2	8.2	9.1
Fixed tannin	31.9	31.6	32.4	32.3	32.4	34.4	31.8
Layaway							
Rendement number	259.1	272.0	267.8	269.8	273.0	277.8	264.0
Tannage number	80.6	88.2	85.1	85.8	87.6	90.3	81.8
Organic solubles	10.7	11.1	11.2	11.4	11.6	11.7	11.6
Fixed tannin	31.1	32.3	31.8	31.7	32.1	32.5	31.0

Table C (condensed) gives the analysis averages of 7 vache leathers each time out of the handlers, "versenk" and layaway. In the Tanning School the leather remains a long time in the handlers and is then already well tanned as the analyses show. After this the increase in weight is largely due to extractable substance, but the leather becomes more solid in the "versenk" and layaway.

The authors promise further studies in this direction, one being a member of the commission on leather analysis chosen at the International Congress held at Paris in September.

The Measurement of the Color of Tanning Extracts. W. EITNER. *Der Gerber.* 1910, (36), 321-3.—In recent times since the introduction of

clarifying processes in extract manufacture, account has been taken of the color in the valuation of extract. Experience has shown that a light colored extract not only gives light colored leather but tans better and quicker and is better utilized. The principle of the colorimetric method by the Lovibond tintometer mostly employed in England consists in matching the color of the extract by a sufficient number of super imposed standard glasses of the ground colors, yellow, red and blue. Professor Procter has improved the method by employment of spectral absorption. In Europe these optical methods are not employed in commercial analysis, but empirical methods by comparison. Dr. A. Gansser in Garessio has devised such a method whereby the coloring effect of the extract may be observed upon animal fiber. An artificial hide "animalized cotton," is prepared from the so-called bachet which is felted on one side and fine wove on the other. This material, 1 mm. thick, is cut in strips 11 cm. wide, 20 m. long and rolled on spools. In a suitable apparatus the material is reeled through boiling water, then pressed by a roll and run through ¼ per cent. formaldehyde solution and from this through a 6 per cent. solution of pure gelatin at 60-65° C.; an attachment scrapes off the excess of gelatin. The dried material is quite stiff, pure white and can be preserved indefinitely in rolls. For tanning experiments, 2 pieces are cut of 2½ grams weight each and softened in water. In testing extracts, 10 cc. of 25° B. with 30 cc. water yielding a liquor of 6° B. are used; for difficult soluble quebracho extracts, 3° B. liquor is taken. The softened strips are placed in the liquor in glass cylinders and shaken for 12 hours at 25 revolutions per minute when the tannage should be complete. The tests are then rinsed 10 min. in running water, pressed and dried like leather, first at room temperature, then at 30°. They may be made smooth by pressing, but ironing, even at moderate warmth, affects the color to some extent.

The author has tested some of Dr. Gansser's original material with very satisfactory results; the shade and depth of color corresponded well with parallel results on hide. As to the reputed uncertainty of tests with hide skivers, etc., the author has found that sufficient regularity in grain coloring may be secured with care. The pelt should be thoroughly cleansed, accurately delimed to neutrality and well dickered, it is then pickled and preserved for use and will keep for months. Before use it is neutralized and well washed to free from salt. The chief advantage of the cotton test is in its rapidity since a hide test requires several days. The author is not of the opinion that this method will enable one to judge the effect of the extract upon rendement and solidity of the leather as Dr. Gansser suggests, but the light proof character of the colors may be determined much more rapidly than with leather. In this way the rapid darkening of colors from sulphited extracts as compared with those from genuine decolorized extracts was observed after exposing a few days to the light.

The optical method, especially with Procter's improvement, seems best suited for control in extract manufacture. It would be well to set the

standards by extracts which had been controlled by tests upon animalized cotton. For the consumers, the dyeing test direct would be preferable.

Chrome-Chamois Glove Leather. B. KOHNSTEIN. *Gerber-Courier. Jubiläums-Ausgabe,* 1910, pp. 36-7.—While the chamois leather manufacture is confined to a few manufactories which produce a high grade product, in America this industry is increasing and with considerable export. The American glove leather is not, however, a genuine chamois but an imitation, the so-called chrome-chamois leather. The native inventiveness of the Americans and their striving toward home production of all necessities, have perfected this manufacture. Live stock in America is exposed to barb wire fencing and the resulting scars on the skins as well as other blemishes are easiest disguised in this form of leather. In the manufacture the hides must be well softened and cleaned. Stale soaks are shunned for it is necessary in chrome tannage to preserve hide substance in all stages of the beam house work; with dry hides, 1½ per cent. salt is added to the soaks of the second day followed by fresh water the third day. The hides are milled in fresh water before liming. Cattle and horse hides are limed 2 days with addition of arsenic, then 6 days in pure lime. Dog and sheepskins need longer liming to avoid natural fat spots which are troublesome with the light shade dyes. After unhairing, fleshing and scudding, a bran drench with addition of a little pigeon dung is of advantage. The pickle for 100 kg. white pelt consists of 40 liters water, 36 kg. salt, 4.5 kg. sulphuric acid. For a second lot of hides, it is strengthened with half the amounts of chemicals. The acid strength must be regularly controlled by the chemist. After pickling, the moisture is pressed out by rollers and the hides are split, then drummed with 3 per cent. salt solution and are then ready for the double chrome bath. For the reducing bath, to 1 kg. pelt, 0.16 kg. sod. thiosulphate, 0.08 kg. HCl and 2 liters water are used. The leather is milled with this 3½-4 hours, let stand over night and milled again 1 hour. It is then treated ½ hour with 2 per cent. borax solution at 40° C. and rinsed in warm water, then pressed, shaved and leveled.

The fat liquor, containing 1.33 water, 2.5 neutral oleate, 4.0 sod. oil chrome-moellon, and 1.2 per cent. borax (sic) is milled with the leather for 30 minutes at 45° C. After drying, the leather is layered grain to grain in sawdust containing 35-40 per cent. water and left under weights for 12 hours. Various machine work follows including a buffing with carborundum. Dyeing is applied by dusting on the table; fine pipe clay is mixed with water, toned for gray with logwood and acetate of iron, or colored to pale yellow with willow and fustic. In order to give the chrome chamois the natural looseness of genuine chamois, the chrome bath is made strong; for 1 kg. pelt, 0.8 kg. bichromate, 0.4 kg. HCl of 22° B., and 1.27 liter water used, milling 3-4 hours. Heating is avoided, else a brittle chrome glue results. The hides are spread smooth over

horses avoiding creases which are sure to show later. Exposure to sunlight is avoided which may cause local reduction.

Glove Leather Manufacture. *Ledertechn. Rundschau*, 1910, pp. 395-7, 404-5, 400-11.—The crude material for glacé leather must be tender, clean grained kid and lambskins from animals still fed by the mother or at least only partially on solid food. Together with the lambskins yearling and sheepskins of the better sorts are used also.

(A) *Lamb Leather.*—The crude skins are carefully sorted by special workmen trained by long experience. After rejecting all skins with dull, dirty or thick flesh or other defects, the sorting is made into primes, seconds and thirds which are minutely described; these are further graded by age. Equivalent lots for working are:

	Sucklings	Lambs	Yearlings
Small	1,400	1,000	650
Medium	1,250	900	600
Large	1,100	800	550

All the skins in each lot must be from the same source which is the care of the sorter.

In the management of the soaks regard is paid to the origin of the skins, whether they be freshly dried or long stored, the season of the year, etc. The softening is complete when all parts of the skin may be equally stretched in both directions. Too long soaking, however, extracts hide substance and gives a flabby leather without strength or gloss and in extreme cases, decay begins and the final leather is brittle and inelastic. With too short a soaking, only the softened parts are loosened and plumped in the limes and the leather lacks in elasticity. If the water is not changed often enough, the blood is not extracted and instead of white, the leather is gray and without gloss. The use of soaks a second time is to be condemned. The normal time is 2, at the most 4 days, with change of water every 12 hours.

The liming likewise should be neither too long nor too short. Old, stale limes are strictly excluded; they produce spongy leather with wrinkled grain. If the swelling in the lime be too lengthy, the fiber does not go back again; the leather is spongy and when pulled, the grain draws up in folds. Too short of too weak liming results in completely inelastic leather. For preparing and bettering the limes, lime that has been stored not less than 2 months after slaking should be used, its action being much milder. In slaking, water is added until there is a permanent layer over the lime. The addition of arsenic to the lime hastens the loosening action and gives gloss to the grain; it also hems the swelling action. An excess injures the wool and still more the tender hide fiber. A lime liquor should not be used over 2-2½ months according to season. The duration of liming for mild natured ware is 8 days at the least, 12 for hard ware and 18 for very hard imported stock. Heed must be given that the temperature be uniform as possible. The apparatus should therefore be under cover in rooms with cool ventilation

in summer and heat in winter. The proper temperatures are 16-19° C. for the liquor and 20-22° for the room. Warming of the liquor does not accomplish the same result as a room of uniform temperature and there is too much variation. The lime vats should be capacious, 50 hectoliters to 900 lambskins with 36 hl. liquor so that the skins swim and are not jammed. The quantities for bettering are computed not from the volume of the liquor but from that of the skins; this is measured by observing the increase in depth of the liquor on immersing the hides and this multiplied by the cross section of the vat gives the volume or cubic contents of the hides. For each hectoliter, 4½-5½ liters thick slaked lime are reckoned and to 100 liters of slaked lime, 2½-3 kg. red arsenic. This is for wool skins; shorn skins take a third more in lime and arsenic. The specified quantities include the total additions (made every other day) for the entire period of liming. For soft hides, the minimum of lime and maximum of arsenic are used, for hard hides, the reverse. For freshly preparing a lime in a vat of 2 × 1.7 × 1.5 m. (liquor 1.3 m. deep) 50 liters thick slaked lime are used. The skins are well drained from the soaks and put in the limes. The next day they receive the first bettering, are turned daily and bettered every other day. When handling, the skins must be thoroughly agitated in the liquor to loosen any deposits of lime.

The subsequent cleansing work must proceed gradually nor should the skins ever go into cold water which shrinks them and makes the removal of lime and dirt difficult or even impossible. On the other hand there should be no delay: 3-4 days from the lime to the bran drench are enough at the most; else putrefaction may begin. The skins are taken in the morning from the lime, drained till afternoon, then thoroughly washed in tempered water (lime temperature) to which a few pailfuls of clean lime liquor have been added. The washing vat is drained, refilled and the above operation repeated. The skins are finally left in a third water over night. The wool is removed the next day, round, polished irons being used; great care is given to this work. The skins then go direct from the beam into tempered water clouded with lime liquor and are well rinsed. Trimming follows and only the coarsest flesh is removed, the real flesh being left for protection during bating. After standing in water over night with renewed agitation the next morning the water is mostly drawn off and the fells are worked or lathered ("gegascht") for 15-20 minutes, then rinsed and piled for bating.

The object of the puer is to remove the remaining lime scum and other dirt. For 100 medium lamb fells, 7-8 liters of dog dung paste which has fermented 2 weeks is used. This is diluted with sufficient hot water that it may run through a fine sieve, the residue being washed again. The whole is further diluted with warm water so it may be filtered through coarse lime. The filtrate is diluted then in the puering vat and regulated to 22½° C. The fells are driven ½-¾ hour, let rest one hour and driven 10 minutes and so on 3½ hours for light fells.

heavier 10 hours. The desired effect is reached when the flesh is easily stripped off by the finger nail. The flesh is then removed on the beam, and the fells placed in a little water and lathered for 15-20 minutes. This is repeated with fresh water, the fells then rinsed, stacked, drained and laid in tempered water. Without delay they are worked on the grain with polished irons, lengthwise of the back and across the sides. Washing, lathering and rinsing follow, then a second scudding of the grain and the fells go directly to the drench.

For 100 medium lamb fells, 1 kg. wheat bran is reckoned; this is softened 2-3 hours in cold water, then washed twice to remove all mealy portions. The cleaned bran hulls are then mixed with hot water which is run off after settling and the prepared hulls put in the drench vat with the necessary water. The fells are first driven for 10 minutes in water of 25° C. to which a portion of the bran has been added and are then hauled, drained and put in the drench at 25-31°; they are driven with poles 15 minutes and the vat is then covered for 7-12 hours. When the fells float because of gas, mild ware is sufficiently bated, harder ware can be pressed down 1-2 times again. The completion of the drenching can be recognized by stretching the fell over the back of the hand, when the bran hulls adhering to the flesh should show through the grain; further the skin readily yields at the back and neck when pulled. The fells are then rinsed in the drench liquor, cleaned from bran with the grain iron and laid out dry from the beam for tawing.

The tawing paste ("Gar") which greatly varies, normally contains 4 kg. alum, 1 kg. salt, 12 kg. wheat flour, 140-150 egg yolks, 30 liters water. It is essential the flour be of the finest; the particles penetrate the fell, serving as filling and "nourishing" material and act on the alum during storage preventing spewing. Fresh egg yolk is the best but barrelled egg yolk is generally used on the large scale. One liter preserved egg-yolk = 50 yolks. The amount of alum must be exactly suited; when too much it deposits crystals in the grain, preventing a gloss and giving a harsh feel. With the sorting in equivalent lots as described at the outset, the computation is the same for all. The salt should never be more than ¼ the alum; with greater amounts the leather attracts moisture from the air and the gloss suffers. For one of the above lots, 12 kg. alum, etc., are used. For economy the tawing may be done in the drum, but for quality, treading by foot in the tub is employed. The leather loses firmness in the drum and becomes too loose. To prepare the paste for the tub, the flour is made up with warm water to a stiff porridge and then well trodden. The egg yolk is diluted with 10 liters luke warm water, sifted, added and trodden in. Then the alum and salt solutions of 56° C. are added and finally water so that the whole is at 40-44° C. All these additions are carefully made in portions, each being fully incorporated before the next is added. For treading, 5 men are required, the first stage being 30 minutes, then 10 minutes rest; 3 such turns are required when the paste should be entirely on the fells. They are let cool a few hours, then folded on the

back grain to grain, and hung over poles to dry; when dry, they are turned to avoid creasing. This drying is at 37-50° C. at the highest in well ventilated rooms; 24-48 hours at the most. The dry hides are let shrink in a cool room and bound in packs. The currying is the same for all and will be described later. Kid leather will next follow.

(To be continued.)

PATENTS.

Process of Preparing Tanning Materials for Extraction. U. S. Patent No. 979,080. HERMANN MECHLENBURG, Köpenick, near Berlin, Germany, assignor to Nitritfabrik Actiengesellschaft.

The process consists in subjecting the material to the action of gaseous sulphur dioxide before leaching.

Leather Stripping and Trimming Machine. U. S. Patent No. 979,219. PETER STEIN, Chicago.

Apparatus for Making Extracts. U. S. Patent No. 979,362. WILHELM WIEGAND, Merseburg, Germany, assignor to Richard Rieder.

The material to be extracted is fed into one end of a long trough, along which it is pushed by a conveyor of the interrupted screw type. Water is introduced at the other end, where the spent material is removed. The liquor flows out of a high opening at end where the new material is introduced.

Belt-Stretching Device. U. S. Patent No. 980,490. GEORGE A. CLENDENNING, Mulberry, Indiana.

Leather-Working Machine. U. S. Patent No. 982,007. ALEXANDER H. KEHRHAHN, Frankfort-on-the-Main, Germany.

Leather Glazing Machine. U. S. Patent No. 982,398. WM. B. TURNER, Melrose, Mass, assignor to the Leather Finishing Machine Co., Boston.

Process of Making Sole-Leather. U. S. Patent No. 983,005. JOHN A. TANNER, Boston; LOUIS L. GREEN, administrator of estate of said tanner, deceased.

The process consists of partial tannage by the two-bath chrome method and then filling with vegetable tanning material.

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EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The opening meeting of this Congress will be held in Washington, D. C., Sept. 4, 1912, and subsequent sessions in New

York City from Sept. 6th to Sept. 13th. A preliminary announcement has just been issued, which will be followed by other announcements as arrangements are completed.

In obedience to a joint resolution of Congress, President Taft extended through Ambassador Reid an invitation to the Seventh International Congress of Applied Chemistry to arrange for holding the Eighth Congress in the United States. The invitation was accepted and the thirteen delegates from the United States to the Seventh Congress were appointed as the nucleus of an Organizing Committee.

Twenty-four sections and subsections have already been organized, not as yet including a section or subsection on leather chemistry. The wish was expressed at the meeting of the American Leather Chemists Association in Chicago, October 1910, that our Association might participate as a Section in this Eighth International Congress. It is not too late for such an arrangement to be made. Members who wish to have our Association participate should urge the Council to take action to that effect.

ON THE COMPOSITION OF TANNING MATERIALS. I.

BIBLIOGRAPHY, 1828-1909.

By Dr. Arthur L. Dean, Sheffield Scientific School, Yale University.

The composition of the tannins, and the nature of the substances which accompany them in nature and appear to have some genetic relation with them, have been the subject of a very considerable number of scientific investigations. Some of these studies have been directed wholly to the problems of organic chemistry and had but remote relation to any practical applications; others have plainly had for their object the identification of tannins in mixtures or the possible equivalence of different tannins.

A practical problem of growing importance to leather chemists is the qualitative examination of tannins in extracts, and with the increasing use of extracts the significance of such examination becomes more evident. As a preliminary to studies directed to this specific practical problem a review of the past work bearing on the subject is indispensable, and as a first step

in such a review the following bibliography is presented, covering the more important contributions up to the close of 1909.

1828 Berzelius, Gerbstoff.
Jahresber., 7, 248.
1829 Geiger, Ueber den Gerbstoff.
Geiger's Mag., 25, 99.
[1](Iron bluing and iron greening tannins.)
Geiger's Mag., 1829, III, 129.
1831 Döbereiner, (Tannin).
N. Jahrb. d. Ch. u. Pharm., 1, 378.
Gerber, Analyse der Eichenrinde.
Arch. d. Pharm., 38, 272.
Nees von Esenbeck, (On Catechu).
Buchner's Repert., 33, 169.
1833 Büchner, Neueste Entdeckungen über die Gerbsäure.
Gekrönte Preisschrift, Frankfurt a. M.
Pelouze, Ueber Darstellung und Zusammensetzung des Gerbstoffs.
Ann. Pharm., 7, 267.
1834 Liebig, Ueber die Zuzammensetzung der Gerbsäure und der Gallussäuren.
Ann. Pharm., 10, 172.
Pelouze, Abhandlung über den Gerbstoff und die Gallussäuren.
Ann. Pharm., 10, 145.
1838 Leconnet, (Preparation of tannic acid from gall nuts).
Journ. d. Pharm., 22, 149.
Robiquet, (Reactions of tannic acid with sulphuric acid and calcium chloride).
Journ. d. Pharm., 22, 483.
1839 Wackenroder, Beiträge zur Kenntniss der Catechusäure.
Annalen, 31, 72.
1841 Hagen, Ueber die Zusammensetzung des Catechins.
Annalen, 37, 336.
Hünefeld, (Transformation of tannic acid to gallic acid by oxidizing agents).
Journ. f. prakt. Chem., 16, 359.
Liebig, Neue Untersuchungen über Gallussäure von Antoine Larocque.
Annalen, 39, 97.
Reinsch, (Pyrocatechuic acid).
Buchn. Repert. 2R., 18, 56.
Zwenger, Ueber Catechin.
Annalen, 37, 320.
Wackenroder, Eigenschaften der Catechusäure.
Annalen, 37, 306.

[1]Titles in parentheses are not exact titles, but indicate the character of the contents of the articles.

1843 Gerber, Ueber das Quercin oder den krystallinischen Stoff der Eichenrinde.
Archiv. d. Pharm., (2) 34, 167.
Larocque, (Conversion of tannic into gallic acid by fermentation).
Journ. f. prakt. Chem., 24, 34.
Stenhouse, On pyrogallic acid and some of the astringent subtances which yield it.
Phil. Mag., 22, 279, also Annalen, 45, 1.
Stenhouse, On some astringent substances as sources of pyrogallic acid.
Phil. Mag., 22, 417.
Wackenroder, (Fermentative change of tannic to gallic acid).
Journ. f. prakt. Chem., 24, 28.

1844 Stahelin und Hofstetter, Chemische Untersuchung einiges Rinden.
Annalen, 51, 63.

1845 Guibourt, (Extraction of tannic acid from gall nuts).
Revue Scient. et Industr., 9, 32.

1846 Dominé, (Tannic acid from gall nuts).
Journ. d. Pharm. et d. Chim., 5, 231.

1847 Guibourt, Mémoire sur les sucs astringents connus sous les noms de Cachou, Gambir, et Kino.
Journ. Pharm., (3) 11, 24, 260, 360; 12, 37, 183, 267.
Mohr, Ueber die Natur der Tanninlösung die bei der Extraction mit Aethererhalten wird.
Annalen, 61, 352.
Wetherill, Recherches sur la transformation de l'acide tannique en acide gallique.
Journ. Pharm., (3) 22, 107.

1850 Laurent, Sur diverses combinaisons organiques.
Compt. Rend., 31, 349.

1851 Gerding, Beiträge zur nähern Kenntniss des Kinogerbstoffs.
Arch. Pharm., (2) 65, 283.

1852 A. Knop u. W. Knop, (Compounds of tannic acid and ammonium sulphate and ammonia).
Journ. f. prakt. Chem., 56, 327.
Laurent, Sur les tannins et les glucosamides.
Compt. Rend., 35, 161.
Robiquet, Recherches sur la fermentation gallique.
Compt. Rend., 35, 19.
Sandrock, (Preparation of tannic acid from galls by the ether method).
Arch. Pharm., (2) 72, 265.
Strecker, Ueber den Milchsäureäther und die Constitution der Gerbsäure.
Annalen, 81, 247.

1853 Grüneberg, (Pyrogallic acid from the extract of Chinese nut galls).
Journ. f. prakt. Chem., **60**, 479.
Hennig, Chemische und pharmakoligische Prüfung des Gummi Kino.
Arch. Pharm., (2) **73**, 129.
Watson, Chemical examination of the berries and bark of *Rhus glabrum*.
Am. Journ. Pharm., **1853**, 193.
Wittstein, (Gallic acid from Chinese nut galls).
Vierteljahrsschr. prakt. Pharm., **2**, 72.
1854 Eissfeldt, Ueber das Kino.
Annalen, **92**, 101.
Hennig, Nachtrag zum Kino.
Arch. Pharm., (2) **77**, 260.
Knop, (Action of ammonium sulphate on tannic acid).
Pharm. Centr., **1854**, 855.
Robiquet, (Tannic acid and gallic acid).
Journ. Pharm., (3) **26**, 29.
Strecker, Untersuchung der Gallaepfelgerbsäure.
Annalen, **90**, 328.
1855 Neubauer, Ueber das Catechu und seine Säuren.
Annalen, **96**, 337.
Rochleder, Notiz über die Gerbsäuren.
Sitzber. d. k. Akad. z. Wien, **18**, 3.
1856 Hennig, Schlussbemerkung über die Natur der Gerbsäure im Kino.
Arch. Pharm., (2) **85**, 150.
Horsley, (Gallic acid from nut galls by the action of sulphuric acid).
Report of the British Association for 1856.
Knop, Ueber Behandlung der nicht flüchtigen organischen Körper mit schwefligsäuren Alkalien.
Chem. Centr., **1856**, 513.
Rochleder, Ueber die Natur der Gerbsäuren.
Chem. Centr., **1856**, 557.
1857 Liebig, Darstellung der Pyrogallussäure.
Annalen, **101**, 47.
Knop, Untersuchung über die Gerbsäure (Schluss).
Chem. Centr., **1857**, 370.
Rochleder, Vorläufige Notiz über den Gallaepfel-Gerbstoff.
Chem. Centr., **1857**, 234.
Rösing, Recherches sur l'acide pyrogallique.
Compt. Rend., **44**, 1149.
1857 Steer, Bereitung der Gallussäure.
Chem. Centr., **1857**, 105.
1858 Kawalier, Ueber den Gallaepfel-Gerbstoff.
Chem. Centr., **1858**, 579.
1859 Lubolat, (Relations of tannic acid to ether).
Journ. f. prakt. Chem., **77**, 357.

1860 Bolley, Das Verhalten der Gallaepfelgerbsäure gegen Aether.
Annalen, **115**, 63.
Delffs, (Moringerbsäure).
N. Jahrb. pr. Pharm., **15**, 166.
Knop, Beiträge zur Kenntniss der Gerbsäure.
Chem. Centr., **1860**, 278.
1861 Sacc, Sur un nouveau principe immediat extrait du cachou.
Compt. Rend., **53**, 1102.
Stenhouse, On some varieties of tannin.
Proceedings of the Royal Soc., **11**, 401.
Wagner, Ueber die Rothgallussäure.
Chem. Centr., **1861**, 47.
1863 Hlasiwetz u. Pfaundler, Ueber das Morin und die Moringerbsäure.
Sitzber. d. k. Akad. z. Wien, (2) **48**, 10.
Kraut u. Delden, Ueber das Katechin.
Annalen, **128**, 285.
1864 Eckert, (On the constituents of oak bark).
Vierteljahresschrift f. prakt. Pharm., **13**, 494.
Hlasiwetz, Ueber das Catechu und das Catechin.
Sitzber. d. k. Akad. z. Wien, (2) **50**, 527.
1865 Hlasiwetz, Ueber das Catechu und das Catechin.
Annalen, **134**, 118.
Luynes et Esperandieu, Sur la preparation et quelques propriétés de l'acide pyrogallique.
Compt. Rend., **61**, 487.
Rösing, Recherches sur l'acide pyrogallique. II.
Compt. Rend., **56**, 1139.
Schützenberger u. Rack, Note sur la catechine, matière colorante du cachou.
Bull. Soc. Chim., (2) **1865**, 5.
1866 Reinsch, (Reaction of sumac tannin).
N. Jahrb. Pharm., **25**, 82.
Wagner, Ueber die quantitative Bestimmung der Gerbsäuren.
Journ. f. prakt. Chem., **99**, 294.
1867 Hlasiwetz, Rembold, Grabowski u. Malin, Ueber einige Gerbsäuren.
Annalen, **143**, 270.
Van Tieghem, Sur la fermentation gallique.
Compt. Rend., **65**, 1091.
1868 Grabowski, Ueber die Gerbsäure der Eichenrinde.
Annalen, **145**, 1.
Löwe, Ueber Gerbsäure und Gallussäure.
Chem. Centr., **1868**, 701.
Watts, (Tannic acid estimations of the iron blacking and iron greening tannins).
Pharm. J. Trans., (2) **10**, 223.

1869 Fellenberg, Notiz über die einwirkung von Essigsäureanhydrid auf Moringerbsäure.
Chem. Centr., 1869, 797.
Löwe, (Rufigallic acid).
Journ. f. prakt. Chem., 107, 296.
Rochleder, Ueber Catechin und Catechugerbstoff.
Sitzber. d. k. Akad. z. Wien, (2) 59, 35.

1870 Dreykorn u. Reichardt, (Alder tannin).
Dingl. pol. Journ., 195, 157.

Jaffé, Ueber Ruffigallussäure.
Ber., 1870, 694.

1871 Ernst u. Zwenger, Ueber Gallussäure Aether.
Annalen, 159, 27.
Sacc, Recherches sur la formation de l'acide gallique.
Compt. Rend., 72, 766.
Schiff, Ueber Natur und Constitution der Gerbsäure.
Ber., 1871, 231.
Schiff, Ueber Gerbsäure und einige Derivate derselben.
Ber., 1871, 967.

1872 Baeyer, Ueber die Verbindungen der Aldehyde mit den Phenolen und aromatischen Kohlenwasserstoffen.
Ber., 1872, 1094.
Löwe, Ueber reine Gallaepfelgerbsäure.
Zeit. f. anal. Chem., 12, 365.
Schiff, Ueber Gallussäure und Gallussäureäther.
Annalen, 163, 209.
Schiff, (Tannic acid) in letters.
Ber., 1872, 291, 437.

1873 Ettinghausen, Ueber *Castanea vesca* und ihre vorweltliche Stammart.
Sitzber. d. k. Akad. z. Wien, (1) 65, 147.
Schiff, Untersuchungen über die Natur und Constitution der Gerbsäure.
Annalen, 170, 43.

1874 Löwe, Catechusäure und Catechugerbsäure.
Zeit. f. anal. Chem., 1874, 113.
Stenhouse, Ueber die Einwirkung von Brom auf Protocatechusäure, Gallussäure und Tannin.
Annalen, 177, 186.

1875 Löwe, Ueber die Gerbsäure der Divi-divi Schoten und deren Beziehung zur Gallussäure.
Zeit. f. anal. Chem., 14, 35.
Löwe, Ueber die Gerbsäure der Myrobalanen und ihre Identität mit den Ellagengerbsäure.
Zeit. f. anal. Chem., 14, 44.

1875 Löwe, Ueber die Gerbsäure der Knoppern und ihre Identität mit Gallusgerbsäure.
Zeit. f. anal. Chem., 14, 46.
Oser, Ueber die Gerbsäure der Eiche.
Sitzber. d. k. Akad. z. Wien, (2) 72, 165.
Rembold, Ueber einige Abkömmlinge der Ellagsäure.
Ber., 1875, 1494.
Schiff, Ueber die Natur und Constitution der Gerbsäure. II.
Annalen, 175, 165.

1876 Etti, Ueber Catechin.
Sitzber. d. k. Akad. z. Wien, (2) 74, 335.
Johansen, (Tannins of willow, oak and elm barks).
Arch. Pharm., (3) 9, 210.
Voelker, An analysis of Raiz del Indio. (Canaigre.)
Am. Journ. Pharm., 1876, 49.

1877 Jean, Note sur la quebracho, nouvelle matière tannifère.
Bull. Soc. Chim., 28, 6.

1878 Barth u. Goldschmiedt, Ueber die Reduction der Ellagsäure durch Zink-Staub.
Ber., 1878, 846.
Etti, Ueber das malabarische Kinogummi.
Sitzber. d. k. Akad. z. Wien, 78, 561.
Etti, Report of the U. S. Commissioner of Agriculture, p. 119.
Canaigre.

1879 Arata, Estudio sobre el acido quebrachotanico.
An. Soc. Cientif. Argent. Buenos Ayres.
Barth u. Goldschmiedt, Studien über die Ellagsäure.
Ber., 1879, 1237.
Proctor, Weselsky's reaction for phloroglucin.
Chem. News, 39, 245.

1879 Schiff, Ueber Digallussäure.
Ber., 1879, 33.
Schiff, Zur Constitution der Ellagsäure.
Ber., 1879, 1533.

1880 Böttinger, Ueber Phlobaphen, Eichenroth, und Lohgerberei.
Annalen, 202, 269.
Etti, (Tannic acid of oak bark).
Sitzber. d. k. Akad. z. Wien, (2) 81, 495.
Lehmann, Vergleichende Untersuchungen einiger Catechu und Gambir-Proben.
Inaugural Dissertation, Dorpat, 1880.
Liebermann u. Tauchert, Zur empirischen Formel des Katechins.
Ber., 1880, 694.

1881 Böttinger, Ueber den Zucker der Eichenrindegerbsäure.
Ber., 1881, 1598.
Etti, Beiträge zur Kenntniss des Catechins.
Monatsh. d. Chem., 2, 547.
Löwe, Ueber die Gerbsäure der Eichenrinde.
Zeit. f. anal. Chem., 20, 208.
Strohmer, Ueber das Vorkommen von Ellagsäure in der Fichtenrinde.
Monatsh. f. Chem., 2, 539.

1882 Barth und Schreder, (Fusion of gallic acid with sodium hydroxide).
Sitzber. d. k. Akad. z. Wien, (2) 86, 565.
Schiff, Ueber Protocatechugerbsäure und über Anhydride aromatischer Oxycarbonsäure.
Ber., 1882, 2588.

1883 Eitner, (On tannic acids).
Der Gerber, 1883, 232.
Kremel, Constitution of Kino.
Am. Journ. Pharm., 1883, 267.
Tauchert, Darstellung von Pyrogallussäure.
Ber., 1883, 2327; D. P. 23347, Aug. 29, 1882.
Young, A distinctive test for gallic acid.
Chem. News, 48, 31.

1884 Bergholz, Ein Beitrag zur Kenntniss der Kinogerbsäure.
Inaugural Dissertation, Dorpat, 1884.
Böttinger, Zur Kenntniss der Hemlockgerbsäure.
Ber., 1884, 1041.
Böttinger, Ueber Digallussäure.
Ber., 1884, 1475.
Böttinger, Erfahrungen uber die Acetylirung der Gallussäure, des Tannin und deren Anwendung.
Ber., 1884, 1503.
Etti, Ueber das Verhalten von Tannin und Eichenrindegerbsäure gegen verschieden en Reagenzien.
Ber., 1884, 1820.
Guyard, The action of the air upon solutions of tannin and on the determination of tannins.
Chem. News, 50, 26.
Nass, (Composition of chestnut wood tannin).
Inaugural Dissertation, Dorpat, 1884.
Nasse, Ein neue Pyrogallol-Reaction.
Ber., 1884, 1166.
Will u. Albrecht, Ueber einige Pyrogallussäure und Phloroglucinderivate.
Ber., 1884, 2098.

1885 Hunt, Preliminary note on the synthesis of tannin.
Chem. News, **52**, 49.
Kohnstein, (Testing of tanning materials with bromine).
Der Gerber, **1885**, 74.
Meerkatz, (Oak and chestnut wood extracts).
Der Gerber, **1885**, 193.

1886 Saul, (Reactions of tannin and gallic acid with thymol).
Pharm. J. Trans., (3) **17**, 387.
Simand u. Weiss, (Investigation of the tanning extracts).
Der Gerber, **1886**, 1.

1887 Böttinger, Ueber Abkömmlinge der Eichenrindegerbsäure.
Annalen, **240**, 330.
Böttinger, Ueber Eichenholzgerbsäure.
Ber., **1887**, 761.
Eitner, Valonia.
Der Gerber, **1887**, 17.
Jacobson u. Julius, Ueber ein Condensationsproduct der Zimmtsäure und Gallussäure.
Ber., **1887**, 2588.
Simand, (Effect of hot and cold extraction on the composition of tanning extract).
Der Gerber, **1887**, 161, 171.

1888 Böttinger, Ueber Verbindungen von Leim und Gerbsäure.
Annalen, **244**, 227.
Böttinger, Einiges über Gallussäure und Tannin.
Annalen, **246**, 124.
Lidow, (Tannic acid content of sumac).
Journ. d. russ. phy.-chem. Gesellsch., **1888**, 607.
Schiff, Ueber Isomere der Gerbsäure.
Annalen, **245**, 35.

1889 Böttinger, Ueber Benzoyltannin.
Ber., **1889**, 2706.
Etti, Zur Chemie der Gerbsäuren.
Monatsh. f. Chem., **10**, 647, 805.
Hoppe-Seyler, Ueber Huminsubstanzen, ihre Entstehung und ihre Eigenschaften.
Zeit. f. physiol. Chem., **13**, 66.
Paterno, (Molecular weights of gallic, tannic and digallic acids).
Zeit. f. phys. Chem., **4**, 457.
Petrowitsch, Kalk im Gerbmaterial.
Zeit. f. anal. Chem., **28**, 606.
Rawson, On some new tests for tannic and gallic acids.
Chem. News, **59**, 52.
Schiff, Zur Kenntniss der Phloroglucingerbsäure.
Annalen, **252**, 87.

1889 Sonne u. Kutscher, Ueber die Einwirkung von Luft. und Wärme auf den Gerbstoff der Weidenrinde.
Zeit. f. angew. Chem., **1889**, 508.
Trimble, (Canaigre).
Am. Journ. Pharm., **1889**, 397.
1890 Böttinger, Ueber einer neue Reaction des Tannins.
Annalen, **156**, 341.
Böttinger, Zur Oxidation der Gallussäure, des Tannins und der Eichengerbsäuren.
Annalen, **257**, 248.
Böttinger, Weiteres uber Gallussäure, Tannin und Eichengerbsäuren.
Annalen, **258**, 252.
Böttinger, Ueber die Einwirkung von Phenylhydrazin auf Gerbextracte.
Annalen, **259**, 125.
Böttinger, Noch Einiges über Gallussäure, Tannin und Eichengerbsäuren.
Annalen, **259**, 132.
Fölsing, Klärung und Entfarbung von Gerbstoffextracten.
D. R. P., **53**, 398.
Kapf, (Canaigre).
Färberztg., **1889**, **1890**, 313.
Smith, Böttinger's new reaction for gallic and tannic acids.
Journ. Soc. Chem. Ind., **9**, 450.
1890 Spence, Notes on gallotannic and gallic acids.
Journ. Soc. Chem. Ind., **9**, 1114.
Villon, The manufacture of colorless tannins.
Chem. News, **62**, 195.
1891 Böttinger, C., Ueber die Gerbsäure des Eichenholzes.
Annalen, **263**, 108.
Böttinger, C., (Some derivatives of tannin).
Arch. Pharm., **229**, 439.
Guignet, Transformation de l'acide gallique et du tannin en acide benzoique.
Compt. Rend., **113**, 200.
Gutknecht, (Separation of Catechin from Catechu).
Chemikerzeit., **1891**, 959.
Klinger & Bujard, Ueber die Canaigre wurzel, ein neues Gerbmaterial und über Gerbstoffbestimmungen.
Zeit. f. angew. Chem., **1891**, 513.
Sabanejew, (Molecular weight of gallic acid and tannin).
J. d. russ. phys. chem. Ges., **21**, 1, 515; **22**, 1, 102.
Sonne, W., Zur Kenntniss der Gerbstoffe.
Zeit. f. angew. Chem., **1891**, 75.
Trimble, Henry, Chestnut-wood tannin.
Chem. News, **64**, 231; Jour. Franklin Inst., **132**, 303.

1891 Zölffel, G., (Tannins of algarobilla und myrobalans).
Jahresber., **1891**, 2210.

1892 Riedel, J. D., Gewinnung und Reinigung von Tannin.
D. R. P., **57**, 633.
Adolphi, W., Zur Kenntniss der Chebulinsäure.
Inaug. Diss. Dorpat.

1893 Eitner, W., (Changes of tanning materials).
Gerber, **1893**, 1.
Sisley, Paul, Sur la préparation du tannin pur et le dosage du tannin.
Bull. Soc. Chim., (3) **9**, 755.
Trimble & Peacock, The preparation of the oak tannins with special reference to the use of acetone as a solvent.
J. Am. Chem. Soc., **15**, 344.

1894 Andreasch, A., (Reactions of the tanning materials).
Gerber, **1894**, 195.
Procter, H. R., On the qualitative determination of tanning materials.
J. Am. Chem. Soc., **16**, 247.
Trimble, Henry, The Tannins. 2 vols. J. B. Lippincott Co.
von Schröder, Bartel, & Schmitz-Dumont., Ueber Zuckerbestimmung und über die Zucker gehalte der Gerbmaterialien, Gerbextracte, etc.
Dingl. pol. J., **293**, 229, 252, 281, 297.

1895 Böttinger, C., Ueber Glucosazon aus Sumach und Vallonen.
Arch. Pharm., **233**, 125.
Fajans, L., Studien über Tannin.
Zeitschr. angew. chem., **1895**, 471.
Günther, F., Das optische verhalten und die chemische Constitution des Tannins.
Ber. d. pharm. Ges., **5**, 297.
Koch, F., Beitrage zur Kenntniss der mitteleuropäischen Galläpfel, so wie der Scrophularia nodosa.
Arch. Pharm., **233**, 48, 240.
Schiff, H., Ueber das optische verhalten der Gerbsäure.
Chemikerzeit, **19**, 1680.

1896 Böttinger, K., Ueber das verhalten der Gallussäure und des Tannins gegen Jodquecksilberchlorid.
Chemikerzeit., **20**, 984.
Gawalowski, Wodurch ist die Erkennung und Unterscheidung der einzelnen Gerbsäurearten, sowie deren chemischer Nachweis ermöglicht?
Chemikerzeit., **1896**, 4.
Günther, F., Das optische Verhalten und die chemische Constitution des Tannin.
Chem. Centr., (1) **67**, 154.

Harnack, E., Ueber eine in Vergessenheit gerathene Farbenreaction der Gallussäure und des Tannins.
Arch. Pharm., **234**, 537.
Merck, E., Ueber die Condensation der Gerbstoffe mit Formaldehyd.
Chem. Centr., (1) **67**, 560.
Perkin & Gunnell, The coloring matter of Quebracho Colorado.
J. Chem. Soc., London, **69**, 1303.
Perkin & Young, Coloring matter of Sicilian Sumach, *Rhus coriaria*.
J. Chem. Soc., London, **69**, 1299.
Schiff, H., Weiteres zur Constitution der Gerbsäure.
Chemikerzeit, **20**, 865.

1897 Dieterich, K., Ueber Gambier-Fluorescin und Gambir-Catechuroth.
Ber. d. pharm. Ges., **7**, 153.
Kunz-Krause, Beiträge zur chemie der sogenannten Gerbsäuren (Glycotannoide).
Chemikerzeit., **21**, 941.
Lepetit, Dollfus und Ganszer, Verfahren zur Umwandlung natürlicher Farb-und Gerbstoffe in neue Verbindungen mittelst Alkalisulfiten.
D. R. P., **91**, 603.
Perkin, A. G., The yellow coloring principles of various tannin matters.
J. Chem. Soc., London, **71**, 1131.
Walden, P., Ueber das optische Verhalten des Tannin.
Ber. d. d. chem. Ges., **30**, 3151.

1898 Alsop & Yocum, Composition of the ashes of some raw tanning materials.
J. Am. Chem. Soc., **20**, 338.
Andreasch, F., (Sicilian Sumac and its adulteration).
Gerber, 1898, 1178.
Flawitsky, Eine Berwerkung über die optische Activität des Tannins.
J. russ. phys. chem. Ges., **30**, 748.
Kunz-Krause, Ueber die Farben-und Fällungsreactionen der Tannoide und deren Abhängigkeit von der Natur, bezw. Constitution des einen, besw. der beiden Reactionscomponenten.
Schweiz. Zeitschr. Pharm., **36**, 424.
Kunz-Krause, H., Versuch einer Classification der sogenannten Gerbstoffe.
Pharm. Centr. H, **39**, 401, 421, 441.
Möhlau & Kahl, Ueber die Producte der Einwirkung von Formaldehyd auf Gallussäure.
Ber. d. d. chem. Ges., **31**, 259.

1898 Rosenheim & Schidrowitz, The optical activity of gallotannic acid.
J. Chem. Soc., London, **73**, 878.
Rosenheim & Schidrowitz, The influences modifying the specific rotatory power of gallotannic acid.
J. Chem. Soc., London, **73**, 885.
Seyda, Anton, Eine empfindliche Gerbsäure reaction.
Chemikerzeit., **22**, 1085.
Walden, P., Ueber die vermeintliche Identität des Tannins mit der Digallussäure.
Ber. d. d. chem. Ges., **31**, 3167.
1899 O'Callaghan & Randall, Sumach and its adulterants.
Jour Soc. Chem. Ind., **18**, 105.
1900 Fernbach, Sur la tannase.
C. R., **131**, 1214.
Pottevin, La tannase, diastase dédoublant l'acide gallotannique.
C. R., **131**, 1215.
1903 Lühm, Malabarkino.
Pharm. Zeitg., **48**, 593.
Ridenour, N. G., Catechu.
J. Frankl. Inst., **156**, 417.
White, E., (Kino: An investigation of its constituents).
Pharm. J., (4) **16**, 676.
1904 Korner, Th., (Proof of adulteration of quebracho extract).
D. Gerberzg., **1904**, Nr. 115.
Trotman, S. R., The mineral constituents of sumac.
J. Soc. Chem. Ind., **23**, 1137.
White, E., (Kino: An investigation of its constituents. II. The constitution of kino tannic acid).
Pharm. J., (4) **17**, 702.
1905 Herzig u. Tscherne, Ueber methyliertes Tannin.
Ber. d. d. chem. Ges., **38**, 989.
Manea, A., (Methode zur Ermittlung der Gallusgerbsaure in den Gerbstoffmaterialien).
Bull. Soc. des Sciences de Bucarest., **14**, 471.
Nierenstein, M., Zur Kenntniss des Quebrachogerbstoffs I.
Collegium, 69.
Nierenstein, M., Zur Konstitutionsfrage des Tannins.
Ber. d. d. chem. Ges., **38**, 3641.
Nierenstein, M., Zur näheren Kenntniss einiger "Blume" gebender Gerbstoffe.
Collegium, **1905**, 21, 197.
Paessler, J., Ueber Malettorinde.
Collegium, **1905**, 224, 232, 237.
Utz, Beitrag zur Frage über die Aufspaltung der Gallusgerbsäure.
Chemikerzeit., **29**, 31.
1906 Dekker, J., Ueber die Konstitutionsformel des Tannins.
Ber. d. d. chem. Ges., **39**, 2497, 3784.

1906 Dekker, J., De Looistoffen, botanischchemische monographie der tanniden.
Bulletin van het Koloniaal Mnseum te Haarlem, No. 35 and No. 39.
Nierenstein, Vorläufige Mitteilung über das chinintannat.
Collegium, 1906, 108.
Nierenstein, M., Zur Konstitution der Gerbstoffe.
Collegium, 1906, 45.
Nierenstein, M., Zur Kenntniss des Quebrachogerbstoffs II.
Collegium, 1906, 141.
Paessler, J., Eine vorläufige Mitteilung über ein Verfahren zur Unterscheidung verschiedener Gerbextrakte.
Collegium, 1906, 287.
Sack, J., Untersuchung auf gerbstoffhaltige Produkte.
Inspectie von den Landbouw in West-Indie, Bulletin No. 5, 1.
Strauss & Geschwendner, Beiträge zur Kenntnis einiger Gerbstoffe.
Zeit. f. angew. chem., 19, 1121.
Thoms, H., Zur Gerbstoffforschung I.
Ber. d. pharm. Ges., 15, 303.
Thoms, H., Zur Gerbstoffforschung II. Ueber das Eutannin.
Apoth.-Ztg., 21, 354.
1907 Alpers, Karl, Untersuchungen über die Bestandtheile der Blätter von Carpinus Betulus (ein Beitrag zur Kenntniss der Ellagsäure und der Gerbsaüren).
Arch. Pharm., 244, 575.
Drabble & Nierenstein, (Ueber die Rolle der Phenole, der Gerbsäuren und der Oxybenzoesäuren bei der Korkbildung).
Collegium, 1907, 179.
Glücksmann, Zur Kenntnis des Tannins.
Collegium, 1907, 282, 287, 294, 301, 313, 321, 325, and 333.
Jean & Frabot, (Einwirkung des Methanal auf Gerbstoffe).
Ann. chim. Analyt. Appl., 12, 49.
Nierenstein, M., Beitrag zur kenntnis der Gerbstoffe.
Ber. d. d. chem. Ges., 40, 4575.
Nierenstein, Zur Konstitutionsfrage des Tannins II.
Ber. d. d. chem. Ges., 40, 916.
Paessler, J., Ueber Valonea-Extrakt.
Collegium, 1907, 309.
1908 Cavazza, L. E., Beitrag zum Studium der Gerbstoffe.
Chem. Centralb., 1908, (1), 1648.
Dekker, J., (The tannin of the bark of Eucalyptus occidentalis).
Archives neerland. sc. exact. et nat., (2) 14, 50.
Eitner, W., Catechu und Gambir.
Gerber, 1908, 85.
Lloyd, S. J., Preliminary note on the Constitution of Gallotannic acid and of the tannins in General.
Chem. News, 97, 133.

1908 Nierenstein, Zur Konstitutionsfrage des Tannins, III.
Ber. d. d. chem. Ges., 41, 77.
Nierenstein, M., Zur Konstitutionsfrage des Tannins, IV.
Ber. d. d. chem. Ges., 41, 3015.
Stiasny, E., Ueber eine Gerbstoff reaktion und ihre Anwendungen.
Collegium, 1908, 419.
Wladika, J., (Die Myrobalane in der Extraktfabrikation).
Gerber, 1908, 250.

1909 Biginelli, (Composition and chemical constitution of artificial tannin).
Gaz. Chim. Ital., 39, [II] 268, 283.
Cavassa, L. E., Mikrochemische und physiologische Studien über die Tannine.
Ztschr. f. wiss. Mikroskop., 26, 59.
Franke, Hans, Die pflanzlichen Gerbstoffe.
See Collegium, 1909, 330.
Herzig & Renner, Zur Kenntniss des Methylotannin.
Monatschrif. f. Chem., 30, 543.
Iljin, L. F., Ueber die Einwirkung von Zinkstaub auf Tannin.
Journ. f. prakt. chem., (2) 80, 332.
Iljin, Ueber die Zusammensetzung des Tannins.
Ber. d. d. chem. Ges., 42, 1731.
Nierenstein, M., Ueber die sogenannte "Blume" der Pyrogallolgerbstoffe und ihre Identität mit der Ellagsäure.
Chemikerzeit., 33, 87.
Nierenstein & Webster, Zum Mechanismus der Phlobaphenbildung.
Collegium, 1909, 337.
Nierenstein, Ueber das Drehungsvermögen des Tannins.
Chemikerzeit., 33, 126.
Nierenstein, M., Zur Konstitutionsfrage des Tannins, V.
Ber. d. d. chem. Ges., 42, 1122.
Nierenstein, M., Beitrag zur Kenntniss der Gerbstoffe, II. Ueber Luteosäure.
Ber. d. d. chem. Ges., 42, 353.
Nierenstein, M., Zur Konstitutionsfrage des Tannins, VI.
Ber. d. d. chem. Ges., 42, 3552.
Paessler, J., Ueber eine neue Gambiersorte.
Collegium, 1909, 16.
Philip, M., Kurze Notiz über eine Gerbstoff reaktion.
Collegium, 1909, 249.
Rosenheim, Otto, Notiz zur Geschichte der optischen Aktivität des Tannins.
Ber. d. d. chem. Ges., 24, 2452.
Sisley, P., (Artificial preparation and constitution of Ellagic acid).
Bull. Soc. Chim., (4) 5, 72.

ON THE USE OF OAK LEAVES IN TANNING.

By the Rev. Mr. Swayne.[1]

(In connection with Dr. Dean's bibliography printed in this number, readers of the Journal may be interested in this article, believed to be one of the very earliest on the subject of tanning chemistry. Mr. Swayne describes one of the first attempts to determine the quantity of tannin in a tanning material, and makes one of the earliest suggestions ever printed in regard to the manufacture of a tanning extract. One would have to consult a very old dictionary to find the meaning of "calx of iron" and "martial vitriol," but the context explains them sufficiently.—Ed.)

Knowing that the bark of the oak was a chief material in the art of tanning leather, and conceiving that every other part of that tree was fraught with the same astringent principle, through which the bark becomes so efficient in that art, the thought had often occurred that the leaves might be advantageously applied for the same purpose. Having in my possession a quantity of those leaves, which had been collected on account of the galls attached to them, I was desirous of ascertaining the proportion of astringent matter contained in them, and of comparing it with that contained in the bark. It was some time before I could think of a method of doing this, and whether the method I at length used was fully adequate to the intention must be left to the determination of those who have more knowledge in chemistry than I can pretend to. The well-known property which this astringent matter possesses, of uniting or striking a black color with the calx of iron, suggested to me that its quantity might probably be ascertained by extracting this matter through the medium of hot water, in which it is known to be soluble, saturating the extract with a known weight of the calx of iron, and afterward filtering, drying and weighing it. Supposing martial vitriol to contain iron in a very proper state for this experiment, the first thing I had to do was to ascertain the weight of iron in a given weight of vitriol, and this I attempted by the following process: I weighed five pennyweights of

[1] Published in the *Transactions* of the Society of Arts, Manufactures and Commerce in 1792 and copied into the *Literary and Biographical Magazine and British Review* for April, 1793, from which we take it.

vitriol, dissolved it in water and added a like weight of vegetable fixed alkali, which immediately precipitated the iron. The mixture was then thrown on a paper filter, the weight of which was noted down, and after being plentifully elutriated with hot water, the residue was dried and weighed. Its weight, exclusive of the filter, was two pennyweights, thirteen grains. This proportion of iron in martial vitriol differs from that given by Professor Neumann from his analysis, but it is necessary to mention that the vitriol which I made use of had been kept in a dry place, uninclosed in a glass vessel, by which it had lost much of its water of crystallization, and this accounts for the difference. At the same time and from the same parcel of vitriol, I weighed several other portions for after experiments.

The weight of iron in a given weight of vitriol being known, I then attempted to follow the process above suggested; but upon trial found that the colored particles were so minute or so intimately mixed that they passed with the fluid through the filter. This I attributed to the presence of vitriolic acid, and its close attachment to the colored particles. With a view, therefore, to destroy this suspected combination by presenting to the acid a substance with which it has a nearer affinity, I added some mild salt of tartar, which instantly produced the desired effect, and brought on an entire separation of the colored mass. I then went on with my intended experiments in the following manner.

I took a half-peck measure full of dried oak leaves well pressed down, from which I had before separated several ounces of mushroom galls, and having put them in a brass kettle with a sufficient quantity of water, boiled them therein for two hours. The decoction was then poured from the leaves and fresh water added to them. This was likewise boiled for a considerable time, till it was judged that the water had extracted all the astringent matter. Both decoctions were then boiled down in the same kettle to one gallon. In a certain measure of this concentrated extract, I dissolved five pennyweights of green vitriol, and afterward added the like weight of salt of tartar. This mixture was then thrown on a filter of sinking paper, the weight of which was three pennyweights, and after being perfectly elixated with hot water, the residuum was dried and weighed.

	Dwts.	Grs.
Filter and contents	6	14
Filter	3	0
	3	14
Calx of iron	2	13
There remains astringent matter	1	1

Two pints of this reduced extract were still farther evaporated to one pint, and a like measure of this was treated as the former, giving 1 dwt. 21 grs. of astringent matter.

I then obtained from a tanner two pounds of oak bark, which was perfectly dry, and after cutting it into thin shavings with a plane, boiled it in three portions of water for several hours, till from the color as well as the taste of the last decoction the astringency seemed to be perfectly extracted. These several decoctions were added together and evaporated to the same quantity as those of the leaves, namely one gallon. An equal measure of this as above produced by the like treatment 2 dwts. 2 grs. of astringent matter.

A quart of this extract was further concentrated to a pint, and an equal measure of this was treated as before, the remainder of astringent matter being 4 dwts. 8 grs.

These experiments do not exactly tally, since in both with the leaves and bark, the amount of astringent matter in the second experiment ought to have been double that of the first. The supposition of a small inaccuracy in the weighing, or a small loss in the process of these experiments, will tend to reconcile them. Where the error lay in the first instance, I cannot pretend to guess. In the first experiment with the bark, the filter caught fire while it was drying, and although it was extinguished almost immediately, yet there must have been a loss of some grains from it. Notwithstanding the experiments do not perfectly accord, yet I think we may fairly deduce from them, provided the method of trial be not objected to, that half a peck of leaves contain nearly as much astringent matter as one pound of bark.

Oak bark was sold in this neighborhood last season for five guineas a ton. In its marketable state it is by no means sufficiently dry for preservation, and the tanners are obliged to dry it more perfectly, and at considerable trouble and expense they

likewise get it cleaned from much extraneous matter. The loss of weight from these operations cannot, I should suppose, be estimated at less than twenty shillings per ton. What I mean is that if a ton of bark cost the tanner in the first purchase five guineas, the same weight of bark when properly dried and cleaned will stand him in six pounds five shillings; for the sake of easier calculation we will say six pounds. I have heretofore had oak leaves collected for the purpose of making hotbeds for melons (for which they are excellent), at three-pence and four-pence per sack of four bushels, or thirty-two half-pecks, which according to the conclusions above are equal to thirty-two pounds of bark, which at six pounds per ton comes to 1 shilling and eight-pence halfpenny and a fraction. If then my premises stand unimpeached, it will follow that the tanner might obtain as much astringent matter in leaves for four-pence as costs him in bark five times that sum. Whether it would equally answer his purpose remains to be proved.

There would undoubtedly be much trouble and some expense in drying the leaves, which would be necessary in order to preserve them, and they would occupy much room. Perhaps for these reasons the most economical plan would be to obtain a concentrated extract from them, on or near the place where they could be collected, which might be conveyed and stored in casks. This likewise remains as the subject of experiment, but before leaves can in any way be legally used by the tanner, it is necessary that the act of parliament be repealed which confines him to the use of ash and oak bark. This restriction was probably laid, not solely from the belief that those substances were the most proper for the purpose of tanning leather, but likewise, to encourage the planting and nurturing of those valuable timber trees. Be this as it may, at present it rather operates to their destruction, than to their preservation or increase, since the high price which oak bark now bears proves an irresistible temptation with needy proprietors to cut down their oaks before they arrive at a proper age for timber. Should oak leaves ever come in much request for tanning, this doubtless would prove an antidote to the rage of felling, and an effectual preservative of timber, since no one

surely would ever think of felling his oaks prematurely whilst they yielded him an annual profit by standing.

N. B. The vitriol was in every case sufficient to saturate the astringent matter, and the quantity of salt of tartar sufficient for the acid.

THE LEATHER CHEMIST OF 1951.[1]

Prof. H. R. Procter.

Few of us remember much of the leather chemist of 1871, partly on account of our age-limit, but mainly because he did not exist! Men there were (all honor to them) like Jackson Schultz in America, and W. Nelson Evans in England, who devoted thought to the study of tanning, and freely gave to the public the results of their labor; and chemists like the late Prof. Knapp who threw valuable light on the theory of the process; but the properly trained chemist who makes the technology of leather his profession was not yet evolved. Those of us whose recollections enable us to judge of the advance which has been made since then, feel that it is a source of pride and encouragement; and knowing the accelerating ratio with which knowledge grows, look forward with curiosity and confidence to a time which only the younger of us will live to see.

To look forward 40 years may indeed be futile, for 10 may carry us beyond the limits which we can at present guess; but it may not be uninteresting to speculate on the road to be travelled by the young and vigorous men who will follow us. Prior to 1871, leather manufacture had indeed made great progress, but principally in mechanical improvements:—today and in the immediate future, it is, I believe, the turn of the chemist. During the last 20 years he has done much in sharpening his tools:—tannin analysis has been brought almost as near perfection as our present empirical methods are likely to carry us, and further progress can only be made through a much extended knowledge of the chemistry of the individual tannins, which is the more imperative since the advent of extracts has made adulteration and mixture so easy. Long before 1951 the

[1] From the *Shoe and Leather Reporter* of March 16, 1911.

chemist will no doubt know the causes of the difference of one tannin from another and will very probably be able to transform and modify them at will, while their economical synthetic production is not impossible; but from their cheapness and abundance in the vegetable world it is at present more likely that they will prove the raw materials for new products. If this is to be done the chemist will have to be versed in the structural formulæ, and the general organic reactions, which at present he is inclined to regard as purely academic.

Apart from tannins, the general methods of analysis and control have been vastly improved, and will go on improving as the need for them becomes obvious. In my own Institute we have a small laboratory in the midst of the tannery, which is devoted to continuous control of limes and liquors, and all the other products which form part of the tanning routine; and we are continually finding new directions in which such control can be applied, and new methods of carrying it out. To develop this work, the future chemist must have a wide experience in the art of chemical analysis, and sufficient general knowledge of reactions, organic and inorganic, to invent new methods for new purposes:—the man who shirks his general analytical work because "it has nothing to do with tanning" will not be the chemist of the future, though he may be his bottle-washer!

Another branch which is usually considered at present superfluous, but which will be an important part of the equipment of the future leather chemist is that of physical chemistry, theoretical and practical, and especially of its modern sub-branch, the chemistry of colloids. To the present-day tanner the very names are repellant, and the idea of measuring electrical conductivities and potentials as an aid to leather manufacture will seem absurd; and I can only assure him that such means are actually in use, not only here, but in one of the most important light leather tanneries of Great Britain with very valuable practical results; and that in this particular direction we are still at the very beginning. To give some instances, the electrometric measurement of the potential of a hydrogen electrode is the only known way of measuring the actual acidity of a tan-liquor as it exists in the vat, which often has no direct relation to that

determined by titration, but which is the only value which really measures the action of the acid on the hides. As this becomes understood we shall be able easily to control it as we wish, and to decide exactly how much or how little the hides shall swell in liming, drenching, or tanning. I may instance the fact that we are in this institute "neutralizing" our chrome stock with a liquid of Dr. Stiasny's invention, which goes exactly far enough, and will go no further if the goods are left in it a week, so that the process, (and the subsequent fat-liquoring) has completely lost its difficulties.

Possibly the future chemist will need to be an expert bacteriologist, but this is less certain, since in 1951 no one will be using dog or pigeon dungs, or bran drenches, and you will sterilize your hides and liquors, and add the required acid by measure. Very possibly by that date there will be no more vegetable tanning, since all the forests may have been converted into newspapers, and it may be necessary to print the *Shoe and Leather Reporter* on thin aluminum foil! It is probable, however, that the aluminium salts may be no longer needed for tanning, and even chrome may have to take a back place before some new tanning agent which we have not yet even considered.

This is a strenuous age, and there is prospect of a busy and useful life for the coming young man; but it would be well for the tanners also to lay to heart the fact that his education will be no less costly, and the needed knowledge no less than that of the physician; and that his pay and social status will have to correspond. Looked at from the public point of view, it is much more important to save the life of an industry than that of a millionaire, though we can hardly expect the latter to hold our opinion!

ABSTRACTS.

Enzymatic Studies. S. P. L. SORENSEN. (Continued).—The three curves relating to mixtures of sodium hydroxide (glycocol + NaOH, citrate + NaOH and borate + NaOH) have a point of inflection at ordinate 5, corresponding to 5 cc. NaOH and 5 cc. respectively of glycocol, citrate or borate. Below the ordinate 5, the three curves (corresponding to mixtures richer in NaOH) approach closely and soon coincide. This shows that in these solutions the

concentration of hydroxyl ions is so great that the hydrolysis of the sodium salts of glycocol, citric acid and boric acid has been suppressed, or nearly so. Under these conditions the sodium salts (the glycocol salt containing one atom of sodium per molecule, the citric acid salt three, and the boric acid salt one) behave like other normal sodium salts not hydrolyzed, (*e.g.* sodium chloride), and the concentration of hydroxyl ions of the solution is determined almost exclusively by the excess of NaOH, taking due account of the incomplete dissociation of this hydroxide occasioned by the sodium salts present.

Table 7 shows the concentration of hydroxyl and hydrogen ions calculated for some mixtures of N/10 NaOH and N/10 NaCl (or other sodium salt not decomposable by hydrolysis). The degree of dissociation in each case is taken as 0.841, (see page 149). The last two columns of the table give the exponent of hydrogen ions calculated for these so-

TABLE 7.

COMPARISON BETWEEN MIXTURES OF THE SODIUM SALT OF GLYCOCOL AND NaOH ON THE ONE HAND, AND ON THE OTHER, MIXTURES OF SODIUM CHLORIDE AND NaOH.

Composition of the mixture of glycocol	For the mixtures corresponding to N/10 NaCl and N/10 NaOH, there have been calculated			Exponent of hydrogen found by experiment for the mixture of glycocol
	Alkalinity alk.	Concent. of hydroxyl ions alk.$\times$ 0.841 $= 10 - q$ q	Exponent of hydrogen ions $14.14 - q = p^1$ p^1	p
0 cc. glycocol + 10 cc. NaOH ..	0.1 norm.	1.075	13.065	13.066
1 cc. glycocol + 9 cc. NaOH (= sodium glycocollate + 8 cc. NaOH).....	0.08	1.172	12.968	12.972
2 cc. glycocol + 8 cc. NaOH (= sodium glycocollate + 6 cc. NaOH).....	0.06	1.297	12.843	12.856
3 cc. glycocol + 7 cc. NaOH (= sodium glycocollate + 4 cc. NaOH).....	0.04	1.474	12.666	12.674
4 cc. glycocol + 6 cc. NaOH (= sodium glycocollate + 2 cc. NaOH).....	0.02	1.775	12.365	12.399
4.5 cc. glycocol + 5.5 cc. NaOH (= sodium glycocollate + 1 cc. NaOH).....	0.01	2.075	12.065	12.095
4.9 cc. glycocol + 5.1 cc. NaOH (= sodium glycocollate + 0.2 cc. NaOH)	0.002	2.775	11.365	11.565
5 cc. glycocol + 5 cc. NaOH (= sodium glycocollate + 0 cc. NaOH).....	0.0	7.070	7.070	11.305

lutions (p') and the exponent of hydrogen ions found by experiment for the corresponding mixtures of glycocol, (p).

The concordance between the values p' and p shows that mixtures of glycocol containing any considerable excess of NaOH are to be considered essentially as solutions containing sodium hydroxide and a normal non-hydrolyzable sodium salt.

That the hydrolysis has not been entirely suppressed is shown by the fact that in every case p is a little higher than p', which certainly cannot be attributed to experimental errors. It is only when the mixtures contain a very small excess of sodium hydroxide that the hydrolysis of the glycocol goes further.

There is no well defined point of inflection on the glycocol hydrochloric acid curve at the point 5 cc. HCl + 5 cc. glycocol, which may be accounted for by the fact that the acid character of glycocol is more strongly marked than its power to form a definite compound with HCl.

The other branch of the curve of citrates presents a well marked point of inflection at the mixture 3.33 cc. of citrate + 6.67 cc. HCl, (corresponding to free citric acid), and also the curve of borates shows a manifest point of inflection at the mixture 5 cc. of borate + 5 cc. HCl, the point at which boric acid begins to be liberated. For mixtures of borates richer in HCl, boric acid has no importance in regard to the hydrion concentration, which is determined solely by the excess of HCl, taking into account the sodium chloride present.

REASONS WHICH LED TO THE SELECTION OF THE STANDARD SOLUTIONS EMPLOYED.

The important part taken in proteolysis by the content of phosphates has already been shown in a research carried out by Fr. Weis in the Carlsberg Laboratory and published in 1902,[1] on the proteolytic enzymes of malt. Weis confirmed the results of A. Fernbach and L. Hubert[2] that the proteolytic power of a malt extract increases with the addition of acid, until all of the secondary phosphate has been converted into the primary salt, but that the further addition of acid diminishes the enzymatic power. The addition of base, however, hinders the proteolysis, the hindrance being greater as the amount added is increased. This effect is especially marked if the alkali added is more than enough to convert all the primary phosphate into secondary.

A series of experiments in the Carlsberg Laboratory by Messrs. Petersen and Sollied in 1902 and 1903 on the enzyme of yeast, also showed that the quantity of primary and secondary phosphates in the medium has an important influence on the speed of proteolysis.

More recently Fernbach has shown that the solvent action of diastase on starch depends among other things on the presence of phosphates,

[1]Comptes rendus, 5, 216.

[2]Comptes rendus, 131, 293, (1900).

the primary favoring the reaction and the secondary tending to prevent it.

It seems scarcely likely that the primary or secondary salts as such can hasten or retard an enzymatic reaction, so we may explain their action by supposing that the concentration of hydrogen or hydroxyl ions in the medium is determined by the ratio of primary and secondary phosphates present. If a small quantity of acid or base be added to such a mixture of phosphates, the only effect is to convert a part of the secondary salt into primary, or the reverse. The hydrion concentration in the solution suffers no change beyond that due to the altered proportions of the two phosphates. Such a mixture of phosphates affords, then, a natural protection against too sudden changes in the hydrion concentration: The mixture serves as a "buffer" ("tampon"). (See page 137, March number of the JOURNAL.)

Mixtures of normal carbonates with acids, as also acid carbonates containing an excess of CO_2 may also serve as buffers, as they often do in nature. A 1/20 molecular solution of normal sodium carbonate has a hydrion concentration corresponding to the index 11.39, while the index of a 1/10 molecular solution of sodium bicarbonate is 8.40, and of this same solution saturated with CO_2, 6.8 to 6.9. As may be seen by a glance at the chart of curves (in the March number), a solution of sodium carbonate containing CO_2 may serve as a buffer over a range of ionic concentrations similar to that covered by the mixtures of phosphates.

In the case of pepsic digestion the optimum hydrion concentration is entirely outside of the range here considered, so that neither phosphates nor carbonates can be used as a regulator in this reaction. In pepsic digestion the buffer is the process of molecular splitting itself, since protein and its decomposition products are capable of fixing both acids and bases.

In selecting liquids of comparison having hydrion concentrations comparable to those which play a part in enzymatic splitting, everything seems to indicate that it will be well to use such substances as serve for buffers in natural processes.

The first liquors of comparison used by the author were mixtures of phosphates and of glycocol. Glycocol was chosen as representing proteids and their decomposition products because it has a simple composition and is easily procured. It will be noticed on the chart of curves, that the curve of phosphates covers the range in which the glycocol curve is useless. It appears that other products of proteolysis as well as the proteids themselves behave essentially like glycocol. In consequence, neutral solutions of these substances to which small quantities of acid or base have been added, deviate much at the neutral point ($p_H^+ = 7.07$), at least if these solutions do not contain phosphates or carbonates capable of acting as buffers.

Examining the chart of curves further, it is evident that while it

is possible by means of mixtures of phosphates and glycocol to prepare liquids of comparison for all ranges of ionic concentration from N/10 HCl to N/10 NaOH, yet in consequence of the form of the curves, from the point where the curve of phosphates ceases to that where the curve of glycocol (with HCl and NaOH respectively) begins, there are ranges of concentration where there is need of other standard solutions. As the chart shows, this need is especially felt in one of these regions, that in the neighborhood of $p_H = 4$, and this is precisely the region of chief interest in the case of many enzymatic reactions. It was therefore necessary to supplement the phosphate and glycocol mixtures with new standard solutions. For this purpose the mixtures of citrates and borates already described were chosen, and served very well.

PARTICULAR CASES WHERE ELECTROMETRIC MEASUREMENTS ARE DIFFICULT.

Even if we employ the apparatus described, and are sure that the hydrogen electrode is working properly, there are yet cases where a precise electrometric measurement is difficult to make, either because the liquid being examined changes of itself during the measurement, or is modified by the action of the platinum electrode. Four cases are discussed.

First. Liquids containing carbon dioxide or carbonates cannot ordinarily be measured electrometrically with sufficient precision, except in cases where the liquid is so acid that all the CO_2 is free and can be expelled by a current of hydrogen, without sensible modification of the hydrion concentration, and in the opposite case where the liquid is so strongly alkaline that no CO_2 is carried out by the current of hydrogen.

A 1/20 molecular solution of normal sodium carbonate may be exactly measured by the electrometric method, but not a 1/10 molecular solution of sodium bicarbonate. A colorimetric measurement of the latter gave $p_H^+ = 8.4$, while an electrometric measurement gave the results which follow. The current of hydrogen was started at 11 o'clock, and π was observed to increase. Exact readings were taken beginning at 11.08, as follows:—

Hour	π	p_H^+
11.08	0.8120	8.22
11.11	0.8218	8.39
11.17	0.8283	8.50
11.30	0.8341	8.60
12.30	0.8475	8.84
1.30	0.8543	8.95
2.30	0.8591	9.04
4.30	0.8682	9.19

These figures show clearly that it is not possible to determine by this

method the hydrion concentration of a solution of this sort, for it would be quite arbitrary to choose the value of $p_H^+ = 8.39$ (after 11 minutes flow of hydrogen), a value which agrees with that found by the colorimetric method. One ought rather to choose the higher value $p_H^+ = 8.60$, because in electrometric measurements constant values of π are commonly obtained after a half hour's flow of hydrogen. By making a colorimetric measurement after the close of the electrometric tests, it was shown that the changes in the value of π were caused by a real change in the hydrion concentration of the solution, and not by a poisoning, so to speak, of the electrode. The value obtained was $p_H^+ = 9.13$, using glycocol mixtures as liquids of comparison, and phenolphthalein as indicator. Solutions liable to give rise to errors of this kind were prepared a day in advance, and hydrogen run through them over night to drive out the CO_2. Both electrometric and colorimetric measurements were then made and the results compared. In the case of sea-water the small percentage of CO_2 was expelled by a current of hydrogen. The hydrion concentration was then measured by both methods, in order to determine the degree of accuracy obtainable by the colorimetric method. These measurements could not be taken as final because the hydrion concentration might have been altered by the passage of the hydrogen. The original liquid was therefore measured colorimetrically, (it being assumed that the accuracy of this method is not affected by the presence of CO_2), and the result corrected if necessary by means of the comparison already made.

This method cannot be employed in the case of some physiological liquids containing CO_2. Blood is an example. It cannot be treated colorimetrically. Protoplasm and serum are other cases, and here the difficulty is that no indicators have been found which are capable of exact results in the case of liquids with a high content of natural proteids. In such instances a slightly modified electrometric method is used. The electrolytic vessel is filled with the liquor to be examined and hermetically sealed. Then a quantity of hydrogen is introduced sufficient to cause the level of the liquid to fall to a certain point, so that a part of the electrode is surrounded by hydrogen. In this way no considerable loss of CO_2 takes place, but ordinarily the electromotive force does not become constant until after a relatively long time (6 to 8 hours, or even more).[1]

Second. In the case of a solution whose ionic concentration is not stable, it is evidently impossible to make direct electrometric measurements. After passing H for half an hour, dependable readings may be made, and if a series of measurements follow, the rate of

[1]According to Carlo Foa (Archivio di Fisiologia, 3, 383, (1906), this is not the case with platinized gold electrodes, and still less with palladium, which rapidly come to constant potential.

change of ionic concentration in the liquid may be determined. If now a curve be made with the measured values, this curve may be extended backward to the time when the solution was mixed.

Third. Influence of toluene or chloroform. In enzymatic researches it is customary to use toluene, chloroform or other antiseptics to prevent the growth of bacteria in the solutions. In measuring such solutions, especially when the gas electrode is freshly prepared, difficulties are encountered, the most notable being that the *e.m.f.* does not at once become constant. Freshly coated electrodes are much influenced by either toluene or chloroform, more strongly in acid than in alkaline solutions. After being used several times, however, the electrode gradually loses this sensitiveness; immunizes itself, so to speak, against these substances. Electrodes thus immunized give nearly accurate results, especially if the quantity of toluene admitted to the apparatus be very small, so that it may be quickly eliminated by the current of H.

Because the toluene introduces a small uncertainty, and because even a large growth of mold in the standard solutions makes no measurable difference in their hydrion concentration, the author has abandoned the use of toluene, and the observations tabulated on pages 151 to 154 were made without it.

Fourth. When the solution to be examined is subjected to the action of hydrogen in contact with platinum sponge, it is evidently possible that the hydrion concentration of the solution may be changed, and that in consequence the electrometric method may become uncertain or even inapplicable. The case is further complicated when the hydrogenization of the solution gives rise to substances which exert an injurious effect on the electrode. An instance of this is found in some experiments on egg albumen, treated with NaOH and then acidulated with HCl. The platinum electrode was at once strongly affected by this solution, which smelled slightly of hydrogen sulphide. Even after the expulsion of the gas by a current of air or hydrogen, the liquid under the combined action of the hydrogen and the platinum electrode, but not in the absence of the latter, continued to evolve small quantities of H_2S, and to exert an appreciable influence on the electrode.

(To be continued.) L. B.

The Drying of Leather. *Gerber-Courier*, **51**, (1911), No. 6, p. 1.— Drying is a very important part of the tanning process. If the water has contained any objectionable matter, such as iron, saltpeter or chalk, these will show on the dried leather. A drying room must above all things be clean, for dust shows on the hides. It is unnecessary to have the drying rooms low, for since the hides are hung on the ceiling they get the warmth no matter how high the ceiling is. The damp air developed by the drying hides should be drawn off by some practical method, such as ventilators or exhaust fans. By this method the ventilator forces warm air from a separate room into the drying

room, whence it escapes out of doors, thus keeping up a circulation and drying the hides very quickly.

Another method which is cheaper is by means of draft boxes placed at intervals around the floor. In this case the room is usually heated by steam pipes at intervals up the walls, and the heavy damp air settles to the bottom, escaping through the flues. These must be warmed by pipes in winter or the air will not go out. Still another method is to place a turret on the roof through which the air escapes. The leather does not become perfectly dry by this method, which, however, does very well for sole-leather; but for skins which are to be glazed, all moisture must be removed. E. A. B.

Report of the Freiberg Research Institute for the Year 1910, by the Director, Prof. Dr. J. Paessler.—The total number of analyses made during the year was 5,640, three-fourths of which were of extracts and tanning materials. In the years 1908 and 1909 all analyses of tanning materials were conducted by both the filter and shake methods, but in 1910 most were done by but one, whichever the sender wished. In the table are given the average tannin content by each method for the samples examined in 1910 and the average difference for the samples of the last 3 years.

PER CENT. TANNIN.

	Filter method 1910	Shake method 1910	Difference 1908, 1909, 1910
Oak bark	11.5	10.6	0.8
Pine bark	12.6	10.9	1.8
Mimosa bark	32.8	29.7	1.5
Mangrove bark	39.9	39.7	1.5
Valonia	34.0	29.2	2.5
Trillo	44.5	40.8	3.0
Myrobalans	37.4	31.9	4.5
Myrobalans, hulled	50.9	47.4	6.0
Divi divi	46.6	37.8	4.0
Quebracho wood	20.8	19.9	1.0
Sumach	27.4	24.3	2.2

Various other substances yielding tannin were examined, including a few samples of oak and chestnut wood. Average results for these in soluble tannin were as follows:—

	Filter method	Shake method
Oak wood	11.3%	10.7%
Chestnut wood	11.0%	.....

The non-tans were much lower in the chestnut wood than in the oak, ranging from 1 to 3 per cent. in chestnut and from 4 to 8 per cent. in oak.

Many samples of tanning extracts were examined during the year. The results of these will be published in a forth-coming work on the sugar-content of various tanning materials and tanning extracts. Some

of the oak-wood extracts showed a very high proportion of non-tans, the highest being 19.7 per cent. non-tans to 20.5 per cent. tannin.

Many chestnut wood extracts were examined, the figures for a few of which are given. The pasty extracts range from 41.9 per cent. tannin, 10.4 per cent. non-tans and 47 per cent. water to 44.7 per cent. tannin, 13.2 per cent. non-tans and 42 per cent. water. The solid extracts range from 73.5 per cent. tannin, 11 per cent. non-tans and 12.3 per cent. water to 55.9 per cent. tannin, 18.5 per cent. non-tans and 24.3 per cent. water.

1,279 samples were examined which came in as quebracho extract, liquid, pasty and solid. Many of these were not pure quebracho, containing myrobalans, mangrove and even molasses. A few instances are given, an extreme case showing 50.1 per cent. tannin, 30.2 per cent. non-tans and 19.1 per cent. water in a solid "quebracho." Solid quebracho regarded as genuine gave 64 per cent. tannin, 5 per cent. non-tans and 26 per cent. water to 77 per cent. tannin, 4 per cent. non-tans and 14.5 per cent. water, insolubles ranging from 0.2 per cent. to 7.3 per cent.

A few figures are given for pine bark extract, the best being 26.1 per cent. tannin, 13.3 per cent. non-tans, 0.7 per cent. insolubles and 59.9 per cent. water.

420 analyses were made of leather and leather articles. The highest content of water-solubles in a leather not "loaded" was 25.9 per cent., 21.8 per cent. of which was tannin. In the loaded leathers, as high as 2 per cent. of magnesia was found, corresponding to 12.3 per cent. crystallized magnesium sulphate. A sample of chrome leather contained 9.1 per cent. sugar, and 13.2 per cent. alkaline sulphates. Another chrome leather had 12.2 per cent. common salt, 10.9 per cent. barium chloride and 1.8 per cent. barium sulphate, a total load of 24.9 per cent. Several samples of brittle leather were found to contain a large amount of free sulphuric acid, in one case as high as 1.87 per cent. A leather with brittle grain contained in the surface layer a considerable quantity of oxalic acid.

A material sold as a deliming agent contained 5.8 per cent. sugar and 20.6 per cent. sulphuric acid. L. B.

Salts of Titanium as Dyeing Materials for Leather. *Le Cuir*, 4, 4, p. 113.—As compared with the salts of aluminum, iron, chromium and copper, titanium compounds are very stable, and therefore make excellent pigments. Titanium salts used as mordants form very durable "lakes" with dyes, and many of the titanium compounds themselves have serviceable colors and are used as dyes. Antimony salts have long been used to fix tannin on the fiber of leather, giving a natural tan color. Titanium salts, however, not only fix the tannin very firmly, but give a deep yellow color, and with the use of a small quantity of material.

Basic dyes cannot be employed at the same time with titanium salts, but acid dyes may be used with them to great advantage. If basic dyes are used, the titanium salt is added afterward, and good results are

thus obtained. The quantity of titanium employed is about one-fourth per cent.

Titanium salts used as mordants with natural dyes such as fustic behave in the same way as with tannin, furnishing very fast colors. Campeachy wood with titanium makes a very good black. L. B.

Artificial Degras. *Chem.-Techn. Fabrikant* through *Ledertechn. Rundschau*, 1911, 34-5.—As a substitute for the genuine article, (the product of chamoisage) oxidized marine oils are emulsionized as follows: (1) 60 parts with 10 crude wool grease, 30 water; (2) 60 parts with 5 bone fat, 10 wool grease, 25 water; 30 parts with 20 wool fat, 20 ordinary whale oil, 20 water. 3-4 hours milling are required. To make the product still cheaper, mineral and rosin oils may be added; a more permanent emulsion is then secured by addition of alkali. An Austrian method consists in tanning hide offal, best with alum, then impregnating this with whale oil and piling the mass in a warm room. Oxidation is complete in 3-8 days; the oil is pressed out and the leather may be re-used. W. J. K.

The Analysis of Degras. W. FAHRION. *Collegium*, 1911, 53-7. I. *Determination of Water and Ash.*—Three grams degras are heated directly in an open platinum crucible until the foaming ceases and a sizzling begins with finally a slight smoking. With practice this end-point may be reached with a concordance of 0.2 per cent. The residue is ashed but for accurate work a charge of at least 50 grams is needed.

II. *Free Fatty Acids, Unsaponifiables, Total Acids and Oxy-acids.*—Three grams degras are weighed in a 100 cc. porcelain dish (outside matt) and titrated with N alkali, N/2 finish, to red (phenolphthalein); this is computed as oleic acid, mol. wt. 282. To the neutral solution 3 cc. 5 per cent. aqueous KOH are added and evaporated on the water-bath, finishing by direct heat cautiously to dryness. The soap is dissolved in 50 cc. 50 per cent. alcohol and extracted successively with 25 + 15 + 15 cc. petrol. ether, boiling below 70°. The united extracts are shaken with 20 cc. 50 per cent. alcohol which is finally added to the soap solution. The residue from evaporation of the petrol. ether extract = unsaponifiable. The alcohol soap solution is evaporated to dryness, the residue dissolved in hot water and when cold shaken well with 25 cc. petrol. ether and 10 cc. 20 per cent. HCl and let stand over night. The acid solution is drawn off and the petrol. ether layer on evaporation yields total fatty acids. The oxy-acids or "degras-former" remain in the funnel; these are dissolved in warm alcohol, evaporated to dryness and weighed, then ashed and again weighed; the difference = oxy-acids. A portion, however, remains in the acid solution and is recovered by evaporating, redissolving in a little alkali or NH_3, not over 10 cc. H_2O, then shaking as before with petrol. ether and HCl. The sum of water + ash + unsapon. + total fatty acids + oxy-acid = 95-96 per cent. of the degras; the difference can be reckoned as glycerine and loss.

The water in degras is normally 15-20 per cent.; English sod oil has 30-40 per cent. Water-free sod oil is sold but from the long boiling is almost black. The ash is slight, 0.3 per cent. at the most; soap was formerly added but seldom now, Traces of Fe are generally present and harmless below 0.03-0.05 per cent.; at times, however, even the smaller amount may be troublesome, probably from precipitation as Fe soap. Marine oils contain mostly 1-2 per cent. unsaponifiable but this can reach 3 per cent. in cod and shark oils. On conversion into degras these ratios are not changed, but they naturally increase on addition of mineral oil or wool fat. Within limits such additions are useful and not adulterations; for instance, a highly oxidized degras will not penetrate leather without mixture with mineral oil. The content of total fatty acids is naturally higher, the lower the unsaponifiable and oxy-acids. The molecular weight determination by titration is not important; it averages 300. The saponification number of the original degras fluctuates according to the degree of reaction since the oxy-acids besides the COOH group also contain weaker acid groups. The iodine number, however, is of value in connection with the resinifying power. This evil feature shows when the oil has been insufficiently oxidized; if the iodine number is below 100 resinification need not be feared. The content of free acid varies much in oils, hence in degras itself. If it exceeds 20 per cent. (reckoned as oleic acid), spewing may result. This consists of a coating on the leather of saturated acids. Views differ as to the desirable amount of oxy-acids (degras-former); the percentage depends upon the iodine number of the original marine oil employed in manufacture and upon the degree of oxidation, 15 per cent. or more may be reached, but 6 to 10 per cent. is best for practical use. The oxy-acids in degras are not free, but present principally as glycerides, hence anhydrous degras is completely soluble in phenol ether. These glycerides are valuable and important in saturating leather after tannage and making it soft. The German degras manufacturers have mutually agreed to furnish two brands of degras:

Moellon, maximum 17 per cent. water, 6 per cent. unsaponifiable; moellon degras, maximum 20 per cent. water, 12 per cent. unsaponifiable. W. J. K.

A Pyknometer for Leather, Tanning Materials and other Solids. GEORG GRASSER. *Collegium*, 1911, 69-70.—Paessler determines the specific gravity of leather by measuring the mercury displaced by a strip of the material 25-30 cm. long, 1-1½ cm. wide. To read this with accuracy, the author has devised a special burette made by Arthur Meissner, Freiberg, Saxony. The weighed solid to be examined which may be in divided form if desired is contained in a displacement tube the stopper of which terminates in an elongated narrow tube bearing the zero point. The tube is connected below by rubber tubing with a narrow burette tube in which the mercury level is read before and after

introduction of the sample. The mercury level is adjusted to zero in the displacement tube at each reading. W. J. K.

Notes on Tannin Solutions. GEORG GRASSER. *Collegium*, 1911, 46-52. —Iodine was first used by Jean for the determination of tannin in alkaline solution, the end-point being ascertained by an external spotting test on starched filter-paper. The author found that an excess of iodine was more easily detected by allowing the test liquid to flow into starch solution contained in a porcelain dish. He employed the method to determine gallic acid (abstract, JOURNAL, 5, 582). He now reports investigations upon the sensitiveness of the reaction for qualitative tests. The various tannin solutions were acidified with 20 per cent. H_2SO_4 and N/50 iodine added drop by drop until a test with starch paste gave a violet color. With solutions containing over 0.1 per cent. the starch could be added directly and iodine added with warming until the violet appeared on cooling the test. The limit of the reaction was found to be 0.001 per cent. of gallotannic acid which gave immediately a weak violet (external test).

Other reagents were compared; tartar emetic alone and with various admixtures was not very sensitive; ammoniacal zinc acetate still gave a slight opalescence with 0.0005 per cent.; gelatine-salt reagent seemed to be the most reliable for used liquors rich in non-tans. In testing various materials, pine was found to give a violet color with iodine alone without starch; the reaction was more decided after boiling.

Finally the author discusses the cause of "detannizing" of tannin solutions on standing. He prepared clear solutions of various materials, mixed these in all possible pairs and observed no clouding due to a mutual reaction. After standing 2 days only those mixtures containing quebracho or valonia gave a slight sediment. W. J. K.

Glove Leather Manufacture. (Conclusion.) *Ledertechn. Rundschau*, 1910, 410-11; 1911, 1-3, 9-10, 17-19, 26-28, 33-34.—*"Fasson" Kid Leather.*— Both lamb and kid fells may be worked and in the same way, the former with more caution. They are carefully sorted, rejecting all without a fresh bright grain as unsuited for this sort of leather, likewise those which held towards the light show streaks in the sides and flanks; these will not withstand the beam work. Ware which has been heated in drying or storage as evident by the dull grain and glued hair is discarded. The soaking must be finished in 2 days; spring water is best. With hard skins once used water may be employed the first day, then fresh water sharpened with 1 kg. caustic soda to the hectoliter. The liming should be complete in 10-12 days; a liquor should not be used over 4 weeks. A series of 5 pits is best. For 600 large (800 medium, 1,000 small) kid fells, 14 hectoliters liquor are needed. The charges for such a lot are 60 liters stiff slaked lime, 1 kg. red arsenic, distributed in the 5 pits so that at each shift 20 l. lime, 550 gm. arsenic go to the fresh liquor, 16 l. lime, 450 g. arsenic to the next best, and to the others 12, 8 and 4 l. lime alone. After liming, the fells are carefully rinsed

and left over night in clean water. The unhairing is done on an elastic beam with a well polished iron, care being taken in scraping away the scud that this be not pressed in and permanently fixed for which there is no remedy. After the beam work (Fassons) which is minutely detailed comes a bran bate at 34-35° C. The tawing is also as with lamb-fells, the proportion of flour and egg being increased; 40 kg. flour, 500 egg yolks, 8 kg. alum, 2 kg. salt, 100 l. water to 600 large fells.

Currying.—The dry fells in packs of 50-100 are dipped in water, untied, covered with cloths and left in the bin 24-36 hours. They are trodden by laborers at intervals for 3-4 days and are ready for the principal operation, moist staking, which must be done very evenly. After partial drying, the fells are again left over night under cover, then smoothed, packed in lots of 10-12 and sent to the white storage (Weisslager). The storeroom should be dry and well ventilated as this leather is extraordinarily hygroscopic and moisture must be guarded against. The leather is stored at least 4 weeks before further treatment.

Flesh Leather ("Chairleder").—This requires denseness and a smooth velvety flesh. Lean or coarse fibered fells are unsuited and cannot be pumiced. The soaking must be quick with water sharpened by sulphide or better caustic; old soaks are excluded. In liming, lime is kept down to the minimum, sulphide being the chief agent. A new liquor is prepared with 15 l. lime paste, 1,800 gm. sod. sulphide to a cubic meter. Five pits are used, shifts every 2 days. For bettering, 10 l. lime paste, 1,440 gm. sulphide are used for the best pit, for the next 5 l. lime, 1,080 gm. sulphide, for the next 720 gm. sulphide only, and the oldest, nothing.

Sulphide is best added from a stock solution of 6 kg. to 100 l. The liming lasts 11-12 days. In dehairing, the fells are drummed with warm water, then washed at 22° C. After sorting and trimming, fleshing and bran bating, the tawing paste is applied as with glacé; 36 kg. flour, 50 egg yolks, 9 kg. alum, 2¼ kg. salt, 90 l. water to 1,000 medium fells.

Mocha Leather.—This is similar to the above, but is curried on the grain which is ground off to give the plush effect. For dehairing, a paste (Schwödebrei) is used; 1 kg. sod. sulphide in 53 l. water and 35 l. lime paste, all to 100 l.; this is applied for 12-14 hours. After unhairing, the fells are given a straight lime for 6-8 days. After shaving, they are delimed with HCl, washed and scudded. Alum alone is used for the first tawing, 2 kg. alum, 200 g. calcined soda, 500 gm. salt to 100 medium fells, trod in warm at 31°. Finally the grain is half removed by polishing with emery and the leather is then again tawed with alum and egg.

Dyeing.—The demands of the trade are much more stringent than formerly; the color must be precise in tone and very uniformly applied. Two methods of dyeing are used: (1) the dip method, coloring

the leather on both sides, used only for light shades since the flesh side takes up dye much faster than the grain; (2) the table method, where the grain only is dyed after applying a ground. For dyeing, pure water free from organic matter is essential; soft water is better than hard. If much lime be present, this is precipitated in the ground, roughening the grain, hindering or preventing dyeing. Careful sorting of the fells is needful; fine grain, thin fells are selected for thin leather and dip dyes. Before dyeing the sorted fells are subjected to the "broschiren" process; this consists in working the leather in water at 30 to 40° according to age until the particles of flour are completely removed from the grain and alum and salt can no longer be detected by taste. Treading gives the best results although the drum is cheaper. After draining, the fells are ready for the dye bath; for table dyeing, each skin first receives a "nourishment" of ½ to 1 egg yolk.

For the dip dye bath, the liquors are always fresh made, a short extraction of the wood or berries being sufficient. The liquor is to be filtered, even when aniline dyes are used. A series of 3, better 4 or 5 vats is used. If the drum be employed, the leather is put in motion with water at 37° and the dye added in 4 to 5 portions at intervals of 10-15 minutes, exhausting the dye each time. The dye may also be trodden in the tub, finally treating the leather with ½ to 1 egg yolk per skin and sufficient water. The drying is finished in 2 hours at 37° C. at the highest. The suspended fells are reversed once in the meantime to insure even coloring. The drying air should be warm but contain no fuel gas. Before staking, the leather is first layered on the flesh with moist sawdust, grain to grain pairwise in a box. Staking, trimming and grain polishing complete the process.

For straw yellow a decoction of wold is used, Brazil wood being added for rose shades; for sea green, privet berries; for flesh color (chamois), beginning with wold then Brazil wood, finally zinc vitriol; for rose, Brazil wood; lilac, elderberry and logwood; mauve, buckthorn-berries; apricot, Persian berries and Brazil wood. More brilliant tones are obtained by combining these various dyes with coal tar colors.

Table Dyeing.—This is carried out on a table covered with lead; the edges are upturned and the surface slopes towards the back for draining. Concentrated dye liquors are used; for black, 40 kg. logwood, 12 kg. fiset, 6.5 kg. fustic, 1¼ kg. soda, 1½ kg. ammonia are boiled with water 2 hours and made up to 500 l.; for blue 50 kg. Domingo logwood, 250 l.; for yellow, 50 kg. fustic, 250 l.; for red 50 kg. Brazil wood, 1½ kg. soda, 250 l.; for brown, 80 kg. fustic, 1 kg. soda, 250 l. It is easier to employ extracts which give more uniform solutions. The fell is smoothed moist and flat upon the table and first brushed with ground which the grain requires before being susceptible to most dyes. For this, human urine is the best medium; for light shades it is diluted with an equal quantity of water containing 1 per cent. borax. The dye is applied with two

brushings, rubbed in, rinsed off and the fell slicked. After a third brushing, a mordant is applied containing in 200 l. 2 kg. green vitriol for black, 1 kg. Salzburg vitriol (iron and copper sulphate mixture) for dark colors, 1 kg. blue vitriol for middle tones, 2½ kg. zinc vitriol for bright red, 5 kg. alum for bright yellow. After drying, the leather is packed in the chest, grain to grain, with moist sawdust on the flesh. When sufficiently moist, it is staked and finally polished on the grain with a roller.

"Chairleder" before dyeing is sorted into fells of the heavier sort which are to have the grain removed and those which are not fitted for this such as the thinner, milder sort. The grain is removed with the paring knife. The next operation is the slicking which can be done by hand with the moon-knife but requires skill. On the large scale emery wheels are used to remove the flesh. After the "broschiren" in the usual way, the flesh is finally ground down on revolving stones of the proper hardness. The dye solutions are prepared rapidly; 15 minutes boiling is sufficient. Alum is used for mordanting. The dye is trodden in from the tub, being added in 5 or 6 portions; finally a "gar" of egg yolk is applied, a third or half that used for glacé leather. W. J. K.

Mangrove Tannin and its Decolorization. ADOLF ROMER. *Ledertechn. Rundschau,* 1911, 26-27.—The varieties of mangrove differ greatly in tannin content. The author quotes analyses of the seven principal varieties occurring in East Africa, ranging from 4 to 52 per cent. tannin. The three richest are Brugiera gymnorhiza, Rhizopera mucronata and Ceriops Candollona, and their tannin content increases with age. The objectionable red color of mangrove has prevented any considerable use of the material in Europe. The author together with Dr. Bosch have successfully solved the problem of bleaching the dyestuff without loss of tannin, the reducing agent being a small amount of chromous acetate. The process is the property of the German Colonial Tannin and Dyestuff Company of Feuerbach-Stuttgart and is patented in all countries. W. J. K.

PATENTS.

Multiple Effect Evaporating Apparatus. U. S. Patent No. 984,226. SAMUEL M. LILLIE, Philadelphia, Pa.

Evaporating Apparatus. U. S. Patent No. 984,754. F. H. EYDMAN, Ryswyk, Netherlands.

Method of Evaporating Solutions. U. S. Patent No. 984,822. SAMUEL M. LILLIE, Philadelphia, Pa.

Leather Skiving Machine. U. S. Patent No. 985,401. F. M. COURSER, Haverhill, Mass., assignor to United Shoe Machinery Co.

Method of Setting Out Leather. U. S. Patent No. 985,466. JAMES T. SMITH, Newark, N. J.

Sectional Work-Support for Leather-Working Machines. U. S. Patent No. 986,497. FRANKLIN J. PERKINS, Woburn, Mass., assignor to Holder-Perkins Company.

Manufacture of Fatty Acids. U. S. Patent No. 987,426. GRACOMO BOTTARO, Genoa, Italy.

A current of steam, air and sulphur dioxide is passed through a lime soap, decomposing it into fatty acid and calcium sulphate.

Apparatus for Color Estimation. U. S. Patent No. 987,148. J. W. LOVIBOND, Salisbury, England.

An improvement on the well-known Lovibond tritometer.

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EXTRACTION OF LEATHER WITH 95 PER CENT. ALCOHOL.

J. S. Rogers.

Mr. G. A. Riker (this Journal, Vol. 5, No. 12, p. 539) describes a method for the extraction of leather, using 95 per cent. alcohol. It stated that the alcohol does not remove the sugars and Epsom salts and consequently avoids the misleading results

obtained when Epsom salts are calculated in the water-soluble and again reckoned in the mineral ash; and also the error in the determination of uncombined tannins, due to the partial absorption of the sugars and Epsom salts by the hide powder.[1]

It is a well-known fact that sugars are purified by recrystallization from boiling alcohol (80-100 per cent.). According to Seidell (Dictionary of Solubilities) 100 grams of 85 per cent. alcohol dissolves 1.95 grams of dextrose at 17.5° C. Trey, (Die Chemie der Zuckerarten 1, 1904, p. 267) found that: 100 cc. of absolute alcohol, boiling temperature, dissolves 1.42 gm. of grape sugar.

Two samples of leather which had previously been analyzed in this laboratory were extracted, following in detail the method given by Riker. Sugars were determined by the usual method in the extract. The sample which gave, by the water extraction, 10.19 per cent. sugar gave 4.32 per cent. by extraction by 95 per cent. alcohol. The second sample which gave by water extraction 12.01 per cent. gave 3.20 per cent. sugar by extraction with 95 per cent. alcohol.

This shows clearly that the sugars are removed to an appreciable extent by 95 per cent. alcohol. In the two cases above, between 25 per cent. and 40 per cent. of the sugars present being extracted.

Comey (Dictionary of Solubilities) states that 100 parts of absolute alcohol will dissolve 1.3 parts of $MgSO_4.7H_2O$ at 3° C. In this laboratory 5 gm. of Epsom salts placed in an S and S thimble and extracted in a Soxhlet extractor for two hours (approximately 12 siphonings) with 95 per cent. alcohol, gave 0.0121 gm. of Epsom salts in the extract. This is 0.24 per cent. of the Epsom salts present. If the extraction had been continued six hours longer, making a total of eight hours (the time used for extracting leather with alcohol), practically 1 per cent. of the Epsom salts present would have been extracted.

[1] H. R. Procter (Leather Industries Laboratory Book, p. 207-8) states that glucose is not absorbed by hide powder, but that on the other hand, it renders a portion of the hide powder soluble and thus increases the non-tannins. Other work has also been done which illustrates this fact; *Collegium*, 1903, pp. 114, 124; 1906, pp. 421, 432, 442, 443; 1907, pp. 50-56, 165.

From these facts, it is evident that the method does not possess all of the advantages over the water extraction method which were claimed for it. For the sugars and Epsom salts are soluble to such a degree that there would be considerable error in the results given if these substances were assumed to be absent from the extract. And since Epsom salts, and especially glucose, have a decided but slow solubility in boiling 95 per cent. alcohol, it would seem probable that the end point of the extraction with 95 per cent. alcohol, of leathers containing Epsom salts and glucose would be less definite than the end point obtained by extracting the same leather with water.

THE COMPARATIVE EFFICIENCY OF CERTAIN TANNING MATERIALS.

By Robert W. Griffith.

The number of tanning materials which are offered to the tanner steadily increases and as the list extends so do the old time tannages of pure bark become less in evidence. Whether the gradual disappearance of the old tannages should be lamented as a sign of decadence in the art of tanning is questionable. The introduction of some new material is evidence of a certain progress and its successful use develops a keener intelligence. It is not conceded that in this industrial development the excellent qualities which distinguish leather from anything else have been sacrificed. On the contrary and as a result of this development the tanner has the choice of tanning materials which will equal the best bark tannage in producing any desirable quality in leather. But it would seem superfluous to enter into a defense of modern development at this stage.

Innumerable circumstances have conspired to bring about present conditions with the result that ocean freights have become an economical factor in the tanning industry and the tannery is no longer a portable proposition trailing the logging camp.

The experience accumulated in the process of development has not been without its price, and the characteristics peculiar to a new tanning material, the tanner has been obliged to ascer-

tain for himself. Now that many of these new materials have a recognized value in the tanning industry, the question of their relative efficiency in the production of leather has to be considered. In judging the economy of various materials which, of course, includes the efficiency as well as the cost of the material, many points have to be remembered.

The analysis of the material offers a good indication of its tanning merits, but its efficiency in leather production has to be tested practically.

Some materials show a considerable difference between the amount of tannin as obtained by analysis and that available for producing leather. Myrobalans and Valonia are specimens of this type, and liquors prepared from these lose a great deal of their tanning strength on standing some time as is shown by the following experiment. A quantity of strong valonia liquor was freshly prepared in a cask and covered with a layer of oil about a quarter of an inch thick. No mould or decomposition showed itself during the experiment, and samples were taken for analyses from time to time.

The loss in tanning strength after standing 56 days amounted to 18.24 per cent. and after 91 days to 23 per cent. The insoluble matter precipitated in the liquor increased considerably. The following is the actual analysis:

ANALYSIS OF VALONIA LIQUOR.

	Fresh liquor	56 days after	91 days after
Tannin	14.64	11.97	11.40
Non-tannins	6.60	6.64	6.72
Insolubles	0.64	2.81	3.68
Water	78.12	78.58	78.20

An experiment was made with myrobalans under exactly similar conditions, but showed a loss in tannin strength, slightly less than valonia. After standing 53 days the loss in tannin strength amounted to 18.42 per cent., and after 90 days to 21.7 per cent. The following shows the actual analysis:

ANALYSIS OF MYROBALANS LIQUOR.

	Fresh liquor	After 53 days	After 90 days
Tannin	14.66	11.96	11.48
Non-tannins	5.98	7.58	7.48
Insolubles	1.52	2.81	3.06
Water	77.84	77.65	77.98

In both the Valonia and Myrobalans liquors the precipitation of insoluble matter commenced after the first day and steadily increased. It is abundantly clear that in the case of liquors prepared from Valonia and Myrobalans that the insoluble matters are formed at the expense of the tannin and not entirely from the original non-tannin matters. It is demonstrated, also, that in practice it would not be economy to leach these materials in the usual way. The deposited matter must have some value in increasing the weight of leather, and the way in which this value is obtained is by the direct contact of the material ground up and used to "dust" in the layers and this results in the deposit of considerable "bloom" upon the surface of the leather.

Valonia and Myrobalans are perhaps exceptional materials in displaying the quality of precipitating insoluble matter, but all tannin liquors do the same, but to a considerably less extent. Certain of the tannin extracts like Quebracho Extract and Hemlock Extract deposit less insolubles on standing in liquors than any other material. Having considered the behavior of the tannin material in its own solution, the next point to investigate in order to arrive at its tanning efficiency, is its leather forming capability. The tannin contained in different materials show a different degree of attraction towards hide fiber, some displaying quick powers of penetration whilst others diffuse through the fiber very slowly. The colloidal character of the particular liquor is perhaps responsible for this, and the amount of non-tannin matter present in the liquor is to some extent an indication of its colloidal properties.

With a view to determine the behavior of certain tannin materials when in solution, towards hide substance, the writer, a few years ago in conjunction with Mr. John Youl, carried out a series of experiments on a practical scale.

In these experiments separate liquors of the different materials were prepared and the hides tanned throughout with the same material. Samples of the liquors were taken regularly and the liquors, having been prepared of the same tannin strength, determined by hide powder analysis, were all strengthened at intervals with the same amount of actual tannin.

As the tanning of the hides proceeded, samples were taken

from the hides and the amount of tannin absorbed was determined by Kjeldahl's Method of Nitrogen Estimation. In this way the speed of tannin penetration could be observed as well as the extent to which the liquor exhausted its tannin strength. The following table shows the results obtained after 34 days:

Material	Bark. °	Tannin	Non-tannin	Insoluble	Per cent. tannin in hides
Valonia.....	12½	1.48	1.12	0.48	33.0
Myrobalans.....	12½	1.82	1.30	0.32	31.4
Oak bark.....	9	1.17	0.89	0.26	30.6
Quebracho ext..	4	1.01	0.35	0.06	38.4
Chestnut ext....	9	1.36	0.74	0.22	33.1
Oakwood ext....	12½	1.56	1.26	0.26	33.9
Hemlock ext....	9	1.15	1.21	0.14	32.9

The barkometer readings of the liquors are given to illustrate that they bear no relation whatever to the tannin strength.

It will be seen from the above table that the Quebracho liquor is the most exhausted of its tannin and the hide shows a corresponding larger absorption of tannin from this liquor or, in other words, the Quebracho tannin enters into combination with the hide to form leather quicker than any of the other six materials. Oak bark tannin is the slowest. There appears to be sound reason for the popularity of Quebracho Extract as a tanning material in this country, and for the purpose of illustrating the respective absorption of the tannin of the other materials by the hides, the following figures are given, obtained by calculation from the above table. For every 100 parts Quebracho Tannin absorbed by hide there are absorbed

86.0 parts valonia tannin
80.0 parts myrobalans tannin
79.6 parts oak bark tannin
86.0 parts chestnut tannin
88.0 parts oakwood tannin
85.0 parts hemlock tannin

The next table shows the condition of the liquors and the hides after 74 days. It should be explained that as the tanning was carried out in a single vat for each material it was necessary to reduce the volume of the liquor by taking from each vat an exact equal quantity of liquor, each time the liquor was strength-

ened. It was, therefore, considered impractical to attempt to account for all the tannin used in the liquors.

Material	Tannin	Non-tannin	Insoluble	Per cent. tannin in hide
Valonia	2.27	1.77	1.04	40.6
Myrobalans	3.02	2.08	0.81	36.8
Oak bark	1.72	2.20	0.45	40.1
Quebracho ext	1.33	0.79	0.13	45.8
Chestnut ext	1.98	1.12	0.55	41.6
Oakwood ext	2.20	1.96	0.34	41.4
Hemlock ext	2.13	1.42	0.15	43.6

It will be observed that Quebracho tannin continues to keep ahead in its absorption by the hide, but at this stage Oak bark tannin has made some progress and myrobalans, which, after 34 days was close to Oak bark, is now the least of the absorbed tannins. The amount of tannin absorbed by the hide in the second period of 40 days is very little compared with the amount absorbed in the first period of 34 days. In fact, in every case considerably over 50 per cent. of the amount of tannin finally taken up by the hide is absorbed within the first 34 days. It is also demonstrated that by the use of certain materials which become readily absorbed by the hide the period of tanning is much shorter than with others, and it is unnecessary to give them all the same length of time. To renew the illustration of the comparative absorption, after 74 days, we have the following figures: For every 100 parts Quebracho Tannin absorbed there are absorbed:

88 parts valonia tannin
80 parts myrobalans tannin
87 parts oak bark tannin
90 parts chestnut tannin
90 parts oakwood tannin
95 parts hemlock tannin

Having regard to the fact that all the liquors were made up and strengthened with equal amounts of tannin, it would appear from the analyses of the liquors that the tannin of some materials is not available as readily as some others. For instance, Myrobalans tannin has been less exhausted than any other and produces more non-tannins and insolubles combined. Myrobalans, however, have some value as acid producers, surpassing all the

others in this respect, but it is worth considering whether acid could not be obtained cheaper from another source.

In our experiments the hides were suspended on sticks for the first 34 days, and for the next 40 days were laid in the vat and handled frequently. Afterwards they passed through a series of four layer liquors and occupied in this process a further 44 days which completed the tannage. The following table shows the figures obtained from the actual weights of the hides.

	Wet weight of hides	Per cent. water	Calculated dry weight of hides	Wt. of rough leather produced	Per cent. water in rough leather
Valonia	23.660	72	6,568	16,299	18
Myrobalans.....	23.772	72	6,599	14,120	18
Oak bark.....	23.081	72	6,407	16,065	18
Quebracho ext..	23.419	72	6,501	15,791	18
Chestnut ext....	23.000	72	6,385	15,547	18
Oakwood ext...	24.001	72	6,662	16,304	18
Hemlock ext...	23.750	72	6,593	15,558	18

	Calculated dry weight of leather	Per cent. gain in leather formation	Calculated hide substance per cent.	Calculated tannin per cent.
Valonia	13.365	103.4	49.1	50.9
Myrobalans. ...	11.579	75.6	56.9	43.1
Oak bark	13.174	105.6	48.6	51.4
Quebracho ext..	12.949	99.1	50.2	49.8
Chestnut ext....	12.750	99.6	50.0	50.0
Oakwood ext....	13.370	100.7	49.9	50.1
Hemlock ext....	12.755	93.4	51.6	48.4

Except for moisture determinations there were no analyses made to arrive at the figures in the above table.

Samples were taken of the leather when the hides were removed from the last layer and those were analyzed in the usual way by Kjeldahling. The following table shows a comparison of the figures obtained by analysis and by direct weighing which show remarkably close results:

	By analyses		By weight	
Material	Hide substance	Tannin	Hide substance	Tannin
Valonia.....	50.6	49.4	49.1	50.9
Myrobalans	58.6	41.4	56.9	43.1
Oak bark	47.3	52.7	48.6	51.4
Quebracho ext..	47.5	52.5	50.2	49.8
Chestnut ext....	51.4	48.6	50.0	50.0
Oakwood ext....	50.3	49.7	49.9	50.1
Hemlock ext....	51.0	49.0	51.6	48.4

To complete the illustration of the comparative absorption of the respective tannins from the basis of the Quebracho tannin, we obtain the following figures from the analysis of the final leather; For every 100 parts Quebracho tannin absorbed there are absorbed:

94 parts valonia
78.8 parts myrobalans
100.4 parts oak bark
92.5 parts chestnut
94.6 parts oakwood
93.2 parts hemlock

These figures indicate the actual combining value of the tannins as they are absorbed by hide fiber to form leather. In the final completion of the various tannages it seems that the tannin, or leather forming substances, of Oak Bark possesses the greatest affinity for hide fiber and has the greatest "combining value." Quebracho tannin runs remarkably close, however, and having regard to its quick powers of penetration, it probably constitutes the most valuable tannin in the economy of leather making. Myrobalans tannin has the least combining value of any of the materials employed.

It must be pointed out that the "combining value" of a tannin material does not, however, indicate its weighing properties. The quality in a tannin material which imparts weight is possessed by the non-tannin matters. Referring to the table showing the hide and leather weights, it will be seen in the column of Percentage Gain in leather formation that Oak Bark liquors possess the greatest weight giving value followed by Valonia and then Oakwood Extract. Myrobalans is the last in this respect also.

These percentage gains are calculated from the difference between the actual dry weight of the hides and the actual dry weight of leather obtained. The percentage hide substance in the leather is obtained by calculation of the dry weight of hide in the dry weight of leather, and the percentage of tannin is obtained by the difference between the dry weight of hide and the dry weight of leather calculated on the latter. Tannin implies leather forming substances.

It is reasonable to suppose that those materials which impart

the greatest weight to leather by virtue of their non-tannins would also show the greatest loss by thoroughly washing the leather.

To test the accuracy of this view, a sample of each of the different leathers was ground up and well washed with cold distilled water. After having been dried, the samples on analysis showed the following loss by washing:

	Per cent.
Valonia	8.0
Myrobalans	2.6
Oak bark	8.0
Quebracho ext	3.2
Chestnut ext	5.4
Oakwood ext	8.1
Hemlock ext	5.8

The value of non-tannins in the direction of weight giving must always be considered so long as the yield of leather is calculated from weights, but it will be observed from the foregoing results that the behavior of these non-tannins towards hide substance are peculiar to the material from which they are derived, and non-tannins as such bear no relation whatever to each other, in which respect they resemble the tannin, so that a material like Myrobalans which is rich in these substances is not necessarily a weight giver.

The difficulty of determining the exact value of non-tannins is not simplified by reference to their solubility because a material like Valonia, which yields a large proportion of insoluble non-tannins, is also an excellent weight producer.

Because of the uncertain action of the non-tannins and the fact that the actual tannin itself contributes under certain conditions in some materials to increase the amount of non-tannins, it becomes impractical to account for each original tannin unit employed in producing leather and, furthermore, as the density of a tan liquor influences the solubility of its leather producing contents, the analysis of the material is at best only an indication of its tanning efficiency, but the behavior of a tanning material under laboratory conditions frequently suggests the manner of its application in practice to obtain the best results.

In the practice of tanning it is not customary to employ only

one tanning material, although a one material tannage is quite practical, but the development of leather making is towards the use of a combination of extracts, and it is already demonstrated that by proper selection and manipulation of the highest efficiency in the art of tanning is being obtained.

THE PRINCIPLES OF LEATHER STUFFING.[1]

By Hugh Garner Bennett.

The stuffing of leather is an essential and critical operation in the various processes of currying, and it is the purpose of this article to point out the scientific principles which underlie this process in the varied forms in which it is found in the practical world. Stuffing leather consists in the permeation of the fibrous tissues with various kinds of greases. This addition of grease to leather has several objects in view, the relative importance of which depends upon the particular kind of leather which is being manufactured. The following, however, are the principal reasons:—

(a) To give to the leather a certain amount of pliability and flexibility. This is desired, in a greatly varying degree, in all curried leathers. The function of the grease from this standpoint is that of a lubricant. The fibers of the leather, and even the smaller fibrils which compose them, have been isolated one from another in the processes of liming and tanning, but, by stuffing, they become coated with the fats and thus glide easily over one another when bending the leather.

(*b*) To give water-proofness to the leather. A certain amount of water-proofness is required in all curried leathers, if only to enhance the wearing properties. In the case of upper leathers, of course, the quality of water-proofness is particularly to be desired so far as it is compatible with a pleasing finish and feel.

(*c*) To give a further tannage. It is not the intention of the writer to discuss in this article the theory of tanning, but there seems little doubt that in some cases the stuffing of leather with

[1] *The Leather Trades Review.*

grease has an additional tanning effect, though, naturally, of a character differing from the primary tannage. Oil tannages are, of course, well known, their action being ascribed, at any rate partly, to the effect of aldehydes formed by the oxidation of the oil. In speaking of currying, Procter says:—"Even the possibility of an aldehyde tannage is not excluded, where the fiber is not already completely saturated with other tanning agents or where these agents, from their nature, have not so firm a hold on the fiber as to be incapable of being displaced by the action of aldehydes."

(*d*) To give weight to the leather. This object is placed last on the list, but it is certainly not least in practical importance. Most curried leathers are even yet bought and sold by weight, both in the rough and in the dressed condition, so that the addition of grease merely to give weight is a fairly obvious aim of the currier. There is, of course, a limit, according to the nature of the leather and the finish that is desired, so that the problem becomes one of making the leather take as much grease as possible without appearing greasy.

The stuffing of tanned leather is very much more easy than the penetration of pelts with oils and fats as in the case of the oil tannages. In the true oil tannages powerful mechanical treatment (stocks, drums, etc.) is absolutely necessary to bring about the penetration of the fats, but in tanned, or partly-tanned, leather the fibers are isolated, and, therefore, the impregnation with greases is much more easy to accomplish. There is, nevertheless, considerable difficulty in getting grease into leather. The penetration of oils and fats into dry leather is not so readily brought about as the penetration of water, and it is necessary for us to consider first of all why this is the case. Although both oil and water are liquids, the former has the greater "surface tension," and that is the reason for the greater difficulty in making it penetrate. The problem of stuffing leather, therefore, is the problem of dealing with the surface tension of the greases used, hence it is necessary that the nature of surface tension should be briefly explained, so that the different ways of overcoming it may be the more readily understood.

In the three states of matter—gaseous, liquid and solid—we

now know that the particles may be considered to be in a state of motion. As the space between the particles is decreased, as in the compression of a gas, the forces of attraction between the particles are increased in magnitude, so much, indeed, as to cause deviation from the gas laws. The motion of the particles in virtue of their kinetic energy independently exercised creates a tendency to fill all available space. This is realized in the gaseous state, but in the liquid state the inter-molecular forces referred to above have attained such a magnitude that they more than counterbalance this tendency. The result of this large increase in the inter-molecular forces is that a liquid is subjected to a force—in many liquids of considerable magnitude—away from its surface towards the interior of a liquid. This force is known as the "internal pressure" of the liquid.

The existence of this pressure will be easily understood when we consider the difference between a particle in the center of the liquid and a particle at the surface. In the center the particle is surrounded on every hand by other particles, all of which attract in their particular direction. If these forces be resolved in any plane they will be found equal in opposite directions. The resultant is, therefore, that there is no force on the particle due to the attraction of other particles. Its motion is, consequently, due only to its own kinetic energy. In the case of a particle at the surface, however, there are particles surrounding it and attracting it only on one side. Those which pull parallel to the surface of the liquid naturally neutralize one another as before, but there is nothing to counteract the attraction of those which fall towards the center, and hence there is exercised on all particles at the surface a strong force inwards—the internal pressure of the liquid. It is in consequence of the resultant of this force—surface tension—that there is the tendency in liquids to decrease the amount of exposed surface, *i.e.*, to assume that condition or shape in which the surface area is at a minimum—the sphere. The effect known as "capillarity" is also a result of the tendency. We have in leather stuffing therefore to consider how to lower the surface tension of the oil in order to make easy the penetration of the grease. There are various methods by which the surface tension of liquids such as oil may be reduced, and each

of these has been applied in practical currying. It is proposed now to consider these in turn.

I.—CONTACT WITH ANOTHER LIQUID.

For theoretical purposes it is often better to measure the surface tension of a liquid with reference to the vapor of that liquid, but in the case of oil, which possesses a small vapor pressure and a large surface tension, the practical problem is its surface tension with reference to air. This high surface tension of oil is effectively lowered for practical purposes by putting it in contact with another liquid—water.

With many pairs of liquids their surface tension one to another is practically zero—*e.g.*, alcohol and water. When shaken together they form an homogeneous mixture, and we say that they are "miscible in all proportions." With other pairs of liquids their surface tension one to another is not zero, but is very small. When such a pair is shaken together two layers separate again, but each layer contains a certain proportion of each liquid. A good illustration is a mixture of ether and water, which, after shaking together, gives a layer of water containing 10 per cent. of ether, and a layer of ether containing 3 per cent. of water. Such liquids are said to be "partially miscible," or "mutually soluble." With other pairs of liquids the surface tension between them is still very appreciable, though very much less than either to air. These are known as "non-miscible" liquids, but there is always some mutual solubility, which varies widely in degree, however, in different cases. Water and chloroform are ordinarily considered as non-miscible liquids, but an appreciable amount of each is dissolved in the other. Water and oil also fall into this last class. The surface tension between them is great, but it is very much less than between oil and air, so that for practical purposes the surface tension of oil is lowered by putting it in contact with water. In stuffing, therefore, the leather is used wet and the grease laid on and the goods hung up to dry. As the water dries out of the leather the grease takes its place following it easily into the leather and between the fibers. This contact with another liquid (water) is the method used for overcoming the surface tension of oil in the oiling of

sole and dressing leather, and it is also the principle of "hand stuffing."

II.—RISE OF TEMPERATURE.

As the temperature of a liquid is raised, the kinetic energy of its particles is increased, the spaces between the particles is also increased, and, on the other hand, the molecular attractive forces are decreased. Rise of temperature in a liquid, therefore, makes it increasingly fluid and mobile, and causes it to approximate slowly to the gaseous state. This involves in consequence a lessening of the internal pressure of the liquid and of the surface tension. With oil we have these effects just as with other liquids. An increase of temperature makes the oil more fluid, so that it runs more freely, and accelerates penetration of the fibers. Hence this method of lowering the surface tension of grease by increasing its temperature has been applied practically in currying leather. It is the principle of what is known as the "burning in" process, which involves the employment of dry, warm leather and hot grease. The process is carried out usually in one of two ways. Either the leather is completely immersed for a short time in the hot grease, or the hot grease is poured on to the warm, dry leather, but in either case the grease penetrates the leather with comparative ease. A practical advantage of this principle is that it becomes possible to employ "hard greases," *i.e.*, those which are solid at ordinary temperatures.

III.—RISE IN TEMPERATURE WHEN IN CONTACT WITH ANOTHER LIQUID.

This method of lowering the surface tension of grease is a combination of the two previous methods. The influence of a temperature increase on the surface tension of two liquids depends entirely upon the nature of the liquids. Some liquids which are "miscible in all proportions" at ordinary temperatures, become "mutually soluble" at higher temperatures. It may happen, indeed, as in the curious case of nicotine and water, that at still higher temperatures the liquids are again miscible in all proportions. The terms "miscible," "partially miscible," etc., apply, therefore, only to a definite temperature. In the case of a

great many pairs of liquids, however, the effect of a rise in temperature on the surface tension between them is similar to the effect of a temperature increase on their surface tension with reference to air, *i.e.*, heat very often lowers the surface tension between the liquids. With aniline and water, for example, there is a mutual solubility at ordinary temperatures, but at temperatures above 165° C. there is complete miscibility. With oil and water the effect is also in the same sense, though not to the same extent. Hence, although contact with water lowers the surface tension of oil, an increase of temperature lowers it still further, as well as making the grease more fluid. The combination of these two factors, therefore, of raised temperature and of contact with water, constitutes a very efficient method of overcoming the surface tension of grease, and of assisting in its penetration into leather. The combination of these two factors is involved in the practical method known as "drum-stuffing," in which both raised temperature and wet leather are employed.

IV.—INFLUENCE OF DISSOLVED SUBSTANCES.

It always happens that a solution has a different surface tension towards another liquid than the solvent alone. In many cases the effect of the dissolved substance is to lower the surface tension between the two liquids. A fourth method, therefore, of helping grease into leather would be to employ some substance, which on solution in water yields a lower surface tension with grease than does water alone. This is often carried out in practice, and is the principle which underlies the process of "fat-liquoring."

If two non-miscible liquids have their surface tension one to another lowered by the presence of some dissolved substance, and the mixture is then agitated very thoroughly, minute drops of one liquid are disseminated throughout the other liquid, and under appropriate conditions considerable time may elapse before these drops coalesce again to form an homogeneous layer, as is normal with non-miscible liquids. This mixture, indeed, may become so intimate that the product might almost be termed an homogeneous mass. Such mixtures are called "emulsions." In the case of oil and water, which is our practical problem, we can dissolve in the water various substances, such as soap, borax,

soda, etc., which lower the surface tension between the water and oil, and give after thorough admixture emulsions of a more or less permanent character. If one employs a relatively large proportion of water, one obtains what is technically known as a "fat-liquor." Raised temperature is often conducive to emulsification, and the practical process of fat-liquoring usually involves, therefore, all of the three methods discussed above for lowering the surface tension of grease. The principle of fat-liquoring hence includes the use of raised temperature, contact with water, and substances dissolved in the water. Natural fat liquors, such as egg-yolk, milk, cream, etc., are often useful assistants in making artificial emulsions. The oxidized fatty acids, moreover, such as occur in dégras, seem very helpful in emulsifying grease.

There are, of course, other points which materially assist in ensuring good penetration of grease into leather. It is perhaps obvious to suggest that, where possible, oils with a naturally low surface tension should be chosen, or oils which readily emulsify. Mechanical motion is also a very valuable assistant in stuffing leather. In drum stuffing the motion to which the goods are subjected results in a more rapid assimilation of the oils and greases than can be the case with evaporation, as in hand stuffing. Drumming is often resorted to after "burning in," to complete the penetration of the grease, and the stuffed leather is frequently made wet before this drumming to assist in the same direction. Fat-liquoring is also usually accomplished in the drum. Naturally the leather itself is also a great factor. The amount of plumping in the limes and early tan-liquors, and the nature of the tannage, are the important factors in isolation of the hide fibers and consequent good penetration of grease.

PROGRESS OF THE CHEMISTRY OF TANNING IN 1908-9-10.[1]

By Franz Ch. Neuner.

I. WORK ON THE THEORY OF THE TANNING PROCESS AND RESEARCHES OF A GENERAL CHARACTER.

The difference of opinion as to tanning, whether it shall be

[1] Condensed from *Zeitschrift für Chemie und Industrie der Kolloide*, Feb. and March, 1911.

considered a physical or a chemical process, continues, and appears likely long to continue. Like all contested scientific questions, this one occasions strenuous work in the opposing camps. E. Stiasny, who may be regarded as the chief advocate of the physical, colloid chemistry idea, still continues to elaborate[2] his theory, put forward as long ago as 1907.[3] According to this theory, tanning consists of two parts; first the adsorption of the dissolved colloid tanning materiais by the gelatine of the hide, and then an irreversible change of condition which the adsorbed tanning material suffers, without however becoming thereby chemically united to the hide. It is well known that however they may differ chemically, tanning solutions in general have a colloidal character.

The results of Stiasny's recent work[4] support his theory. Fahrion holds[5] that the hide fiber must be oxidized before or during the tanning process in order to make serviceable leather. This view is opposed by researches which show that the adsorption of acid, alkali and tan-stuffs by hide powder or hide is independent of any previous oxidation of the hide fiber. Stiasny shows further that the products of decomposition of collagen which undoubtedly contain the reactive groups NH_2 and COOH in freer form than the collagen itself, are not precipitated by tan-stuffs. The single exception to this is glutin, whose precipitates with tan-stuffs are now generally regarded as colloid precipitates. Acids are adsorbed much less freely by hide powder from alcoholic than from aqueous solutions, and in the former case no swelling takes place. Very recently Stiasny has shown that the adsorption curve holds for the taking up of acid by hide powder. R. A. Earp[6] has shown the application of the adsorption law for the equilibrium between water, tan-stuff and hide powder, while the non-tans show a much more crystalloid character.

In opposition to W. Fahrion[7] who holds that the surface development of the material to be tanned is of importance in the

[2] *Koll.-Zeit.* 2, Heft 9, (1908).
[3] *Chem. Ztg.*, No. 95 ff, (1907).
[4] *Coll.*, 1908, 117.
[5] *Zeit, f. angew. Chem.*, 665, (1903).
[6] *Coll.*, 1907, 175.
[7] *Zeit. f. angew Chem.*, 665, (1903).

tanning process only in so far as it concerns the extent of the surface and the masses of the reacting parts, Stiasny shows that the *condition* of the surface is of great importance. H. Wislicenus[8] found that "sprouted" and ignited oxide of aluminum shows higher adsorption of tan-stuff than freshly precipitated hydroxide, although the latter certainly has the greater chemical activity. According to E. Stiasny[9] sprouted alumina takes more tan-stuff out of aqueous solutions than from solutions in glacial acetic acid, thus showing that the aqueous solution is colloid, while according to E. Paterno,[10] tannin in glacial acetic acid shows the molecular weight of digallic acid. He has also shown that hide takes less silicic acid from an α-silicic acid solution than from a β-silicic acid solution of the same concentration, the latter being colloid, while the former is not.

R. O. Hertzog in collaboration with J. Adler[11] and G. Rosenberg[12] has published two related contributions to our knowledge of the tanning process. He points out that the taking up of silver nitrate and certain dye-stuffs by hide powder are typical reversible adsorption processes. The taking up of phenol also apparently follows in the main the adsorption scheme, but the results obtained make it evident that other features are present. In the case of phenol the process is at least more complicated, and in the opinion of the author these irreversible processes can never depend solely on adsorption. The adsorption of colloids by hide powder follows the rule of W. B. Hardy, that oppositely charged colloids are adsorbed, while those similarly charged are not. In two cases (sugar and albumen solution) negative adsorption by hide powder may be observed. From this circumstance R. O. Hertzog[13] concluded that the surface of chromed hide powder must be covered with a more or less semi-permeable membrane which permits the passage of the solvent but not of the dissolved material.

Since further research shows that chromed and unchromed hide

[8] *Koll.-Zeit.*, 2, Sec. 1, (1907).
[9] *Coll.*, 1908, 117.
[10] *Zeit. f. phys. Chem.*, 4, 475, (1889).
[11] *Koll.-Zeit.*, 2, Sec. 2, III, (1908).
[12] *Koll.-Zeit.*, 7, 222, (1910).
[13] *Zeit. f. physiol Chem.*, 57, 315, (1908).

powder are in essentially the same condition, Hertzog regards the question as no longer open. Stiasny[14] opposes this view of Hertzog. He also had found that white hide powder in the presence of albumen solution behaves entirely like chromed hide powder. The former indicates negative adsorption, although here one can scarcely suppose there is a semipermeable membrane. Hide powder takes from a solution of egg albumen as much water as white hide powder in a damp condition contains, that is, about 71 per cent., and this whether it is brought dry into contact with the solution or is moistened first.

E. Stiasny applies this apparent negative adsorption to the estimation of the plumping effect of acids.[15] It is clear that the hide powder must take away as much of the water of the acid albumen solution as its condition of plumpness due to the then present acid content permits. According to this research the water absorption depends on the increase of concentration of the albumen solution.

It appears from this that with increasing acid concentration from 0 to N/20 H_2SO_4, the plumping increases, reaching a maximum at about N/20 and decreasing again with further increase in acid concentration. The taking up of acid by hide powder follows fully the anticipated adsorption curve. An analogy in the behavior of hide powder with that of white hide cannot however be established. In the latter case, it is true, the water absorption by the white hide (plumping) also increases with increasing acid concentration, reaching a maximum at about N/10 H_2SO_4 (N/2 CH_3COOH). If the acid concentration is further increased, so great a decrease of plumping results that the hide may even shrink, that is, in consequence of the presence of a larger quantity of acid, the white hide holds less water than if it were in contact with water alone. The taking up of acid by white hide also follows the adsorption law, and for each acid there seems to be a maximum plumping concentration which is a specific constant of the acid.

An important contribution has been published by J. von Schroeder,[16] who has studied the adsorption of tannin under

[14] *Coll.*, 1909, 302.
[15] *Coll.*, 1909, 302.
[16] *Kolloidchem Beihefte*, 1, 1, (1909).

various circumstances by charcoal, sprouted alumina, gelatine and hide powder, in order to draw inferences in regard to the nature of the tanning process. It was shown that the taking up of tannin from alcoholic solution by charcoal or sprouted alumina takes place in the manner of the adsorption process; that this also holds for water solution in the case of the sprouted alumina, while for charcoal and water solution it only holds in the case of extreme dilution. In the adsorption of tannin from water solution by sprouted alumina, the end concentration became constant after some time, (in the research in question, four days) but when charcoal was used as the adsorbent, the concentration of the tan solution continued to decrease during the whole time covered by the experiment.

Hide powder takes tannin from alcoholic solution according to the adsorption law only for the first hour; later the law does not apply. The same is true for water solution. The amount taken from alcoholic solution is much less than from water. The addition of acids scarcely influences the adsorption of tannins, while alkalies cause a marked decrease. The abundant formation of gallic acid in the process of adsorption of tannin from water solution by hide powder may be entirely suppressed by the addition of acid or by sterilizing the tannin solution and the hide powder.

The adsorption of tannin by gelatine follows the adsorption isotherm and appears independent of the previous history of the gelatine. (Fresh gelatine solution, gelatine jelly and soaped gelatine solution were used.) While inorganic acids do not hinder the precipitation of gelatine by tannin, organic acids have a great influence in this direction. In this case, however, the previous history of the gelatine has a notable effect; gelatine gel taking a higher acid concentration to hinder precipitation than soaped gelatine, which in turn requires more than freshly dissolved gelatine.

The glue-tannin precipitate, dried and extracted with alcohol, dissolves easily without residue in luke-warm water. This seems to prove that tannin can be completely washed out of the glue-tannin precipitate, that the components of this precipitate are loosely bound together, and that tannin is not adsorbed by gelatine from alcoholic solution.

From these researches J. von Schroeder comes to the following conclusions. The adsorption of tannin by hide powder is a so-called indirect ("versteckte") colloid precipitation; that is, before the hide can be precipitated by tannin it must first be brought into a kind of soluble swelled condition. Therefore the taking up of tannin is far less when the hide powder is first treated with formaldehyde, because this makes the collagen completely insoluble. For a similar reason the taking up of tannin by hide powder proceeds much more slowly than in the case of glue. In the former case equilibrium is established much more slowly because in glue the collagen is already broken down, while in the case of the hide powder the outer layers must first become swollen before the precipitation of tannin by these layers takes place, and they in their turn because of their tanned condition hinder the swelling of the interior layers.

J. T. Wood[17] has also published an extensive research on the compounds of gelatine and tannin. Since various early writers gave very various figures for the proportions of gelatine and tannin in the gelatine-tannin precipitate, J. T. Wood reëxamined this matter, and found, as Sir Humphry Davy had, that the quantities of tannin precipitated depend on the concentration of the solution, and upon the amount of excess tannin. J. T. Wood's maximum to 100 parts gelatine was 240 parts tannin. According to Davy this should be 85 parts tannin, Lipowitz 65, Rideal 137, Mulder 135, Williams 78, and so on. By washing with cold and hot water until gelatine gives no precipitate in the wash water, a considerable part of the tannin is removed, so that the proportions in the washed precipitate were 100 parts gelatine to 136 parts tannin. The assertion of A. L. Lumiere and A. Seyewetz[18] that tannins and gallic acid render gelatine insoluble only in the presence of air was confirmed for gallic acid but negatived for tannin.

By chroming gelatine with solutions of chrome salts of varying concentration and basicity it was found that the Cr_2O_3 content of the resulting insoluble substance depends upon both the concentration and the basicity of the chrome solution, and

[17] *J. S. C. I.*, No. 30, (1908). (Reprinted in this JOURNAL, 1908, p. 183.)
[18] *Coll.*, 1906, 205.

that this is true also for the chrome tannage of hide. It was shown also that the maximum given by Lumiere and Seyewetz[19] of 3.2 to 3.5 grams Cr_2O_3 per 100 grams of gelatine may be much exceeded, (up to 13.6 per cent. Cr_2O_3). Chromed gelatine takes as much tannin out of its solutions as unchromed. This is observable in the case of gelatine plates, which can take up less tannin than gelatine solutions. J. T. Wood inclined to the opinion that the basic chrome groups unite with the COOH group of the gelatine molecule, while the acid tannin molecule adhere to the amino group of the gelatine. The equal capacity for tannin of the chromed and unchromed gelatine would thus be explained. This view, which he had expressed tentatively, J. T. Wood abandons in a later paper[20] in which the gelatine-tannin precipitate is considered as a colloid precipitate. The necessity of the presence of an electrolyte[21] for the formation of the precipitate is explained as follows. According to Wo. Pauli,[22] perfectly salt free gelatine has no electric charge, but the positive charge conferred by the material adsorbed from the electrolyte first enables the gelatine to form a precipitate with the negative tannin. This precipitate then adsorbs more tannin, and hence appears a reason for the dependence of the quantity of combined tannin on the concentration of the tannin solution.

R. A. Earp[23] found that continued heating in water rendered gelatine insoluble, and that an old gelatine solution precipitates considerably less tannin than a fresh one.

Lüppo-Cramer[24] describes the tanning effect on gelatine of dissolved colloid Ag_2O and Ag_2O_2. The insoluble gelatine compound of silver superoxide is of surprising permanence. The oxides of mercury and copper also tan gelatine to complete insolubility. By treatment with alkalies, this tanned gelatine is detanned and brought into solution.

A. Ricevuto[25] investigated the influence of electric charge on

[19] *Bull. Soc. Chim.*, 1077, (1903).
[20] *Coll.*, 1908, 494.
[21] Weiske, *Zeit. f. physiol Chem.*, 7, 460.
[22] *Pflüger's Arch.*, 78, 315, (1899).
[23] *Coll.*, 1907, 379.
[24] *Coll.*, 1908, 24.
[25] *Koll.-Zeit.*, 3, 114, (1908).

tanning. He found that gelatine solution only gives a precipitate with tannin when a *small* quantity of acid is added. With higher acid concentration, no precipitation takes place. This he explains by assuming that gelatine and tannin carry opposite electric charges only in the presence of low acid concentration. A substance must possess a negative electric charge in order to precipitate gelatine or hide. Therefore, Ricevuto asserts, chrome tannage must take place in alkaline solution in order for the chromic hydroxide to confer a negative charge.

Ricevuto's research, however, does not appear to justify the conclusion which he has drawn from it. This is especially true of the gelatine precipitate made with neutralized tannin solution.

Professor Henry R. Procter in "Problems of the Leather Industry," (Collegium, 1910, No. 313, reprinted in this JOURNAL, V. 242) makes some observations on the theory of the tanning process. In the case of tannage by sulphuric acid and salt pickle, he believes that the amphoteric hide forms a chemical compound with the acid, which is semipermeable to the salt and is dehydrated by its osmotic pressure. Aluminum and chrome salts, because of the weakness of their bases, are easily hydrolyzed. The hide takes up the free acid thus formed, as it does the acid from pickle, and fixes it. Continued hydrolysis results in the formation of colloid insoluble basic salts, which coat the hide fibers or possibly form adsorption or chemical compounds with them. Procter regards aldehyde tannage as essentially a chemical change, for "it is difficult to see how a volatile substance like formaldehyde can form a resistant coating on fibers."

B. Kohnstein[26] also gives a very interesting view of the probable nature of formaldehyde tannage. He considers that the condition of the fibers in formaldehyde leather is similar to that brought about by alcohol tannage, (according to F. Knapp), the gluing together of the fibers in drying being hindered by the union of the soluble protein of the hide with formaldehyde, forming a precipitate which surrounds the hide fibers,

On the contrary, L. Meunièr,[27] who has proposed a purely

[26] Personal communication.

[27] *Coll.*, 1908, 195.

chemical theory for quinone tannage, thinks with U. J. Thuau that formaldehyde tannage consists purely of the adsorption by the hide fiber of colloidal polymerization products of formaldehyde.[28] Formaldehyde leather shows comparatively little resistance to warm water.

A new purely chemical theory of tannage has been proposed by L. Meunier and A. Seyewetz,[29] based on the observation that a leather can be made either with quinone in the presence of air, or with a weak alkaline solution of phenol, which has even greater resistance to boiling water than chrome leather. Meunier and Seyewetz have not only turned this discovery to practical account (see their patent described in this number of the JOURNAL), but also make use of it as the basis of a theory. They assume that the quinone oxidizes the animo group of the hide (the formation of hydrochinon was observed), and that this oxidized hide unites with a second quinone molecule.

The chief representative of the chemical conception of tanning is now, however, W. Fahrion, who supports his views with a very extensive and valuable array of facts. Especially valuable are Fahrion's researches on the nature of chamois tannage, which afford several new points of view. In 1903[30] he published his first comprehensive theory of tanning as a salt-formation between a tan-stuff and oxidized hide fiber. In 1908[31] he advocated the view that after the preliminary physical processes (diffusion, adsorption, etc.), the secondary phenomena are of a chemical nature. He held that these changes do not relate, as Stiasny thought, to the adsorbed tan-stuff alone, but also to the hide, in consequence of the chemical action of the tan-stuff. Fahrion especially urges the view that tanning is preceded by a partial hydrolysis of the proteid bodies in the hide, by which chemically active groups are formed which react with the tan-stuff. This conception is similar to Suida's[32] color theory, and as already mentioned is opposed by Stiasny.

[28] *Coll.*, 1909, 211 ff.
[29] *Coll.*, 1908, 195.
[30] *Zeit. f. angew. Chem.*, 665, (1903).
[31] *Chem. Ztg.*, No. 28, (1908).
[32] *Zeit. f. Farbenindustrie*, **2**, Heft 9, 257, (1908).

Meanwhile W. Fahrion[33] published a new method of leather testing. In making tanning experiments with hide powder it is necessary to have some criterion by which to determine when the hide powder shall be said to be tanned. Fahrion uses for this purpose the behavior of the hide powder toward hot water. The hide powder is shaken up with water and then kept for 10 hours on a boiling water-bath, after which the percentage of dissolved organic matter is estimated, (called a). The undissolved part, expressed in per cent., $(100-a)$, is then the water resisting power, (Wasserbeständigkeit, "W. B."). The higher this number, the more complete is the true tannage in Fahrion's opinion. For pure white hide powder the W. B. is zero, and for quinone leather above 90. Between these lie the W. B. of vegetable tanned, oil tanned and chrome tanned leather, in an ascending series.

With the help of these criteria and many experiments, W. Fahrion comes to the following view in regard to the nature of the tanning process.[34] First it is granted that the primary process of tannage are of a physical nature. The preliminary processes depend on capillarity, diffusion and adsorption. The real tannage is a secondary process. Fahrion makes a distinction between true tannage, (which is a condensation process wherein the tan-stuff contributes O and the hide H to form water which splits off), and pseudo-tannage. The latter does not involve a chemical combination between hide and tan-stuff, but under the catalytic influence of the hide the tan-stuff splits off water, and the anhydro-derivative thus formed is precipitated in an insoluble condition on the hide. Fahrion's pseudo-tannage is comparable to Stiasny's secondary irreversible change of condition. Pseudo-tanned leather has slight water resistance, while that of really tanned leather is high.

1. *Chamois Tannage.*—True tannage is here brought about by the peroxyacids of marine animal oils, ("Tran"), which are formed by the oxidation of fatty acids in the air. The first phase of the reaction may be the union of the carboxyl group of the acid with a basic group of the hide. At least the deriva-

[33] *Coll.*, 1908, 495.

[34] *Zeit. f. angew. Chemie.*, 2083 ff., 2135, 2187 ff., 1909. *Coll.*, 1910, 16 ff., 249. Abstr. this JOURNAL, 1909, p. 326, 1910, pp. 72, 414.

tives of the peroxyacids with replaced carboxyl hydrogen, (salts and esters), and also other colloid and unsaturated peroxides without the carboxyl group do not tan thoroughly, while leather tanned with the peroxyacids of marine animal oils shows high water resistance. All these peroxyacids which are used technically contain the group —O—O— at least twice. In the second stage of true tannage, an active oxygen atom of the peroxyacid oxidizes two NH_2 groups of two hide molecules to NH groups, and the resulting water in the form of OH + H saturates the two valences which have been freed by the splitting off of the active oxygen. This assumption of Fahrion's is supported by the observation that the percentage of active oxygen in the peroxyacid becomes notably less during the tannage, and is in analogy with the results of Bamberger's[85] researches on the oxidation of amino groups by active oxygen.

As a third phase in oil tannage, Fahrion supposes a complex body to be formed by the splitting off of a second O_2 group, which then combines with both of the NH groups. This conception is based provisionally on a supposed structural analogy with the dianilino-quinones, since the structure of the hide molecule is still so slightly investigated as to afford no sure basis for reasoning. Besides this true tannage there is a pseudo-tannage. W. Fahrion found in hide powder tanned with fatty acids of fish oils, a completely neutral nitrogen free oil, soluble in petroleum ether. Leather so tanned resembled chamois leather in appearance but had small water resistance. On further examination these oils proved to be rearranged fatty acids, lactones, some of which were insoluble in all solvents. As these lactones are formed first by means of the tanning process itself, the hide must have the power to split off water catalytically, and the insoluble lactone thus produced brings about the pseudo tannage of the precipitated hide.

2. *Aldehyde Tannage.*—Following Nierenstein's opinion, W. Fahrion conceives this to be a true tannage, for which the equation holds:—

$$HCHO + 2XNH_2 = H_2O + CH_2(NHX)_2.$$

3. *Quinone Tannage.*—Fahrion points out that during the pro-

[85] *Berl. Ber.*, 1898—1902.

cess of quinone tannage, the proportion of active O in the quinone becomes less, and that by means of this O the quinone must operate to change the hide. The hide on its part must act through its amino group, since only such fibrous materials as contain the amino group (wool, silk, hide,) bring about the reduction of the quinone molecules. The analogy with dianilino quinone is here closer than in the case of chamois tannage, and corresponds to the following equation for the true tannage:—

$$2XNH_2 + 2C_6H_4O_2 = C_6H_6O_2 + C_6H_4(ONHX)_2.$$

There is here also a pseudo tannage. Quinone when allowed to stand a long time with water forms an almost black amorphous body scarcely soluble in water which is freely taken up by hide powder, to which however it gives only a very slight water resistance.

4. Vegetable Tannage.—It is known that vegetable tan-stuffs are related to the phenols, while they contain no ready formed quinone. Since, however, tanning research with phenol shows that the water resistance of the product is in all cases proportional to the capacity of the reacting phenol to form quinones, Fahrion assumes that true vegetable tannage may likewise be conceived as quinone tannage, especially since he found that the *o-* and *p-* polyphenols are oxidized to quinones without atmospheric oxygen by water alone.

Beside this true tannage, which depends on the ability of the phenol derivative of tannin to form quinones, a pseudo tannage also takes place, through the agency of the phlobaphenes. "By the reaction between hide, tannin and water, a hydrolysis of the tannin takes place, and then under the catalytic influence of the hide, causing water to split off, the formation of a difficulty soluble anhydro derivative follows." By intensive action of water, this anhydro derivative is again hydrolyzed, and becomes easily soluble. Hence the possibility of detanning bark leather, and its comparatively low water resistance.

5. Mineral Tannage.—By researches similar to those for the other modes of tannage, W. Fahrion comes to the opinion that mineral tannage is first a pseudo tannage, and that it later passes over into true tannage. This is done by the hide splitting

off water catalytically from the chrome salt in solution, and precipitating the anhydride so formed upon itself. This process is promoted by neutralization. Fahrion's views on mineral tannage are less convincing and his researches less extensive than on chamois tannage for example.

Among new tan-stuffs which have been investigated during the three years are the basic salts of the rare earths, cerium, lanthanum, etc., which in their tanning effect are very similar to chrome. F. Garelli[36] made some investigations, and shortly afterward his pupil, M. Parenzo[37] published the results of some tanning experiments with these materials. It was suggested that the abundant cerium bearing residues from monazite which has been worked for thoria (used in the manufacture of gas mantles) might be utilized as a source of tanning materials. It now seems probable that they will find a more profitable use in the manufacture of pyrophoric cerium alloys.

With the view that the adsorption of tanning materials depends chiefly on their physical properties, F. Neuner and E. Stiasny[38] studied the diffusive power of vegetable tan-stuffs, obtaining results as follows. Non-tans diffuse more rapidly than tannins, but a complete separation by dialysis is not practicable. The different tannins have considerably varying facility of diffusion through membranes, and many of them suffer in passing through a parchment membrane a partial splitting up into non-tans. In the case of many tannin solutions dialysis produces a cloudiness which seems to be due to diminished solubility caused by the removal of the more easily diffusible parts. In such cases the dialyzed solutions are sometimes difficult or impossible to detannize with hide powder. With increasing concentration and with increasing age of tannin solutions diffusive power decreases. By boiling solutions changed by age, the diffusive power may be restored. Sulphited quebracho shows less diffusive power than the untreated extract. From the diffusion of tan mixtures no conclusions can be drawn in regard to the conduct of the components. Non-tans seem to be without influence

[36] *Acad. dei Luicei,* vol. XVI, 1 sem. ser V.
[37] *Coll.,* 1910, 121.
[38] *Coll.,* 1910, 129.

on the diffusive power of tannins. In the process of dialysis the parchment membrane increases in weight, the amount of increase varying considerably with different tannins.

In regard to the diffusion of chrome, iron and aluminum salts through gelatine jelly, H. R. Procter and D. J. Law[39] have made a report. They showed that the diffusion of acid and base proceed separately, as already suggested by E. Stiasny, because through hydrolysis the chrome salt is split into acid and base, and the former in conformity with its crystalline character diffuses much more rapidly in the jelly than the latter. The jelly was colored with weak phenolphthalein, so that the advance of the acid could be observed by the fading of the color and that of the chromic hydroxide by the green tint which it produced. In the case of chromium chloride solution, it was notable that the speed of diffusion both for acid and base appeared independent of the basicity of the solution, while for chrome alum solution only the acid diffusion was independent of the basicity, the speed of diffusion of the basic portion decreasing conspicuously with increasing basicity. A great difference was found between boiled and unboiled alum solutions. In the boiled solution the violet crystalloid modification being changed over into the green colloid form, the sulphuric acid now completely split off by hydrolysis showed a much increased rapidity of diffusion.

Of work of a general character there remains to be mentioned only that of L. Meunier and his pupils, which relates to the important subject of emulsions, treated from the standpoint of the tannery.

II.—GREEN HIDES AND THEIR PRESERVATION.[40]

The much disputed question of an interfibrillar substance in the hides of mammals appears now to have been solved by E. H B. van Lier.[41] It is a mucoid, similar to that found in sinews or the umbilical cord. It gives a weak acid reaction, is soluble in

[39] *J. S. C. I.*, Mar. 31, 1909. Reprint this JOURNAL, 1909, 157 and *Coll.*, 1909, 199.

[40] Pure theoretical researches on hide substance, having no direct relation to tanning, are not mentioned in this report.

[41] *Coll.*, 1908, 337.

alkalies and in dilute lime-water and is precipitated by acetic acid. By long continued hydrolysis with dilute HCl it yields a substance which reduces Fehling's solution. The interfibrillar substance may be completely extracted from cow or horse hide by dilute lime-water in eight days. In this respect it is not identical with Reimer's[42] coriin which was apparently a decomposition product of connective tissue produced by the action of concentrated lime-water. The difference between sole and upper leather has often been explained as due to the presence or absence of this interfibrillar substance, determined by the previous treatment of the hide. Yet this explanation appears not to suffice, since the interfibrillar substance would doubtless be for the most part removed by liming. E. Stiasny and G. Abt,[43] in a work on the action of lime salt and acetic acid on green, sweated, limed or bated hide[44] come to a like conclusion about Reimer's coriin. The authors find that saturated lime solution exerts a solvent or hydrolytic action on hide fiber, and that this action continues during repeated extractions. The splitting up effect seems to be considerable. By fractional "salting out," primary and secondary gelatoses and gelatopeptones were recognized; also a compound of collagen and lime which may be called calcium albuminate. Lime-water shows a sterilizing action with reference to the ferments of the dung bate and of putrefaction. Salt solution, (10 per cent.), by itself has no solvent action on the hide substance. Repeated extractions with it gave less and less result in hide substance. Only when the hide without liming was put into the salt solution directly from the sweating or bating did the salt solution seem to dissolve any considerable amount of hide substance. This is really due to the insufficient sterilizing effect of the 10 per cent. salt solution. The hydrolysis of the so dissolved hide substance is slight, but is greater if there has been a previous liming. The degree of hydrolysis was estimated by Stiasny's method.[45] Acetic acid (N/10) produces a considerable swelling effect, but no great chemical change. The dis-

[42] *Coll.*, 1909, 321.
[43] *Dingl. polyt. Journ.*, 205, 143, (1872).
[44] *Coll.*, 1910, 189. Abstr. this JOURNAL, 1910, 384.
[45] *Coll.*, 1908, 371 and 1910, 181. Abstr. this JOURNAL, 1910, 345.

solved portion is largely acido-gelatose. The action of bacteria in the sweated and bated hides is quickly checked.

The Brussels Congress of 1908[46] referred the question of proper preservation of hides to a commission, who should test the various methods of preservation and disinfection and work out new methods. This commission made a first report to the Paris Congress in 1910. J. Paessler reports on the damage to hides by unsuitable preservation.[47] S. R. Trotman[48] found that certain stains are due to microörganisms. J. Abt[49] finds two kinds of so-called salt stains. The first, gray and irregular, he ascribes to a yeast. The other, brown and visible on the flesh side, to various kinds of bacteria which act on the blood and make the coloring matter from it. A. Seymour-Jones[50] has studied the influence of mode of living and kind of food on the quality of sheepskins. He found that the cause of a frequently occurring eruption, ("Cockle"), was the feeding of the sheep on oil cake and other artificial foods. A few days after shearing the cockle disappears, and cockle is not found in goats or hairy sheep. Seymour-Jones suggests that the wool withdraws from the hide the more liquid parts of the fat, and that the excess of solid fat left behind is the cause of cockle. Breckle[51] suggests that the spores of authrax in hides may be destroyed by permitting the hides to lie in a warm damp room for some hours. The spores are thus made to germinate, and the resulting bacteria may be destroyed with lime.

J. H. Yocum[52] finds fault with the methods of disinfection suggested by the government, and recommends for wet salted hides immersion for five minutes in a 0.1 per cent. solution of bichloride of mercury saturated with common salt. The bichloride alone forms insoluble compounds with the hide. Not only

[46] *Coll.*, 1908, 398.

[47] *Ledertechnische Rundschau*, 1909, No. 51. Abstr. this JOUR., 1910, 198.

[48] *J. S. C. I.*, **28**, 1238. (1909). Reprint this JOURNAL, 1910, 216.

[49] *Le Cuir*, 1910, 527.

[50] *Coll.*, 1908, 191.

[51] *Zentralbl. f. Bact.*, 50, 101, (1909)

[52] This JOURNAL, 1910, 507.

does the salt prevent this, but the hides after immersion are as thoroughly salted as before.

III.—SOAKING, LIMING AND SWEATING.

L. Meunier and Hue[53] found that dry imported sheepskins which had been soaked, sweated, unwooled and again dried, lost when again soaked by the tanner from 25 to 30 per cent. They recommend the use of sulphurous or hydrochloric acid in the second soak. The skin substance which would otherwise be lost is thus converted into a gel, and in subsequent liming there is no more loss of skin substance than from fresh skins.

U. J. Thuau[54] describes the unhairing effect of sulphurous acid which acts chiefly on the Malpighian layer, and loosens the hair very well. For lessening or preventing swelling, common salt may be used. Further work on this line was done by E. Nihoul[55] who also used hydrochloric, acetic and formic acids, controlling the swelling by sodium sulphate etc. He attributes the effect to the ability of the acids to produce hydrolysis.

L. Levi and E. Manuel[56] find that high temperatures must be avoided in the use of technical arsenic sulphide and lime.

R. W. Griffith[57] gives a detailed explanation of the liming process from the scientific standpoint, with reference also to practice.

In order to estimate the quantity of dissolved hide substance in soaks and limes, R. A. Earp[58] precipitates the liquid with chrome alum and estimates the nitrogen in the precipitate by the Kjeldahl method. This method, however, does not precipitate the amino acids. F. Kopecky[59] titrates the soak water before and after use with normal acid, and finds in the difference between the amounts of acid used a measure of the dissolved hide substance, since the putrefaction of the hide forms alkaline substances.

[53] *Coll.*, 1909, 217. Abstr. this JOURNAL, 1909, 242.
[54] *Coll.*, 1908, 362. Abstr. this JOURNAL, 1908, 407.
[55] *Bourse aux Cuirs de Liege*, 1908, No. 38, 8.
[56] *Coll.*, 1910, 309.
[57] This JOURNAL, 1910, 109.
[58] *Coll.*, 1907, 412. Abstr. this JOUR., 1908, 63.
[59] *Coll.*, 1907, 311.

J. T. Wood and S. R. Trotman[60] place 50 cc. of filtered lime liquor in a 100 cc. cylinder with 10 cc. glacial acetic acid and 40 cc. concentrated solution of common salt, and estimate the precipitate from its volume.

E. Stiasny[61] titrates the lime liquor with and without the addition of formaldehyde, and finds in the observed difference a measure of such material of an amino-acid character as has been produced by the hydrolysis of the hide. He supports his method by the results of a research by S. P. L. Sorensen.[62] This method however is not applicable to old limes which contain sodium sulphide. It is not practicable to remove this substance with zinc sulphate, for that would precipitate a part of the hide substance. E. Stiasny therefore recommends the destruction by means of iodine solution[63] of the H_2S released by acetic acid, neutralization of the acid, addition of formaldehyde and then titration with NaOH. This method is only available where amino acids are already formed. By completing the hydrolysis of an equal sample (boiling with 20 per cent. HCl) and subjecting it to the same analysis, the difference in the amounts of NaOH used gives a measure of the extent of the hydrolysis of the first sample. By determining the total N before and after complete hydrolysis, an estimate may be made of the proportions of mono-amino and di-amino acids in the decomposition products.

H. Garner Bennett[64] in the technical control of limes estimates their basicity by the use of methylorange and phenolphthalein as indicators. While phenolphthalein is only sensitive to the strong base, lime, methylorange also shows ammonia, amino-acids, peptone, etc. The difference between the amounts of acid used with the two indicators gives a measure of the dissolved hide substance. This very rapid method is not, as the author admits, very trustworthy. The end point is difficult to strike, and sodium sulphide exerts a disturbing effect.

H. G. Bennett[65] recommends a modification of the Kjeldahl

[60] *J. S. C. I.*, **28**, 1304, (1909). Reprint this JOURNAL, 1910, 272.
[61] *Coll.*, 1908, 371. Abstr. this JOUR., 1908, 398.
[62] *Biochem. Zeitschr.*, 1907, 45.
[63] *Coll.*, 1910, 181. Abstr. this JOUR., 1910, 345.
[64] *Coll.*, 1909, 194. Reprint this JOURNAL, 1909, 143.
[65] *Coll.*, 1909, 197. Reprint, this JOURNAL, 1909, 140.

method. After the action of the sulphuric acid is complete, the mixture is neutralized with caustic soda, phenolphthalein as indicator, and then a neutral solution of formaldehyde is added, liberating the sulphuric acid of the ammonium sulphate, as shown:—

$2(NH_4)_2SO_4 + 6HCHO = 2H_2SO_4 + N(CH_2.N : CH_2)_3 + 6H_2O$. Hexamethylenetetramine is quite neutral to phenolphthalein, and free sulphuric acid is then titrated with soda.

IV.—DELIMING, PLUMPING AND PICKLING.

Of acids newly made available for these purposes, butyric acid has been prominently mentioned. It has lately been produced cheaply from distillery refuse by Effront's fermentation process, and is quite equal to other organic acids heretofore used, beside having valuable properties peculiar to itself.[65a]

E. Giusiana[66] uses sodium bisulphite for deliming, with an equal quantity of HCl. The sodium bisulphite forms with sodium sulphide and lime, H_2S, sodium sulphite, calcium sulphite and NaOH, which are changed into the respective chlorides by the HCl. This method avoids the danger of plumping by excess of HCl.

In the case of the acid swelling of white hide, R. W. Griffith and A. H. Claflin[67] found that the speed of plumping is directly proportional to the hydrion concentration. Gelatine and glucose do not diminish the plumping by acids, but they add to the restraining influence of NaCl. The influence of salts on acid plumping depends both on the nature of the salt and the kind of acid. In a 0.5 per cent. solution of sulphuric, formic, or lactic acid, 2.5 per cent. of sodium lactate prevents plumping, while 2.5 per cent. disodium phosphate hinders plumping in the case of formic and lactic acids, but not in the case of sulphuric acid. Analyses of sour yard liquors confirmed these observations. For example, a liquor containing 0.5 per cent. lactic acid and 0.5 per cent. calcium lactate showed no plumping effect.

[65a] Among the latter may be mentioned its odor, which is little short of terrifying. Ed.

[66] *Coll.*, 1910, 14. Abstr. this JOUR., 1910, 200.

[67] This JOURNAL, 1908, 154.

A. Besson[68] has reported on the lactic acids and methods of analyzing them. The technical acid is digested with KOH. If this is done with boiling, the KOH acts on the foreign substances present, but if allowed to stand in the cold, the KOH takes up the lactic acids and hydrolizes the anhydrides without acting on the other substances.

V.—BACTERIOLOGY OF TANNING AND BATES.

Detailed researches on the role of bacteria in the tannery have been made by H. Becker,[69] G. Abt[70] and J. T. Wood.[71]

The action of microörganisms in destroying acid in tan-liquors was studied by L. Balderston,[72] who found that yeasts growing on the surface and not fermenting sugars, rapidly destroy the acid in liquors exposed to the air.

L. A. Groth[73] studied the influence of bacteria on tannin. Balland and Droz[74] recommended the use of a layer of oil on the surface of vats to prevent the growth of mold.

In recent years a number of artificial bates have been devised to replace the dung bates.

VI.—VEGETABLE TANNING MATERIALS.

Many researches on the constitution of the tannins, having no direct relation to practice, have been made. These are not mentioned.

J. Jedlicka[75] in an extensive research on the sugars of oakwood extract showed that the non-hydrolyzed non-tans of oakwood extract had a reducing power on Fehling's solution corresponding to an average content of 3.2 per cent. glucose in the extracts, while after hydrolysis the percentage of glucose rose to 7 per cent. This seems to mean that a part of the non-tans consists in the first instance of non-reducing di- and poly-saccharides.

[68] *Coll.*, 1910, 73.
[69] *Coll.*, 1909, 169.
[70] *LaHalle aux Cuirs*, 1909, 53, 87, 105. Abstr. this JOURNAL, 1909, pp. 86, 110, 165, 189.
[71] *J. S. C. I.*, 29, 666, No. 11, (1910). Reprint this JOURNAL, 1910, 366.
[72] This JOURNAL, 1910, 326.
[73] *Leather Trades Review*, 1910. Reprint this JOURNAL, 1910, 269.
[74] *Jour. Pharm et Chimie*, 1909, 6 Reihe, 29, 573.
[75] *Coll.*, 1909, 112. Abstr. this JOURNAL, 1909, 162.

If the extract itself be hydrolyzed before being de-tannized, the percentage of glucose is 9.2 per cent. This higher proportion is explained by supposing either that a part of the saccharides are of a glucoside character, and are so combined with the tannin as to be precipitated by the hide powder; or that the removal of tannin with lead acetate also precipitates some gummy bodies which by subsequent treatment with sulphuric acid are converted into sugar.

(Here follows mention of many articles on the production of extracts etc., and of many patents relating to extracts.)

J. Paessler and Ch. Veit[76] have investigated the solubility of the commoner tanning extracts at various concentrations, and find that the "utilization," that is the proportion of really soluble tannin to that shown by analysis varies very much with different extracts. In some it is 100 per cent., but in most lower. In many it increases with increasing concentration of the solution, while with others it falls, and with still others it at first falls, and as the concentration is further increased it again rises.

In another study which deals with the colors which various tanning materials give to leather, J. Paessler[77] tested the leather colors in a Lovibond tintometer.

VII.—TANNIN ANALYSIS.

The official methods of the I. A. L. T. C. have now been published by authority of the Paris Congress, 1910. In 1908 Zeuthen[78] proposed an improvement in the official method, which was later modified by J. Paessler.[79] This method was tested by the commission of the I. A. L. T. C. on tannin analysis.[80] The A. L. C. A. has an official method of tannin analysis[81] which differs slightly from that of the I. A. L. T. C.

Karl J. Swick[82] proposes to make approximate determinations

[76] *Coll.*, 1908, 295. Abstr. this JOURNAL, 1908, p. 358.
[77] *Coll.*, 1908, 48. Abstr. this JOURNAL, 1908, 109.
[78] *Coll.*, 1908, 366. Abstr. this JOURNAL, 1908, 395.
[79] *Coll.*, 1909, 201, 305. Abstr. this JOURNAL, 1909, 298.
[80] *Coll.*, 1909, 201; 1910, 157. Abstr. this JOURNAL, 1909, 247, and 1910, 342.
[81] This JOURNAL, 1911, 3.
[82] *Coll.*, 1908, 281. Abstr. this JOURNAL, 1908, 355.

of tannin content by examining the refractive index of solutions before and after treatment with hide powder, the fall in the index being approximately a measure of the tannin taken up. The instrument employed is the Zeiss immersion refractometer, with means for maintaining constant temperature.

R. Lepetit[83] precipitates tannin with ammoniacal zinc acetate solution. M. Philip[84] reports on certain color-relations of different tannins. E. Stiasny[85] found a very sensitive colloidal reaction with certain metallic salts. To 2-5 cc. of a dilute solution of an aluminum salt, 5 cc. of a 1/10 per cent. tannin solution is added followed by 10 cc N/1 Na_2SO_4, and the whole is boiled. A flocculent precipitate forms even when only 0.01 mgr. Al_2O_3 per cc. is present. This is regarded as a good test for the presence of genuine tannin.

H. Procter and S. Hirst[86] detected sulphite cellulose liquors in tanning extracts by means of the lignin reaction with anilin and HCl.

M. Nierenstein and T. A. Webster[87] give a chemical method of recognizing the adulteration of sumac depending on the fact that the pyrogallol tannin of sumac gives a precipitate with diazobenzol-chloride, while the catechol tannin of pistacia and other adulterants does not.

Cavazza[88] uses thallium carbonate and uranyl nitrate for the microchemical examination of various tanning materials. W. Appelius and F. Merkel[89] have prepared tables for the valuation of willow bark by von Schröder's hydrometer method. W. K Alsop[90] reports on the analysis of chestnut wood.

Much work has been done on color estimation of extracts. H. Procter[91] has devised a modification of the tintometer method, which English chemists have adopted.

[83] *Coll.*, 1910, 375. Abstr. this JOURNAL, 1910, 527.
[84] *Coll.*, 1909, 249. Abstr. this JOUR., 1909, 249.
[85] *Coll.*, 1908, 348. Abstr. this JOURNAL, 1908, 400.
[86] *J. S. C. I.*, 1909, 293. Reprint this JOURNAL, 1909, 146.
[87] *Coll.*, 1907, 244. Abstr. this JOURNAL, 1907, 308.
[88] *Chem. Zentralbl.*, 1, 1648, (1908). Abstr. this JOURNAL, 1908, 245.
[89] *Coll.*, 1909, 22. Abstr. this JOUR., 1909, 62.
[90] This JOUR., 1909, 95.
[91] *J. S. C. I.*, 1910, 663. Reprint this JOURNAL, 1910, 352, *Coll.*, 1910, 292.

A. Gansser[92] employs "animalized" cotton fabric, while H. C. Reed and G. A. Kerr[93] use white woolen cloth for testing the coloring effect of extracts.

H. G. Bennett and C. D. Wilkinson[94] recommend the use of lead oxide for the estimation of acids in tan liquors, which precipitates the tannin and forms soluble salts with the organic acids. The quantity of these acids is estimated by titration with potassium ferro-cyanide.

A. Seymour-Jones and H. R. Procter[95] titrate the liquors direct with KOH, using fluorescin as indicator.

G. Grasser[96] proposes a method by which several of the acids often found in tan liquors may be estimated separately.

VIII.—VEGETABLE TANNAGE.

J. Gordon Parker[97] shows that sole leather tanned with liquors extracted at atmospheric pressure is firmer and has a higher water resistance than that tanned with materials extracted under pressure. The former kind he finds also tan more rapidly. He also decides that the value of non-tans in the tan-liquors, viewed from the standpoint of leather quality is at least extremely doubtful.

IX.—CHROME AND ALUM TANNAGE.

E. Stiasny[98] has published an extended study of the chemistry of chrome tanning. At the beginning of the one-bath process the sulphuric or hydrochloric acid from the hydrolized chrome salt is adsorbed because of its crystalloid character. Then adsorption of the basic chrome salt begins, an irreversible process, and this adsorption gradually increases. The basicity of the liquor therefore at first increases and afterward diminishes, and finally the liquors become more acid than at the beginning. The

[92] *Coll.*, 1909, 37.

[93] This JOURNAL, 1908, 382 and 1910, 94.

[94] *J. S. C. I.*, 1907, 1186. *Coll.*, 1907, 441. Abstr. this JOURNAL, 1908, 68.

[95] *Coll.*, 1910, 298. Abstr. this JOUR., 1910, 411.

[96] *Coll.*, 1910, 406. Abstr. this JOUR., 1910, 581.

[97] *J. S. C. I.*, 1910, 313. Reprint this JOURNAL, 1910, 297.

[98] *Der Gerber*, 1908, No. 823, 1909; Nos. 826, 827. Abstr. this JOURNAL, 1908, 401.

more dilute the solution of chrome or aluminum alum, the more basic is the part taken up by hide powder. Added salts and colloids have no marked effect on the amount of chrome taken up. The addition of electrolytes to the first bath in the two-bath process causes a reduction in the amount of bichromate taken up, while the addition of mineral acids causes a great increase.

J. T. Wood and D. J. Law[99] report on a colorimetric method of determination of chrome in one-bath liquors, and H. Ballenbach[100] on a volumetric method with the use of potassium permanganate.

X.—LEATHER ANALYSES.

The Paris Congress of the I. A. L. T. C. appointed a commission to study the subject and work out an official method for the association. The official method of the A. L. C. A. was published.[101] For the qualitative estimation of grape sugar, in leather, B. Kohnstein[102] applies the Hoppe-Seyler method, employing orthonitrophenylpropiolic acid, which in alkaline solution reacts with grape sugar to form indigo. For the quantitative estimation of sugar, H. G. Bennett[103] recommends a modification. The copper oxide reduced in the Fehling's solution is shaken up with ferric sulphate, reducing an equivalent amount to ferrous sulphate, which is then titrated with potassium permanganate.

For the estimation of nitrogen in leather, U. J. Thuau and P. de Korsak[104] follow the usual Kjeldahl method as far as the formation of ammonium sulphate, which substance is broken up by sodium hypobromite and the released nitrogen measured in a specially constructed nitrometer.

XI.—MISCELLANEOUS.

Boulanger[105] has differentiated between the hide fiber and the cementing materials by means of the microscope, staining a thin

[99] *J. S. C. I.*, 1910, 398. Reprint this JOURNAL, 1910, 295.
[100] *Coll.*, 1907, 428. Abstr. this JOUR., 1908, 70.
[101] This JOURNAL, 1911, 12.
[102] *Coll.*, 1910, 310. Abstr. this JOUR., 1910, 467.
[103] *Coll.*, 1909, 289. Reprint this JOUR., 1909, 259.
[104] *Coll.*, 1910, 364. Abstr. this JOUR., 1910, 527.
[105] *Bull. Soc. Ind. du Nord de la France*, 1907.

section of leather with Weigert's solution. He draws conclusions in regard to the swelling and tanning of the hide, and the constitution of corium.

M. C. Lamb[106] has made an extensive study of the injury done to book-binding leathers by the products of combustion of illuminating gas.

THE BACTERIOLOGY OF THE LEATHER INDUSTRY.[1]

(See J. S. C. I., June 15, 1910, pp. 666–672.)

By J. T. Wood.

BIBLIOGRAPHIC APPENDIX.

At the request of friends who are interested in the subject, I have been induced to print the following short bibliography of works bearing on the bacteriology of leather manufacture especially in connection with the bating or puering process. It was put together originally with a view to form part of a treatise on the subject, but as the prospect of publishing this is remote, I give the list as it stands in the hope that it may prove useful to other investigators. It does not profess to be complete, but I think it includes most of the important works. I shall be glad if those interested will inform me of any omissions, or make additions to the list, which will render it more complete.

For particulars of some of the earlier works (Nos. 1, 2, 4, 5, 6, 7, and 8) I am indebted to Dr. E. Stiasny of Leeds University.

1. La Tannerie et la preparation des Cuirs. (MS.) Desbillettes. 1708.
2. L'art du tanneur. De la Lande. 1764.
3. The art of tanning and currying leather, with an account of all the different processes made use of in Europe and Asia for dying leather red and yellow, collected and published at the expense of the Dublin Society. To which are added Mr. Philipo's method of dying the Turkey leather as approved of by the Society for the Encouragement of Arts, etc., and for which he had a reward of £100, and their gold medal for the secret. Also the new method of tanning invented by the late David Macbride, M.D., London, reprinted for J. Nourse in the Strand, Bookseller to His Majesty. 1780.
4. Lohgerberei, Ignatz Bautsch. Dresden, 1793.

[106] *Coll.*, 1908, 400.

[1] From J. S. C. I. Supplement to article reprinted in this JOURNAL, 1910, p. 360.

5. Ueber die Bearbeitung der Tierhäute zu allen Gattungen von Leder. K. T. Kasteleyn. German translation from the Dutch. Leipzig, 1797.

6. Chemisch technologische Grundsätze der gesammten Lederindustrie. Hermbstädt. 2 vols. Berlin, 1805 and 1807.

7. Dictionary of Chemistry and Mineralogy. Aikins, 1825.

8. Hand-Encyclopädie füd das Gerben, Zurichten, etc., des Leders. L. F. Kummer, Berlin, 1830.

9. Handbuch der Gesammten Lohgerberei. Vom Dr. Ch. H. Schmidt. Weimar, 1847.

10. Lehrbuch der Sohlledergerberei. Dr. G. W. Bichon, Berlin, 1848.

11. "Das Beizen der Glacé-Felle" in Handbuch der Weissgerberei. Anton Brüggemann. Quedlinburg and Leipzig, 1857. p. 21.

12. Erfahrungen auf dem Gebiete der Gerberei. J. C. H. Lietzmann, Berlin, 1862.

13. "Das Behandeln in der Kleienbeize" in Handbuch der Weissgerberei. Dr. W. F. Gintl, Weimar, 1873. p. 51.

14. Mistbeizen. Der Gerber, 1884. p. 197.

15. The manufacture of Leather. Davis, Philadelphia, 1885. p. 335, etc.

16. Traité pratique de la Fabrication des cuirs et du Travail des peaux. Villon, 1889. p. 407.

17. Die Englische Methode für die Chevrettengerbung. Beizverfahren, Der Gerber, Bd. XV, 1889. p. 267.

18. Methods of Bacteriological Research, with some accounts of Bran Fermentation, by J. T. Wood. Jour. Soc. Chem. Ind. IX, 1890. p. 27.

19. The Theory and Practice of Tanning. W. J. Salomon. Tech. Quarterly, 1892. 5 (1 and 2), 81—88.

20. Further contribution on the Nature of Bran Fermentation, by J. T. Wood, and W. H. Willcox, B.Sc., London. Jour. Soc. Chem. Ind. XII, 1893. p. 422.

21. The Chemistry of the Grainer Pit, by T. Palmer and P. G. Sandford. J. Anal. and Appl. Chem., 1893, 7, 87—95.

22. Fermentation in the Leather Industry, by J. T. Wood. Jour. Soc. Chem. Ind. XIII, 1894. p. 218.

23. The Bacteria of Stable Manure and their Action. Dr. E. Herfeldt, Bonn. Jour. Soc. Chem. Ind. XIV, 1895, pp. 449—452. Translated with foreword by J. T. Wood. (This paper contains a Bibliography of 21 items.)

24. Uber die Beziehung der Bakteriologie zur Gerberei. Dr. F. H. Haenlein. Cent. Bl. f. Bakt. II, 1895. p. 26.

25. Die im Miste vorkommenden Bakterien und deren physiologische Rolle bei der Zerzetzung desselben. S. A. Severin. Central Bl. (II), Vol. I., 1895, pp. 97, 160, 799. Vol. III. pp. 628, 706.

26. Gährungserscheinungen in Gerbbrühen. Fr. Andreasch. Der Gerber, 1895-7.

27. W. Schmitz Dumont. The Sweating Process in the Tannery. Ding. Polyt. Jour. 1896, 300, 139—144. J. S. C. I. 1896, p. 461.

28. On a pure cultivation of a Bacillus fermenting Bran Infusions, by J. T. Wood and W. H. Willcox, B.Sc., London. Jour. Soc. Chem. Ind. XVI, 1897. p. 510.

29. The Rationale of Bating, by J. T. Wood, Leather Industries. September, 1898.

30. Notes on the constitution and mode of action of the Dung Bate in Leather manufacture. J. T. Wood, Jour. Soc. Chem. Ind. XVII, 1898. p. 1010.

31. "Schwitzen" in Gerberei Chemie, Sammlung von Aufsätzen Professors Dr. Julius von Schröder, 1886—1895, published 1898.

32. Beizen und neue Beizmittel, W. Eitner, Der Gerber. Bd. XXIV, No. 563—567, 1898.

33. The Rationale of Drenching, by J. T. Wood. Leather Trades Review, Nov. 15, 1898.

34. Cantor Lectures on Leather Manufacture, by Prof. H. R. Procter, F.I.C., Society of Arts. Lecture II., April 24, 1899.

35. Further notes on the Action of the Dung Bate, by Joseph T. Wood. Jour. Soc. Chem. Ind. XVIII, 1899. p. 990.

36. Das Beizen der Blössen in Handbuch der Chromgerbung, Jos. Jettmar. Schulze and Co., Leipzig, 1900.

37. J. Borgmann. Die Feinleder Fabrikation, Berlin, 1901. Das Beizverfahren, p. 65.

38. Das Beizen der Blössen in Praxis und Theori der Leder Erzeugung, von Josef Jettmar, Julius Springer, 1901.

39. Micro-organisms and Antiseptics in Tanning. F. Jean, Rev. Chim. Ind., 1901.

40. The Principles of Leather Manufacture, by Professor H. R. Procter. E. and F. N. Spon, London, 1903. Chap. XIII.

41. La Tannerie, par Louis Meunier and Clément Vaney, Gauthier-Villars. Paris, 1903. p. 125, etc.

42. Bakteriologische Vorgänge in der Lederindustrie. 1904, H. Becker. Zeitschrift f. Offentliche Chemie. Heft. XXIII, Jahrgang X.

43. Untersuchungen über die Bakterien im Verdaugskanal des Rindes. P. Ankersmit. Centralbl. f. Bakter. I, O, Bd. 39, 1905. p. 359.

44. Uber anaerobe Bakterein im Rinderdarm, Neubauer. Archiv. f. wissensch. u. prakt. Tierheilk. Bd. 31, p. 153, 1905.

45. Studien über fäulnisserregende anaerobe Bakterien des normalen menschlichen Darmes, und ihre Bedeutung. F. Passini. Zeitsch. f. Hygiene. Bd. 49, p. 135. 1905.

46. A new process of puering or bating hides and skins. Allen Rogers. Jour. S.C.I., p. 103, 1906.

47. Recent advances in the Bacteriology of Putrefaction, by J. T. Wood. Jour. S.C.I. XXV, 1906, p. 119. (Contains a bibliography of 21 items.)

48. Uber den Bakteriengehalt menschlicher und thierischer Fäces. M. Lissauer. (Archiv. f. Hyg. Bd. 58, p. 136.) See also Koch's Jahresbericht, 1906, p. 195.

49. Character of the Bacterial Flora of Carnivorous and Herbivorous animals. A Herter. (Science N.S. Vol. 24, p. 859. 1906.)

50. Leather Trades Chemistry. S. R. Trotman. Griffin, 1908. p. 79.

51. Le Rôle des Microbes dans la putrefaction des peaux en poils et en tripe et dans les confits. par Dr. G. Abt. Bull. Mens. du Synd. Gen. de cuirs et peaux de France. Nov.—Dec., 1908. p. 416.

52. Bakterein in der Lederindustrie. H. Becker, Collegium, 1909. p. 169.

53. A new Chromogenic Organism. S. R. Trotman, Jour. S.C.I., 1909. p. 1238.

54. Problems of the Leather Industry. Prof. H. R. Procter, J.S.C.I., 1910. p. 329.

55. Les Anaerobies. par M. Jungano et A. Distaso. Paris, Masson and Cie., 1910.

56. The Bacteriology of the Leather Industry. J. T. Wood, J.S.C.I., June 15, 1910. p. 666.

57. The Seymour-Jones Anthrax Sterilization Method, by Alfred Seymour-Jones. Bradbury, Agnew and Co., Ltd., December, 1910.

Index of Author.

ABSTRACTS.

Depreciation of Skins in Process. CARL. E. SCHMIDT, in *Shoe and Leather Reporter,* March 6, 1911.—During storage and treatment, skins lose a part of their substance by liquefaction through the action of bacteria. This may be prevented by the use of zinc chloride, which is a deliquescent substance and must be bought in sealed bottles. The skins are first piled in low narrow piles after salting with coarse salt, and allowed to lie one or two days. The salt to be used for the second salting is sprinkled with a solution of 1 lb. zinc chloride in 1 gallon water until on squeezing the salt with the hands some liquid oozes out. Skins treated thus may be kept one year with practically no loss of skin substance.

If skins from a distance are found when received to have been heated so that the hair slips, they may be prevented from decaying further by dipping in a solution of 2 ounces of zinc chloride to a barrel of water.

A comparison of the zinc chloride method with the cold storage method was made. One lot of skins were kept at 30° F., another at zero F., and a third lot put in pack with zinc chloride as first described. At the end of a year the three lots were in equally good condition, and the leather made from the skins preserved with zinc chloride was in every respect equal to that made from fresh skins.

Fat-Liquoring. M. C. LAMB in the *Shoe and Leather Reporter,* March 16, 1911.—Incomplete absorption of the fat liquor by chrome leathers causes a greasy feel on the exterior and a "tinniness" or undertanned feel of the skin as a whole. This is sometimes due to insufficient neutralization, the acid acting upon the soap and oil emulsion and breaking it up, thus preventing penetration. Any over action of the borax or other neutralizing agent must be avoided, for if the leather is made alkaline the basicity of the contained chrome salt is changed and the leather will be rubbery if slightly alkaline, or it will seem undertanned if there is much excess of alkali. The writer approves of borax for neutralizing, but prefers sodium phosphate because it is less liable to produce the rubbery effect, and also because it is cheaper. If chrome leather is piled wet after neutralizing, dissociation of the contained chrome salts causes it to become acid again.

A soap and oil emulsion to be used as a fat liquor must not be in the slightest degree alkaline, or the dye will not hold on the leather. The writer prefers soft or potash soaps for making fat-liquors. Too much soap causes a cementing together of the fibers, producing a dead feel.

Acid fat-liquors possess some advantages over soap and oil emulsions. They work perfectly on leathers in which the acid is imperfectly neutralized. The material best known for this purpose is Turkey-red oil, prepared by sulphonating castor or olive oil. For the better class of leather, such as glace kid, sulphonated oils are not good enough lubri-

cators, but this difficulty may be at least partly overcome by adding degras or neatsfoot.

A number of new materials unaffected by acids are now on the market, prepared by patented processes from mineral or resin oils by "saponification" under pressure. A properly fat-liquored skin should be completely penetrated, and every fiber lubricated.

New Qualitative Test for Tanning Materials. HUGH GARNER BENNETT in *Shoe and Leather Reporter,* March 16, 1911.—There are two types of tannins, called the pyrogallol and catechol tannins, the former yielding pyrogallol and the latter catechol on being heated to 200° C. Pyrogallol tannins deposit "bloom," (ellagic acid), give a blue black color with iron salts and no precipitate with bromine water and contain about 52 per cent. carbon. The catechol tannins yield no bloom, but deposit "reds," (phlobaphenes), give greenish black precipitates with iron salts and a precipitate with bromine water, and contain about 60 per cent of carbon. Some natural tanning materials seem to contain both classes of tannins, giving a blue black iron precipitate, and yet forming a precipitate with bromine water. Some writers class these as a third group.

The attempts at subdivisions of these main groups have not thus far been very successful. In the case of the catechol tannins, a division into two subgroups may be effected by the copper sulphate and ammonia test. A little copper sulphate is added to the tannin solution and then an excess of ammonia. The precipitate at first formed dissolves with excess of ammonia in the case of one group and does not in the other case. The color of the solution in the first case or of the undissolved precipitate in the other, helps in identifying the individual tannin. Other tests which are usually sufficient to complete the identification are made with vanillin, lime-water and sodium sulphate.

In the case of the pyrogallol tannins the copper ammonia precipitate is in every case insoluble in excess, and is in most cases very dark, so that there are few or no characteristic color reactions. All the important members of the pyrogallol group respond to the nitrous acid test, and none of them to the stannous chloride and hydrochloric acid test. The sulphuric acid test gives yellows or yellow browns in every case, so that none of these can be used in distinguishing the members of this group, neither do the color tests with sodium sulphite and with lime-water themselves serve as a basis of subdivision.

It is certain that with materials differing so widely as myrobalans and valonia, or sumac and chestnut extract, there must be some difference in chemical constitution. The subdivision of the pyrogallol tannins into at least two groups is made possible by the author's discovery of a new color reaction for solutions of tanning materials, which is carried out as follows. A solution of the tanning material is made of the same strength used for tannin determination. To a few cc. of this solution in a test-tube, an equal or somewhat smaller quantity of a 10 per cent. solution of sodium bisulphide is added, and after shaking one or two

drops of a 10 per cent. solution of potassium chromate is added. With some tanning materials nothing is observed but a greenish or greenish brown color, evidently due to the reduction of the chromate to chromic salts by the sulphurous acid present. This is the behavior of all the catechol tannins examined by the writer. With some pyrogallol tannins a rich blood-red color is obtained, but this rapidly fades through orange to yellow brown. This transient blood-red color is characteristic of myrobalans, sumac and their extracts, of gallotannic acid and also of gallic acid. With other pyrogallol tannins a deep red violet color is obtained, which is much more permanent, and is easily destroyed by dilute mineral acids. This color is given by valonia and its extracts, by chestnut extract and by oakwood extract.

The Use of Sulphur Tannage in the Manufacture of Leather. W. EITNER. *Der Gerber,* 37, 1-3, 15-17, 43-5, 59-61.—In reducing with sodium hyposulphite in the double bath chrome process, sulphur separates as a fine powder, a portion being included within the fiber of the leather. The author has earlier shown that this last involves a sort of tannage. Although sulphur is not a tanning agent, it acts like the flour used in glacé leather manufacture, making the leather soft and fuller. The product is analogous to the leather obtained by Knapp on treatment of hide with an alcoholic solution of stearic acid which is even useful for some manufacturers, for instance the valves of wind musical instruments. By using a solution of sulphur in CS_2 and evaporating, a leather may be obtained which can be staked and resembles stearine leather although not so soft.

The auxiliary tannage effected by sulphur is the cause of the double bath chrome leather being found suitable for check-straps; for driving belts such leather stretches too much. In France a special superior leather of this sort has been made for automobile pneumatic leather. In ordinary two bath chrome leather, the author found the ratio of Cr_2O_3: S to be 3.8: 0.2 per cent. or at the highest, 3.1: 0.8 while a French leather gave 3.0: 3.8 per cent. The best grade of French check straps analyzed 0.66 Cr_2O_3, 0.23 Al_2O_3, 2.82 per cent. S; the fat was slight, hence the sulphur must be the real softening agent.

To secure the maximum amount of sulphur *within* the leather and to avoid its deposit on the surface, it is desirable to reduce the amount of acid used in the second bath. One process reaches this result by partially tanning in the first bath which contains for 100 kg. pelt, 3 kg. chrome alum, 1 kg. bichromate; 2 kg. HCl; for the reducing bath, 150 l. water, 8 kg. hypo are used, without acid addition. No sulphur separates and the bath can be strengthened for re-use. The product contains only 0.7 per cent. S but this is all within the leather which is markedly soft. The green color of such leather is not liked in the trade, hence to secure a whiter product, the following process is substituted. Each kilo pelt is pickled with 1.5 l. water containing 20 per cent. NaCl, 5 per cent. H_2SO_4 for 1-2 hours, then 4 per cent. bichromate is gradually added. The re-

ducing bath contains only hypo hence all the available acid for reduction is within the fiber, derived from the first bath. The leather ought to be well washed to remove SO_2 although manufacturers sometimes leave this to be neutralized in liquoring, thereby increasing rendement; the result is spew and spots on the leather which is hygroscopic.

Another method employed to increase the deposit of sulphur consists in treating the hide first with acid then with hypo, or in the reverse order, before the tannage proper. 100 k. pelt are drummed 3-4 hours with 100 l. H_2O, 20 k. NaCl, 8 k. HCl, or suspension vats are used. The drained pelts are next drummed 6 hours in 20 per cent. hypo and let stand 6 hours more. The reversed order of process is also employed. The same amount of hypo is gradually applied and then the acid bath which contains 3 parts salt to 1 of acid in order to raise the density of the liquor and prevent extraction of the hypo by diffusion. This second bath is always employed in vats, the drum agitation being unsuitable. By this process, the S content may be raised to 4 per cent. and the tannage rapidly finished with chrome or vegetable tan.

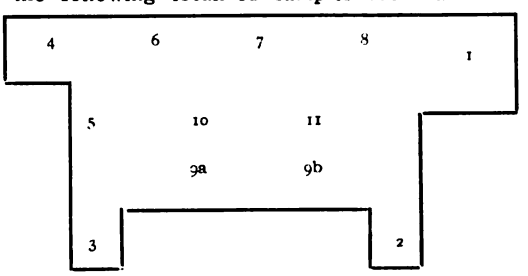
In the manufacture of automobile leather which is the most important application of sulphur tannage, a product is required which can withstand 60° C. for the "vulcanizing" or cementing of the rubber pneumatic. The sulphur of the leather itself facilitates this process; the leather must not contain free fat. For original material, steer or buffalo hides are best. The soaks are sharpened with sulphide and likewise the limes. Only the croupons are used and they are evenly shaved by hand or machine before the sulphur tannage. In this the hypo is applied first, 25 per cent., gradually. After the acid treatment, the hides go direct to a preliminary chrome bath, 1-2 days suspension. The tannage is best finished in a series of vats, but the drum may be used. A moderately basic Cr salt is needed since the leather is acid and a basic tannage at the finish determines the heat resistance of the leather. The salt is prepared by dissolving 10 parts chrome alum in 50 hot water, adding gradually 1 chalk; the solution is drawn off after settling of the gypsum. A soft white leather, but not so resistant to heat is obtained by a combined tannage of chrome and alumina salt. For the currying, a fat liquor is indispensable, but an excess of alkali is used; castor oil soap is used for its preparation.

The sulphur fore-tannage is also employed in the manufacture of check and hitching reins, etc., finishing with the double chrome bath, although this is an unnecessary complication since the special advantage of the second bath is already secured. These leathers which were formerly made exclusively by alum or alum-fat tannage are now most generally made by the sulphur fore-tannage, finishing with a combination of chrome and alumina; the alum gives the softness, the chrome the resistance and endurance. The currying is carried out in two stages to suit the varied requirements. For the soap liquor, 3 per cent. soap, 0.3 potash, 25 water (pelt = 100) are drummed until taken up. After partial drying, the desired fat is applied to the flesh and drummed in.

To make the leather look very dry and clear and yet give weight, a special grease is prepared by milling 10 parts stearine with 5 boiling water, then gradually adding 0.8 ammonia diluted with 3 parts water. This may be applied alone, after soap liquoring, after both soap liquor and greasing. The above dressings are all used above 37° C.

The combination of sulphur and vegetable tannage is of recent development. Steer or buffalo hides are used. Salted hides are given a lengthy liming; for foreign hides sulphide is added to the limes In England dung bates are used but not in France where a bate of 6 per cent. salt, 1.3 HCl (pelt = 100) is used. The sulphur tannage may be carried out in either order as described. Another variation consists in giving a light vegetable fore-tannage before the sulphur impregnation. The vegetable tannage proper is effected in vats or the drum, but the main difficulty is to avoid too rapid a saturation of tannin at the outset. A series of 10-14 vats are used, liquors 5-20°, barkometer. The tannage is finished in lay-aways or the drum. Formerly vegetable tanned rein leather was saturated with grease; even after the introduction of mineral tannage, sometimes as much as 25 per cent. was found. French leather now made by the combined process described gave 10 per cent. fats. If a soap stuffing be used, this must be neutral to avoid darkening the leather. W. J. K.

Leather Rendement and Examination. L. JABLONSKI. *Ledertechn. Rundschau,* 1911, 41-3.—Referring to the recent paper by Appelius and Manstetten (abstr. ante, p. 160), the author agrees that the practical yield cannot be deduced from the analytical rendement number. The analytical results have a value for the tanner, however, although not always appreciated. The rendement number is of no value whatever, but the tannage number is of fundamental importance not in giving actual weights, but ratios. The lack of agreement of the number determined by analysis with practical estimates is due to our imperfect knowledge of the composition of hide substance. The author believes it may be possible to ascertain the composition of the entire hide from the examination of an oriented sample and refers to the "Jahrbuch der Deutschen Leder industrie" for 1911 for details. His method (preliminary) is to determine hide substance, specific gravity and sometimes moisture in the following localized samples from a half hide:



(1) forehead, (2) forefoot, (3) hindfoot, (4) tail, (5) rump, (6)

crup, (7) back, (8) shoulder, (9a) flank, (9b) belly, (10) (11) ribs, shell. A table of hide substance percentages in 3 ox hides is given; if these apparently irregular results are plotted graphically, complex curves but of very similar forms are obtained. Corresponding values from Appelius and Manstetten's data interpolate well. The usual assumption that an average of the analyses of various portions of the hide is representative, the author holds to be faulty; these variations here reach to 33 per cent. of the whole. The curve varies in type with different animals and some examples are given. Further investigation and reports are projected.

Fundamental Rules of Practice. (Continued.) L. MANSTETTEN. *Ledertechn. Rundschau*, 1910, 57-9.—Although a considerable amount of the substance dissolved at high temperatures separates on cooling, hot extraction is almost universal in practice. It has not yet been precisely ascertained at what stage the extraction ceases to be economical, hence the tendency is to push it in order to obtain everything useful, and on the other hand to let the extract settle well to obtain a clear solution.

The usual way of clearing is to allow the hot liquor from the spent bark to flow over less extracted bark and so on, in a battery or series of vats, thereby cooling, enriching and filtering the liquor. The filtering effect increases with the number of vats, but decreases with rapid flow. Since the usual practice is to hasten the extraction, slow filtration is not possible here and the liquor is unlikely to be well cleared when extraction and filtration are effected in the same round. Moreover the sediment deposited in filtration becomes redissolved in the hot extraction, leading to a great accumulation of difficult soluble matter.

The labor expended in carefully clearing a liquor is repaid by the rapid and perfect tannage. The so-called extract spots can be shown to be caused by separation of resinous, difficult soluble phlobaphenes, probably from poorly cleared liquors. The chief fault, however, is in employing hot liquors direct from the extraction. If warm liquors are to be used for steeping, these should have been previously completely cooled and filtered. To secure good clearing, the best plan is to conduct the extraction and filtration in two separate rounds, say 4 vats for hot extraction and 4 more for filtration of the product. Still better results are obtained by allowing a day's cooling and settling before filtration; the filter material is thereby kept cleaner for the hot extraction. The division between extraction and filtration not only gives better filtration but better extraction; the filter bark by transfer to the extraction vats becomes loosened. W. J. K.

Bacteria and Mould Fungi in Tanning. O. DROSIHN. *Ledertechn. Rundschau*, 1911, 59-60.—The author does not agree with Hugo Kühl that mould on leather originates from imperfect drying. He has repeatedly observed that leather stored through the winter and spring and apparently dry first showed mould during the sultry months of July and August. Not only the leather but the flooring, which was assuredly previously

dry, was covered with mould. When vache leather moulds on storage during summer, the thinnest parts first mould, although they are naturally the driest. The germs of the growth may originate during the fermentation accompanying the tannage process and lie dormant, but the direct cause lies in the weather conditions and it is desirable that the subject be scientifically studied. It would be of interest to ascertain whether mould develops on leather which has been plumped with mineral acids. W. J. K.

The Pickling of Sheep Skins. *Lé March des cuirs,* **23,** (1911) 99-100.—After de-liming in a bran bate the skins may be preserved for some time in the soft condition by treatment with a pickle of 40 k. NaCl, 2.7 l. H_2SO_4, 400 l. H_2O. The salt is essential and must be maintained, else the pelt will swell. After thorough draining the pickled pelts are best stored in closed casks; moisture must be excluded. When required for tannage they are milled with 15 k. NaCl, 3 k. whiting, 400 l. H_2O and well rinsed. W. J. K.

Enzymatic Studies. S. P. L. SORENSEN. (Concluded.)—B. Colorimetric Method. a. Method employed. When a solution is to be examined, the ionic concentration of which is altogether unknown, preliminary trials are necessary to determine the liquids for comparison and the indicator suitable to the particular case. The most convenient method of operation is to commence by examining the reaction of the solution on litmus paper, if an alkaline reaction is obtained, several drops of phenolphthalein are added to the solution, if, however, the litmus shows an acid reaction, the behavior of the solution towards methylorange is determined. The result of these trials shows what other indicator to use in order to fix the ionic concentration more exactly. Suppose, for example, that we have found a reaction acid to litmus but alkaline to methyl-orange, and then with *p*-nitrophenol, the turning point of which is between that of litmus and that of methyl orange, the solution takes on a moderate yellow color. The ionic concentration of the solution is then such that *p*-nitrophenol will probably serve as the proper indicator for the measurement.

There are then measured out into test-tubes (of colorless glass and alike in all respects) the following mixtures of phosphates: pure primary phosphates, with 0.25 sec., 0.5 sec., 1 sec., 2-3-4 and 5 sec. (Note. The mixture 0.25 cc. of primary phosphate with 9.75 cc. of secondary phosphate is designated by the abbreviation "0.25 sec." and analogous abbreviations are used not only with phosphates, but also with those of glycocol, citrates and borates.) These mixtures correspond in ionic concentration to the region embraced by *p*-nitrophenol. A few drops of the indicator added to each of these mixtures gives a series of colors gradually increasing to deep yellow. After measuring similarly 10 cc. of the solution to be examined, there are added to each solution an equal number of drops of the indicator solution, and after

mixing, the color of the solution which is being examined is compared with the series of standards.

If the solution examined is but faintly colored, more of the indicator may be added in equal amounts to all the tubes. If the color lies between that of two of the standard tubes, new standards may be mixed giving the interval more closely. The exponent of the hydrogen ions corresponding to the mixture whose color matches the solution examined can be found from the curves. (p. 136.) To make an accurate comparison, at least four standard solutions are necessary such that the color of the solution examined falls between the limits of the standards selected.

b. Sources of error of the method.

1. Color of the liquid itself.

If the solution examined is not colorless, it is necessary, before adding the indicator, to color the standard solutions as nearly as possible like the former, and then, to mask the inevitable slight differences of tint by using a large quantity of the indicator. For this purpose coloring matters may be used which may themselves be indicators, provided that their turning points are sufficiently removed from the ionic concentration of the solution. The following substances are available for this purpose.

(*a*) Bismark brown. (0.2 gr. in 1 liter aq.)
(*b*) Helianthin II. (0.2 gr. in 800 cc. alcohol, added to 200 cc. aq.)
(*c*) Tropeolin 0. (0.2 gr. in 1 liter aq.)
(*d*) Tropeolin 00. (0.2 gr. in 1 liter aq.)
(*e*) Curcumein. (0.2 gr. in 600 cc. alcohol, added to 400 cc. aq.)
(*f*) Methyl violet. (0.02 gr. in 1 liter aq.)
(*g*) Belgian blue. (0.1 gr. in 1 liter aq.)

In case the solution is turbid, an analogous turbidity must be produced in the standards. This has been done by means of freshly precipitated barium sulphate, prepared by mixing equal volumes of N/10 solutions of barium chloride and potassium sulphate. If more than a few drops of coloring solution or barium sulphate suspension must be added because of the strong color or turbidity in the solution being examined, then an equal number of drops of water must be added to it. Of course the accuracy of the method is greatly decreased by the necessity for such precautions.

2. Influence of neutral salts.

We have already seen, (pp. 134-135) the effect of neutral salts upon other methods for determining ionic concentration; in the colorimetric method also neutral salts may act in unequal ways, and, perhaps as well, differently upon different indicators. (Bohdan von Szyskowsky, Zeit. phys. Chem., 58, 420, (1907), and Lenor Michaelis and Peter Rona, Zeit. f. Elektrochem., 14, 251, (1908). This influence can be determined by a "blank test."

3. Influence of toluene or chloroform.

Since toluene, chloroform or other antiseptics are often used in enzymatic studies, it is important to know whether the indicator employed is influenced by them. Experiments have shown that, in general, the acid indicators of the azo-group are not affected, while the basic members are quite useless. Further, phenolphthalein, *p*-nitrophenol rosolic acid, alizarin-sulphonic acid, and azo-lithmin are unaffected.

4. Modifications of the shade or of the intensity of the indicator.

If a few drops of methyl-violet are added to a N/10 solution of hydrochloric acid, the solution is colored green with a tinge of blue; but both the intensity and the shade gradually change. After an hour the solution is almost colorless. In using this indicator, therefore, as well as its analogs, mauvein, gentian violet, and methyl-green, which act the same way, it is necessary to work rapidly, and to be careful to add the indicator simultaneously to the solution and the standards. This bleaching is proportional to the ionic concentration, so that it is possible to work with precision even when the comparison is made after the lapse of considerable time. This modification of color, therefore, occasions less inconvenience than that from other causes.

It is otherwise, however, with indicators such as "Azosäureblau," chrysamine G, and pyrogallol-phthalein, with which the modifications of color depend on other factors than the hydrion concentration. Such indicators are useless for this purpose.

In case the indicator is difficultly soluble in water, a modification of color may result from the partial precipitation of the indicator. To use this class of indicators, they must be dissolved in rather dilute solution in alcohol, a procedure which involves an additional source of error, for it is scarcely probable that the hydrion concentration of the standards and the liquid investigated will be modified in the same way by the alcoholic solution.

Thus it is that on the one hand the acid indicators of the azo-group (tropeolin oo, for example) can generally be employed in the form of aqueous solutions, and give tints which are stable for a day at a time, while, on the other hand, the basic indicators of this same group (such as di-phenyl-amino-azo-benzene) must be used in alcoholic solutions, and give colors which gradually diminish in intensity due to the gradual precipitation of the indicator. The more complex the indicator, the less, generally, is its solubility in water, and the more, consequently, does this source of error make itself felt.

It may be added that, although phenolphthalein must be used in alcoholic solution, it is nevertheless sufficiently soluble in water so that the small additions necessary are not precipitated. On the contrary, in using the analogous and otherwise excellent indicator, thymolphthalein,[1]

[1] Made by Grüber & Co., Leipzig. Constitution not given. Its melting-point is 240°, so that it is doubtless different from the thymolphthalein prepared by P. Jakimowiez: *Ber.* **28**, 1876 (1895), which melts at 85°.

this difficulty is encountered, so that one must work as rapidly as possible.

5. Influence of the proteins and their decomposition products.

A more important fact than any of the above, in colorimetric measurements, is that the proteins and their decomposition products often render the method difficult or even impossible. This is doubtless due, on the one hand, to the colloidal nature of the proteins and of a large number of the more complex indicators, and on the other hand, to the amphoteric character of the proteins whereby they can unite with both acid and basic coloring matters. Such combinations of protein and color-indicator are sometimes precipitated, but even if the combination remains dissolved—probably in the colloidal state—it generally presents a peculiar tint so that the colorimetric measurement becomes uncertain, or even valueless.

The behavior in this respect is very different with various groups of indicators. Methyl-violet, and its analogs are influenced only to a slight degree by the natural proteins, while the numerous indicators of the azo-group are almost all useless, in their presence. Here again the less complex indicators give the least error.

In taking account of the sources of error in the colorimetric method, it is seen what care is necessary in the choice of indicators, and how, if need arises, a comparison of electrometric and colorimetric methods must be employed in order to establish the value of the indicator chosen for the particular kind of solution with which one has to work. There arises then the question of what concordance must be obtained between the colorimetric and electrometric methods in order to establish the utility of a certain indicator. We have seen that in the measurement of protein solutions and the like, by the electrometric method, one can scarcely count on an accuracy greater than $\pm$ 0.05 in the exponent of the hydrogen ions. The colorimetric method is not as precise as this, both in principle and because its accuracy depends upon the electrometric method as the standard. We consider, therefore, that an indicator is suitable under the existing conditions when the variation between the measurements by the two methods does not exceed $\pm$ 0.1 in the hydrion index.

c. The indicators examined.

(The author here gives the results of his extended investigations on the applicability of a large number of indicators in the presence of various neutral salts and proteins, the hydrion index as determined by the indicator being compared with that determined by the electrometric method. As a result the following indicators are selected as giving results most free from the errors discussed above.)

1.	Methyl-violet	$p_H^+ = 0.1—3.2$
2.	Mauvein	0.1—2.9
3.	Diphenylamino-azo-benzene	1.2—2.1
4.	Diphenylamino-azo-parabenzenesulphonic acid	1.4—2.6
5.	Diphenylamino-azo-metabenzenesulphonic acid	1.2—2.3
6.	Benzylanilino-azo-benzene	2.3—3.3
7.	Benzylanilino-azo-parabenzene sulphonic acid	1.9—3.3
8.	Metachlordiethylanilino-azo-parabenzenesulphonic acid	2.6—4.0
9.	Dimethylanilino-azo-benzene	2.9—4.0
10.	Dimethylanilino-azo-benzenesulphonic acid	3.1—4.4
11.	*a*-Naphthylamino-azo-benzene	3.7—5.0
12.	*a*-Naphthylamino-azo-parabenzenesulphonic acid	3.5—5.7
13.	*p*-Nitrophenol	5.0—7.0
14.	Neutral red	6.8—8.0
15.	Rosolic acid	6.9—8.0
16.	a-Naphthol-azo-parabenzenesulphonic acid	7.6—8.9
17.	Phenolphthalein	8.3—10.0
18.	Thymolpthalein	9.3—10.5
19.	*p*-Nitrobenzene-azo-salicyclic acid	10.1—12.1
20.	Resorcino-azo-parabenzene sulphonic acid	11.1—12.7

In the selection of an indicator from this list which we recommend it is necessary to make a judicious choice, taking especially the following facts into consideration:

a. The indicators of the methyl-violet group (Nos. 1 and 2) are particularly sensitive to the action of neutral salts; in addition it should be remarked that the color changes gradually, more rapidly the greater the acidity of the solution.

b. The basic indicators (Nos. 3, 6, 9, 11 and 14) dissolve in toluene or chloroform; in addition the first four separate partially from the solution on long standing.

c. In the presence of large amounts of natural proteins most of the indicators are useless, although several of them may serve; Nos. 1, 2, 13, 16, 17, 18.

d. In the presence of the products of protein decomposition, even in considerable proportion, the entire series of indicators may render real service; however, even in these conditions several of the acid azo-indicators can give rise to noticeable errors (Nos. 4, 5, 7, 8, 10) in which case one may have recourse to the corresponding basic indicators.

e. When the solution contains but small proportions of proteins or their decomposition products, the acid azo-indicators are usually preferable to the basic, because the former are not influenced by either toluene or chloroform, and because they do not separate from the solution on standing.

f. In all doubtful cases—for example in the colorimetric measurement of solutions whose behavior towards the indicator considered is un-

known—the electrometric method should be used as a standard, and the value of the indicator determined by a comparison.

(Section C of the original paper deals with "The importance of hydrogen ion concentration in enzymatic reactions." Since the subject as treated hardly lies within the scope of this journal, the results will be given simply in the summary of the entire publication which follows.)

SUMMARY.

1. It is very necessary to distinguish between acidity and hydrogen-ion concentration; it is the latter alone which plays a role in enzymatic reactions.

2. When the normality of the hydrogen-ions is designated by 10^{-p}, we propose for the numerical value of the exponent the name "hydrion index," and the sign p_H^-.

3. In enzymatic reactions the mean hydrion concentration plays a role analogous to that of the temperature at which the experiment is performed. The hydrion concentration curve of an enzyme is that which is obtained by taking as ordinates the quantity of material split up in unit time under the conditions of the experiment, and as abscissae the mean hydrion index. The hydrion concentration curves proceed in a manner analogous to the temperature curves.

4. To measure the hydrion concentration of a solution any method whereby the ionic concentration changes during the operation cannot be used; consequently all the ordinary methods of acidimetry and alkalimetry are inapplicable. The "catalytic" methods also are not generally suitable; in rare cases they can be used only with all the requisite precautions.

5. As methods of measurement of the hydrion concentration in enzymatic reactions we recommend two procedures, each of which supplements the other: the electrometric method, very precise but rather complicated, and the colorimetric method, less precise but nevertheless extremely simple.

6. Electrometric method.

a. If π denotes the e.m.f. at 18° of a cell composed of a calomel electrode in N/10 potassium chloride and a hydrogen electrode (platinized platinum) in an electrolyte having a hydrion index p_H^+, we have seen that the equation

$$\pi = 0.3377 + 0.0577 \times p_H^+$$

expresses the relation at 18° between the e.m.f. of this element and the hydrion concentration of the electrolyte, if $p_H^+ - 0$, then $\pi_0 = 0.3377$.

b. In the principal table of curves (p. 136) the line which expresses graphically the above equation is designated by the name "line of exponents." With the aid of this line one can, in a manner purely graphic,

without the need of any calculation, convert a measured value of π into the corresponding value of p_H^+ and conversely.

c. By electrometric measurements of the hydrion concentration of dilute caustic soda solutions the dissociation-constant of water was found to be $0.72 \times 10^{-14} = 10^{-14.14}$.

d. By dissolving in water certain substances of simple composition, substances whose purity can easily be verified and which can be obtained commercially of guaranteed purity, it is possible by mixing in determined proportions to prepare standard solutions having any hydrion concentration whatever between about 10^{-1} and 10^{-13}, exactly determined in advance by the electrometric method. On the principal table of curves one can easily read graphically the hydrion exponent of any one whatever of these mixtures.

The choice of the substances entering into these standard solutions has been confined to those that are protected against sudden changes in ionic concentration. We have shown the importance in enzymatic reactions of the presence of these "buffers."

e. We have cited a certain number of particular cases in which difficulties are encountered in the course of electrometric measurements of solutions such as are involved in enzymatic reactions.

7. Colorimetric method.

a. We have described the method to follow in colorimetric measurement where mixtures of the standard solutions mentioned serve as liquids for comparison.

b. The method is infected with a certain number of errors, the chief of which is due to the tendency of the natural proteins and their decomposition products to combine with the indicators, an inconvenience which in certain cases renders the colorimetric measurement difficult if not altogether impossible.

Because of these sources of error it has been necessary to verify with the greatest care just how far each indicator can serve under various conditions, with the view of rejecting those which are not useful, and of determining the degree of precision possible with those proving useful. In the control measurements the electrometric measurement of the hydrion concentration has served as the fundamental method.

c. The indicators examined, several of which have not been recognized hitherto, are divided, principally according to the position of the turning point, into five groups, for each of which we give a suitable choice of control measures effective at least for the most important and the best of the group.

d. Several of the common indicators, congo-red, for example, must be considered as altogether useless for measurements of this kind.

e. Based upon all the effective methods of control, we advise the use of twenty indicators. Since they are not equally available under all conditions it is necessary always, when it is a question of choosing an

indicator appropriate to a given case, to take notice of a certain number of facts explicitly mentioned. See p. 263.

8. The importance of the concentration of the hydrogen-ions in decompositions by the aid of invertase, of catalase, and of pepsin, is shown by examples:

a. Under conditions otherwise equal, the optimum hydrion concentration for the inversion of sucrose has been recognized as very nearly independent of the kind and of the quantity of the invertase, as well as of the acid present. Under the conditions used the optimum ionic concentration of the inversion corresponds to $p_H^+ = 4.4$ to 4.6.

b. By a series of experiments upon invertase we have shown the necessity, in studies of reaction velocity, to take account of the hydrion concentration, and we have pointed out that the very different manners in which our predecessors have viewed the inversion of sucrose are attributable at least in part to the lack of recognition of the importance of the ionic concentration for this enzymatic reaction.

c. After having drawn attention to the importance of spontaneous decomposition of enzymes in studies of this nature, we have shown the resulting dependence between the length and the temperature of the experiment and the mean concentration of the hydrogen-ions.

According as the time is prolonged the optimum hydrion concentration is displaced towards the alkaline side.

d. At the temperature of 0° the optimum hydrion concentration of catalase is found near the neutral point, but a prolongation of the time appears to displace it towards the acid side.

e. At 37°, the optimum concentration for peptic decomposition is clearly dependent upon the time: for short duration the optimum point has a hydrion index slightly less than 2; but when it is prolonged, the optimum point is displaced towards the acid side.

J. H. H.

PATENTS.

Tanning. U. S. Patent No. 987,750. ALPHONSE SEYEWETZ and LOUIS MEUNIER, Lyons, France.

The method involves producing oxidation products of a phenol, including a substance of the quinone type, having a cyclic structure, and treating hide with the said products.

Process of Manufacturing New Organic Acids. U. S. Patent No. 988,032. HEINRICH ROSSNER and WILLIAM COTTON, Germany.

The process involves treating unsaturated fatty acids of high molecular weight, such as ricinoleic acid, in the presence of a mineral acid with formaldehyde or other body containing the carbonyl group, which renders them capable of combining with phenylhydrazine and hydroxylamine.

Stretcher for Leather. U. S. Patent No. 988,331. E C. GREULICH and THEODORE G. STEINKE, Milwaukee, Wis.

Process of Tanning Leather. U. S. Patent No. 989,252. JABES A. HAMRICK, Hot Springs, Ark.

The hides are treated first with a liquor made from gambier extract, to which are afterward added at intervals extract of black alder, extract of persimmon and extract of black haw.

Machine for Treating Hides, Skins and Leather. U. S. Patent No. 989,278. DANIEL P. O'BRIEN, Woburn, Mass.

Combined Burette Holder and Pinch-cock. U. S. Patent No. 989,503. H. E. HILDEBRAND, Chicago, assignor to E. E. Behlke, Chicago.

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ON THE ACTION OF DILUTE ACIDS AND SALT-SOLUTIONS UPON GELATINE.[1]

By Henry R. Procter.

The investigation which forms the subject of the following paper was begun in 1897, and much of the experimental work was done in 1898 in conjunction with Mr. Richard Paget, who, it was hoped, would share in the authorship of the paper. Circumstances, however, prevented its completion in coöperation, and the work has been carried on at intervals, with various assistance, up to the present time; and although there remain many points still unsolved, it seems desirable, in consideration of the present interest in colloid questions, no longer to delay the publication of what is already completed.

The investigation was originally undertaken in the hope that the study of comparatively simple cases of colloidal swelling and contraction might throw some light on the complicated phenomena of the tanning process, and especially on the very curious results of the treatment with acid and salt known as "pickling," and on the mineral tanning processes in which acids and salts are employed; but as it proceeded it became obvious that much wider and more important scientific issues were involved, which included the whole theory of colloid swelling.

The pickling process consists in principle in treatment of the skin with a very dilute bath of sulphuric acid, in which the connective tissue fibers are strongly swollen; and subsequent immersion in a concentrated solution of common salt, in which not merely the swelling disappears, but the fibers become greatly dehydrated, and the skin converted into a kind of leather. As even saturated solution of common salt has no dehydrating effect without the preliminary acid treatment, the effect is at first sight striking and unaccountable.

The swelling action is complicated in skin by its anatomical structure, which allows it to absorb liquids not merely by colloidal swelling, but capillarily in the interstices between the fibers, and it was obvious that no quantitative study could be made, unless

[1] This article was published in German in Kolloidchemische Beihefte, Bd. II, Heft 6-7, 1911. Professor Procter has kindly furnished the original manuscript for publication in the JOURNAL.

means were devised to separate the two effects. Fortunately, however, gelatine behaves in a manner at least qualitatively identical with hide-fiber, and the very close chemical relationship between the two justifies the assumption that the same chemical affinities are involved, while from the absence of structure, capillar absorption is excluded. Comparative experiment confirmed this anticipated identity of behavior; and as the experiments were only intended as a preliminary investigation, ordinary commercial thin sheet gelatine was selected as a material. For the same reason, and to avoid complicating the work, slight variations of laboratory temperature, and other secondary disturbing causes such as adhering moisture, were neglected, and a method of experiment adopted which was capable of comparatively rapid execution. Sheets of thin French gelatine of the purest kind were cut, air-dry, to portions of about 1 gram in weight, and soaked in the requisite solutions, their gain in weight determined after draining as far as possible from adhering moisture, and both the gelatine and the residual solution analyzed as regards acid and salt, and the whole calculated to ash-free gelatine dried at 110°, and to milligram-molecules per gram. The air-dry gelatine in the earlier experiments contained 16.07 per cent. of moisture, which, as it was kept in a stoppered bottle was practically constant; and 1.19 per cent. of ash consisting mainly of lime with traces of sulphites and phosphates. It was, no doubt, a bone-gelatine. For all the earlier experimental work the same sample of gelatine was used, but for some later series of determinations other gelatines were employed of the same character but not actually of the same parcel. This may account for some variations between different series of experiments, while any single series gave as a rule very consistent curves.

The Swelling of Gelatine in Water.

The extent to which a gelatine will swell in cold water at a given temperature is to a great extent a specific quality of the particular sample, influenced by the proportion of partially hydrolyzed gelatine-products which are always present in the commercial article. These indeed cannot wholly be avoided, since they are formed to some extent whenever the gelatine jelly is heated so as to melt it, and they are unquestionably the main

cause of those variations in character which have been attributed to what has been called the "*Vorgeschichte*" of the jelly. Traces of soluble electrolytes also affect it osmotically, and perhaps chemically. That gelatine and other gelatinizing substances do not swell to infinity, and become colloid solutions like gum and dextrine is due to the solid but elastic structure which is formed at setting, the cohesion of which finally balances the attraction of the gelatine for water. Under these circumstances it seemed not improbable that the swelling maximum of any given jelly would be influenced by the volume of its structure at the moment of setting; and this is proved to be the case by the following experiment.

Solutions containing approximately 5, 10 and 20 per cent. of air-dried gelatine were cast in glass tubes on wire spirals for convenience of handling, and were then dried for some days in a current of dry air, weighed, and allowed to soak in water at laboratory temperature, and weighed at intervals. Taking the weight of actual dry gelatine as unity the amounts of water absorbed were as follows:—

TABLE 1.—ABSORPTION OF WATER BY GELATINE.

	5 per cent.	10 per cent.	20 per cent.
Dried in air	0.1	0.1	0.2
After soaking 24 hours	8.4	4.3	3.7
After soaking 72 hours	11.7	6.0	5.1
After soaking 96 hours	12.6	6.5	5.4
After soaking 120 hours	13.2	6.9	5.5
After soaking 144 hours	13.6	7.2	5.7
After soaking 168 hours	14.6	7.7	5.8
In original jelly	23.2	11.1	5.0

As will be seen from the figures, and still more plainly from the graphic curves, the original setting volume has considerable influence on the maximum swelling, but is evidently not the sole determining cause.

Action of Alcohol on Gelatine Jelly.

It is well known that the swelling of gelatine jelly can be reduced by treatment with alcoholic solutions, and with absolute alcohol it becomes a hard and apparently dry mass. As there is no reason to suppose any chemical action of alcohol on gelatine, which on soaking in water returns to its original jelly-condition,

the case seems a favorable one for the study of the effect of purely physical forces on jellies. Gelatine is practically quite insoluble in cold alcohol either pure or dilute, and conversely, even quite weak jellies are semipermeable to alcohol in solution. Alcohol placed in a porous cell lined with gelatine, and immersed in water, develops a considerable osmotic pressure, and masses of gelatine-jelly dehydrated by alcohol absorb scarcely any of the latter.

In order to get some idea of the effect of alcohol upon swelling, weighed portions of air-dried thin sheet gelatine were immersed in a series of mixtures of alcohol and water for 24 hours and again for 24 hours in renewed portions of the same solutions. This length of time had been found sufficient in previous experiments to establish practical equilibrium. The portions were then drained and weighed to determine the swelling; the gravity of residual alcohol taken, and its percentage calculated by the ordinary tables, and the pieces dissolved in hot water, and distilled to a volume of 25 cc. of distillate of which the gravity was taken to determine alcohol in the gelatine. Only in the case of the 100 per cent. alcohol did the gravity of the distillate fall so low as 0.999; and in this case only to 0.9979, so that any alcohol found may very well have been that merely adhering to the surface of the gelatine, and more exact methods of experiment must be adopted before conclusive evidence of any solubility of alcohol in gelatine-jelly can be obtained, though it seems possible that when the gelatine is nearly dehydrated, some alcohol is absorbed.

A second series of experiments were also made in a similar way, in which the gelatine was swollen in water for 24 hours before treatment with the alcoholic solutions. The results, which are given below are almost precisely similar to those of the first series, except that in the 90 per cent. and 100 per cent. alcohol complete equilibrium does not appear to have been reached. No evidence of penetration of the alcohol into the jelly was obtained, the gravities of the distillate ranging from 0.9996 to 1,000. The equilibrium appears to be completely reversible.

Table 2 and Fig. 1 give the weight of swollen gelatine obtained from 1 gram of dry. It will be observed that the curve is quite a regular one. The weight of the gelatine from

absolute alcohol is slightly less than its weight air-dried.

TABLE 2.—ACTION OF MIXTURES OF ALCOHOL AND WATER.

Original mixture		Gelatine air-dry		Gelatine first swollen	
"absolute" alcohol cc.	water cc.	Per cent. alcohol in solution after soaking	Wt. of 1 grm. dry gelatine after soaking grms.	Per cent. alcohol in solution after soaking	Wt. of 1 grm. dry gelatine after soaking grms.
100	0	99.04	1.20	92.63	1.84
90	10	84.08	1.36	81.76	1.80
80	20	73.30	1.50	70.64	1.60
70	30	.....	....	60.88	1.68
60	40	51.56	1.70	48.73	1.96
50	50	43.04	2.24	39.80	2.36
40	60	33.22	2.86	30.84	2.52
30	70	24.46	3.14	22.77	3.06
20	80	16.20	3.72	15.17	4.42
10	90	7.93	5.72	7.42	5.96
0	100	0.00	7.23	0.00	7.23

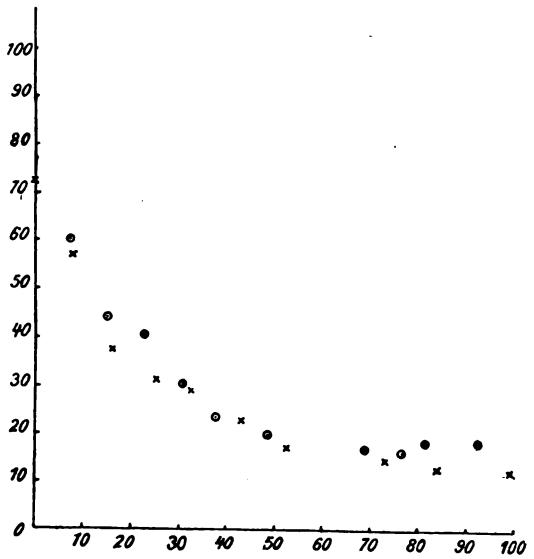


Fig. 1. (Table 2.)—Ordinates; weight of 10 g. dry gelatine after experiment o Abscissas; alcohol content of the solution after the experiment, in per cent. x = air-dry gelatine; • = previously swelled gelatine.

It is of course impossible to calculate theoretically the osmotic pressures of alcohol in such concentrated solutions as were here used, but the curve is such as would be expected from osmotic pressure acting on a material with a certain elastic rigidity of its

own; and there seems no reason to invoke other forces. Probably if the osmotic pressures of the alcoholic solutions were independently determined, such experiments might furnish a means to calculate the elasticity of the jelly. Neglecting any small attraction of the alcohol for the gelatine, the equilibrium is probably

$$\left.\begin{matrix}\text{Cohesive attraction of jelly}\\ +\\ \text{Attraction of alcohol for water}\end{matrix}\right\} = \text{attraction of gelatine for water.}$$

This is of course merely an inverse way of stating the osmotic view, since osmotic pressures are "partial" kinetic pressures, and may be expressed as "minus internal pressures" of the solvent; just as in a mixture of air and water-vapor at atmospheric pressure, the pressure of air in the mixture is lowered by that of the water-vapor, which is equivalent to a minus atmospheric pressure.

Alcohol, though it precipitates hot gelatine solutions when added in large quantity, can be mixed in moderate proportions without causing separation, and the mass sets to an apparently homogeneous jelly, which, if alcohol is insoluble in jelly, must really consist of alcohol-water solution of such concentration as corresponds to the equilibrium just discussed, enclosed as an emulsion in a jelly-medium. Such an emulsion should swell more in water than a plain jelly, since not only will the jelly absorb all the water necessary for its maximum swelling, but the alcoholic emulsion-globules will become diluted, and exert an outward pressure on the jelly mass. On the other hand if the action of the alcohol were a chemical one, lessening the absorptive power of the gelatine, the swelling should be reduced whether the alcohol were introduced from without, or were already present in the mixture. Experimentally, it was found that of two somewhat concentrated jellies of equal strength, one made with water alone, and one with a mixture of water and alcohol, the latter swelled much the more, thus confirming the emulsion-character of alcoholic jellies. It is almost certain that such jellies would show microscopically the cellular structure which has been attributed by Bütschli and van Bemmelen to jellies in general.

The Action of Acids on Gelatine.

It is well known that gelatigenous fiber is swollen by all dilute

acids which are sufficiently ionized, although very feeble acids such as boric, carbonic and sulphydric, have little or no swelling effect, and the same is true of many of the weaker organic acids.

Gelatine is similarly affected. A gelatine which absorbs 7 or 8 times its weight of pure water, may absorb over 50 times its weight of very dilute hydrochloric acid. For the most detailed experimental work, hydrochloric acid was chosen, as a highly ionized and typical monobasic acid, which could be easily estimated both acidimetrically and by silver nitrate. A further reason for the selection was that although in the commercial pickling process already mentioned sulphuric acid is used in conjunction with excess of common salt, yet the acid principally active must necessarily be hydrochloric; and as a satisfactory pickling can be produced by this and salt alone, nothing could be gained as regards principle by complicating the equilibrium with the presence of sulphuric acid and sulphates.

The general method of experiment was similar to that which has been already described. Pieces of air-dried sheet-gelatine of about 1 gram in weight, of which the content in dry ash-free gelatine was known, were soaked in solutions of acid of known volume and concentration for 48 hours, which was found a sufficient time to produce a steady equilibrium. The volume and strength of the residual solution was determined acidimetrically with standard KOH solution and phenolphthalein, the swelling of the jelly was measured by weighing after draining, and it was subsequently melted and the absorbed acid similarly titrated, it having been proved by preliminary experiments that the whole of the acid present could be thus determined, and that no difference in result was caused by melting the gelatine. Any slight variations from this procedure are noted in connection with special series of experiments.

In an early series of experiments it was found that though the whole of the acid present in the jelly was estimated using phenolphthalein as indicator, yet only a portion was determined when methyl-orange was used, although to free hydrochloric acid both indicators are equally sensitive. It is therefore clear that in the jelly a portion of acid is combined either chemically or by adsorption, in such a way that it is less ionized as regards H-ions than the remainder which behaves as if merely dissolved in the

jelly, and of course varies with the degree of swelling. In order to get rid of the complication thus introduced, it was assumed as a first approximation that the absorbed volume of liquid was of the same concentration as that of the surrounding acid solution, and that the excess which was always found on the titration with phenolphthalein was "fixed" or more closely combined with the gelatine. This "fixed acid" proved to be usually somewhat lower but roughly approximate in quantity to that estimated by phenolphthalein but not by methyl-orange, and obviously represents the excess of acid absorbed by the gelatine, though it does not accurately determine what portion is attached to the gelatine and what to the absorbed water, and it will be shown later that the quantity of acid really fixed by the gelatine is greater than that so determined. Still it affords a ready means of comparing the character of the absorption; and as such, is given in the tables.

TABLE 3.—GELATINE AND HYDROCHLORIC ACID.

Series No.	Mgr-mols. HCl in 1 grm. solution after use Phenolphth. a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols HCl absorbed by 1 grm. dry gelatine Phenolphth. c	Mgr-mols. HCl absorbed by 1 grm. dry gelatine Methyl-or. d	Acid "fixed" by 1 grm. dry gelatine c—ab	Acid of 1 grm. dry gelatine not indicated by Methyl-or. c—d
XXVI 1	0.2692	18.25	5.780	.....	0.867	.....
XXVI 2	0.2089	17.72	4.460	.....	0.758	.....
XXVI 3	0.1546	18.23	3.613	.....	0.795	.....
XX 1	0.1425	21.70	3.798	.....	0.706	.....
XX 2	0.1250	21.35	3.400	.....	0.731	.....
X 1	0.1066	23.87	3.291	2.413	0.746	0.878
XXVI 4	0.1009	21.84	3.060	.....	0.856	.....
X 2	0.0879	25.27	2.989	2.074	0.768	0.915
X 3	0.0655	26.98	2.527	1.680	0.759	0.847
X 4	0.0548	29.56	2.392	1.568	0.772	0.824
XXVI 5	0.0483	31.33	2.387	.....	0.874	.....
X 5	0.0331	34.80	1.937	1.126	0.778	0.811
X 6	0.0134	45.31	1.431	0.609	0.824	0.822
X 7	0.0096	50.43	1.319	.....	0.835	.....
X 8	0.0060	54.16	1.176	.....	0.851	.....
XX 3	0.0028	45.38	0.963	.....	0.834	.....
X 9	0.0024	54.67	0.954	.....	0.823	.....
X 10	0.0006	35.27	0.622	.....	0.601	.....

Table 3 represents the results of more than one series of ex-

periments, the Roman numerals of the first column indicating the series. These experiments were made in 1899 and 1900 on

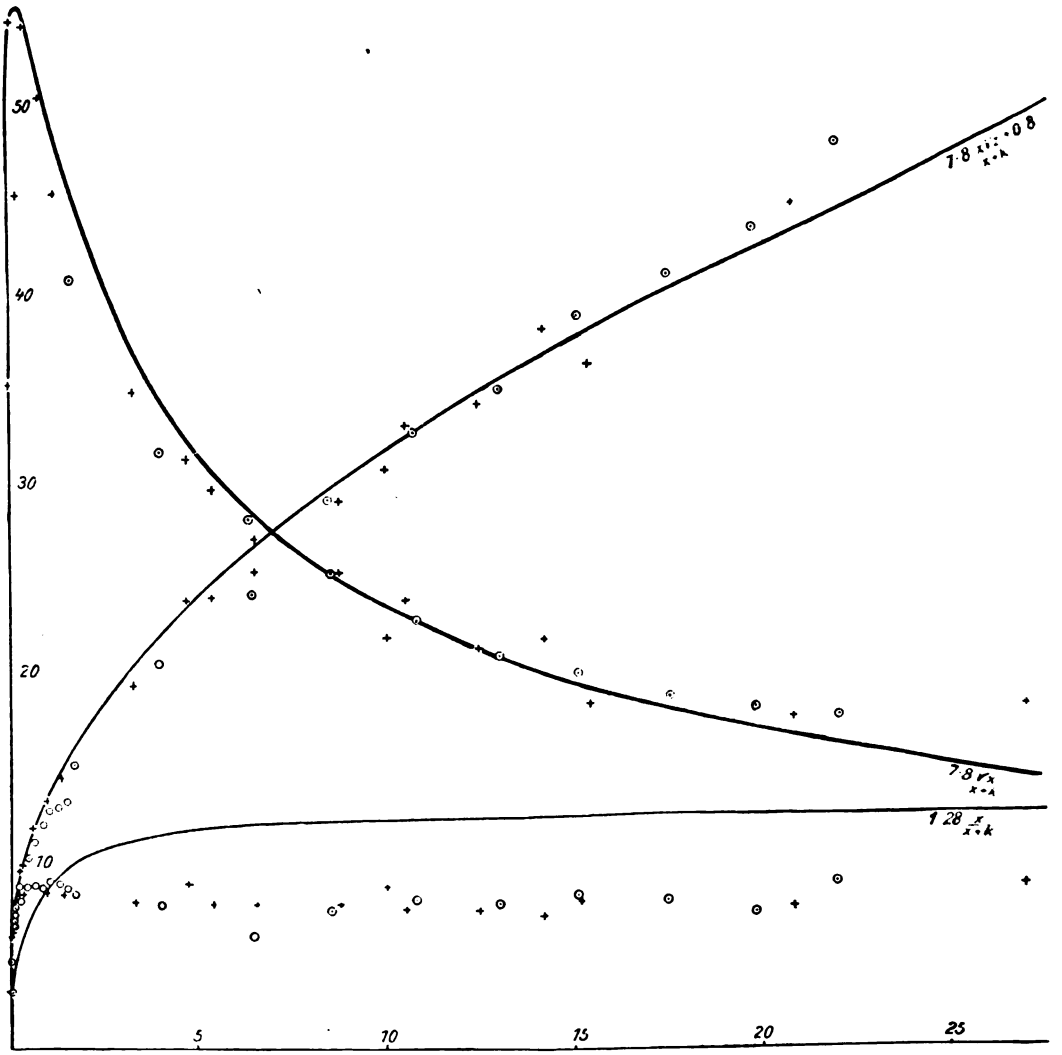


Fig. 2. (Table 3 and 4.)—Abscissas; mgr. molecules HCl in 1 gr. solution. Ordinates; + = results from table 3, • = results from table 4.

one sample of French gelatine, the titrations being done mostly by Mr. Pagett. Table 4 represents experiments made more re-

TABLE 4.—GELATINE AND HYDROCHLORIC ACID.

Series No.		Mgr-mols. HCl in 1 grm. residual solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in 1 grm. solution (Methyl-orange.) d	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Methyl-orange.) e	Mgr-mols. difference HCl in gelatine (Phenolphth. and methyl-orange.) c—e	Mgr-mols. HCl in excess of solution absorbed by gelatine (Phenolphth.) c—ab	Mgr-mols. HCl in excess of sol. absorbed. Sol. estimated with m.-o. c—db
β	1	0.2217	17.63	4.790	0.2193	3.875	0.915	0.876	0.915
	2	0.1082	18.12	4.332	0.1064	3.203	1.129	0.734	0.773
	3	0.1755	18.74	4.089	0.1733	2.901	1.188	0.793	0.841
	4	0.1533	19.92	3.875	0.1516	2.706	1.169	0.817	0.855
	5	0.1306	20.74	3.485	0.1289	2.415	1.170	0.770	0.818
	6	0.1081	22.75	3.252	0.1066	2.064	1.188	0.788	0.827
	7	0.0801	25.13	2.901	0.0841	1.752	1.149	0.733	0.793
	8	0.0644	28.23	2.414	0.0625	1.480	0.934	0.593	0.650
	9	0.0403	31.65	2.045	0.0385	1.111	0.934	0.763	0.823
	10	0.0171	40.81	1.519	0.0154	0.565	0.944	0.821	0.890
α	1	0.0152	30.10	1.315	0.0142	0.610	0.705	0.857	0.888
	2	0.0129	32.28	1.298	0.0120	0.498	0.800	0.881	0.890
	3	0.0107	37.79	1.268	0.0098	0.520	0.748	0.899	0.903
	4	0.0084	38.37	1.196	0.0076	0.409	0.787	0.874	0.904
	5	0.0060	36.12	1.096	0.0054	0.352	0.744	0.877	0.901
	6	0.0041	37.94	1.016	0.0035	0.352	0.664	0.862	0.883
	7	0.0023	33.49	0.860	0.0018	0.194	0.666	0.783	0.793
	8	0.0015	31.15	0.751	0.0010	0.000	0.751	0.704	0.720
	9	0.0012	26.54	0.685	0.0007	0.000	0.685	0.655	0.668
	10	0.0006	18.36	0.467	0.0001	0.000	0.467	0.457	0.466
	11	0.0004	9.17	0.304	0.0000	0.000	0.304	0.300	0.304

cently, with slight variations of method suggested by experience, on another sample of gelatine of a slightly more acid character, and with apparently a greater solid cohesion, as the maximal swelling is in all cases less, though the character of the curves and the position of the maxima in general show good agreement with the earlier results. Especially in the lower concentrations of Table 4 some ambiguity is caused by the acidity of the gelatine, consisting mainly of bisulphites which amounted to 0.282 mgr-mols. per gram as indicated by phenolphthalein, but did not affect methyl-orange, and of which at least a portion diffused into the outer solution, and affected its molecular acidity as determined by phenolphthalein, but could hardly have much influence on the acid "fixed." Determinations of the strength of the outer solution by methyl-orange, which certainly represent the whole of the acid present as HCl, are therefore given, with corresponding calculations of "fixed" acid, and of the acid absorbed in the gelatine as determined by the two indicators.

In reference to this work attention must be drawn to a paper[1] by Dr. Wolfgang Ostwald on the swelling of gelatine, in which he gives curves for the swelling of gelatine plates in acids and alkalies of different concentrations. In both cases he shows the existence of a maximum such as has just been described, but he also observed a minimum with very dilute solutions of which the present writer has found no trace. Ostwald himself ascribes this tentatively to the originally acid reaction of the gelatine, and in this he is probably correct, as the acidity is usually due to bisulphites, which are acid to strong bases and basic to strong acids, and of which neutralization in either sense would probably diminish the original swelling in water. The plates he employed were much thicker (3-4 mm. as compared to about 0.25 mm.) than those used in the present research, so that it is doubtful if real equilibrium was reached.

Table 5 gives the results of a series of experiments intended to test the reversibility of the equilibrium gelatine-acid-water. The gelatine was swollen for 48 hours in a solution which when equilibrium was reached was of 0.2253 mols. per mil concentration, and then for 24 hours in solutions of varied (lesser) con-

[1] Wo. Ostwald, Ueber den Einfluss von Säuren und Alkalien auf die Quellung der Gelatine. Archiv fur die ges. Physiologie. Bd 108. Bonn, 1905.

centration. The latter time does not seem to have been quite sufficient for equilibrium to be again attained, but there is no reason to suppose the absorption as other than completely reversible. The lowness of the "fixed acid" as calculated by deducting the calculated acid of the solution absorbed is somewhat remarkable, and it is unfortunate that in this series no parallel determinations were made with methyl-orange. Several possible explanations may be suggested, but it seems best to defer discussion for further experimental investigation. The portions which were only treated for 48 hours in one solution are normal in respect of "fixed" acid.

TABLE 5.—GELATINE SOAKED FOR 48 HOURS IN HCl OF APPROX. 0.275 MGR-MOLS. PER GRAM, AND NOS. 4-16 AFTERWARDS FOR 24 HOURS IN WEAKER SOLUTION.

Series No.	Mgr-mols. HCl in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine. c−ab=f
1	0.2253	20.33	5.411	0.830
2	0.2253	20.14	5.411	0.873
3	0.2253	21.18	5.506	0.734
	Then 24 hours in weaker solutions.			
4	0.2333	22.00	5.683	0.541
5	0.2146	21.61	5.125	0.488
6	0.1950	21.10	4.616	0.502
7	0.1754	22.77	4.567	0.573
8	0.1561	23.44	4.274	0.615
9	0.1383	25.04	4.039	0.576
10	0.1182	24.37	3.531	0.650
11	0.0984	26.89	3.218	0.571
12	0.0807	27.90	2.944	0.692
13	0.0629	28.94	2.465	0.644
14	0.0526	29.33	2.220	0.673
15	0.0476	32.87	2.230	0.667
16	0.0462	31.18	2.083	0.643

Although no exact quantitative result can be expected from the somewhat crude method of experiment, it is evident that graphic plotting of Tables 3 and 4, Fig. 3, represents the curves of a regular equilibrium, the figures being fairly consistent for any one series of determinations, and the errors of experiment not greater

than may be expected, considering the influence of various undetermined factors, such as the cohesive elasticity of the jelly, and the extremely small forces involved in considerable changes of volume near the swelling maximum. The approximately horizontal course of the "fixed acid" line, after a certain concentration of acid is reached, strongly suggests the idea of a definite though hydrolyzing chemical compound, rather than a merely physical one; and the determinations of "fixed acid" by the difference of reaction of phenolphthalein and methyl-orange prove a decided change of concentration of the H′ ion at or near that particular point. The occurrence of a very marked maximum of the swelling volume (S) is striking, and this follows naturally from the combination of the two regular curves, of "total acid" per gram of gelatine (a) and of "fixed acid" (f) since by the mode of calculation $S = \frac{a - f}{x}$; x being the concentration of the external solution given in column a.

As regards other acids, only a limited amount of work has been done. With weak acids like acetic and lactic, no definite maximum of swelling has been observed, the absorption of liquid increasing with the concentration till solution of the jelly begins. With formic acid a maximum occurs at a concentration of about 0.07 gram-mols. per liter, but it is less marked, and the rise to it is much more gradual than in the case of hydrochloric acid. Owing to the fact that no repression of swelling takes place with the weaker acids, a greater total swelling can be obtained by concentrating the solutions with acetic and probably with lactic acid than with hydrochloric, though it is evidently accompanied with greater solution, and possibly by structural changes of the gelatine.

As regards the fixation of acid, the methyl-orange method is inapplicable to any but the strongest acids, but calculating the absorbed solution as of equal strength to the external, figures for the excess-absorption are obtained which for acetic acid of medium concentrations are somewhat lower, and for lactic and formic about the same or slightly higher than those for hydrochloric. At the higher concentrations, the total absorbed acid is so large that experimental error makes the determination of "fixed acid" irregular and unreliable, and from the lowest concentrations the

value rises to a fixed average much more gradually than in the case of strong acids.

As regards sulphuric acid, but few determinations have been made, but these show that it produces a maximum swelling effect at a low concentration of which the value has not yet been determined, and the apparently "fixed acid" is also somewhat larger. No experiments have yet been made on the determination of "fixed acid" by methyl-orange, but as the change of color of this indicator is gradual it is evident that determination by mere titration is somewhat rough, and it is proposed to investigate the subject further by the actual determination of ionization-constants.

The following tables 6-9 give the results of the work which has already been done on acids other than hydrochloric.

Table 10 (xxix 1-3) gives a few determinations on sheepskin and shows that a maximum exists, the weaker solution swelling more than the stronger; and the acid "fixed" is very similar in amount to that fixed by gelatine. The skin was unwoolled in the customary way, freed from lime, and dried at 80° C., and soaked in water till soft, before use.

TABLE 6.—GELATINE AND ACETIC ACID.

Series No.	Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid fixed by 1 grm. dry gelatine ca—b=f
XV 1	0.1050	46.97	5.570	0.638
2	0.0873	44.29	4.520	0.653
3	0.0693	43.90	3.747	0.705
4	0.0513	37.27	2.527	0.615
5	0.0340	32.98	1.679	0.558
6	0.0161	25.36	0.874	0.466
	New Sample of Gelatine.			
A 1	1.0050	62.97	62.54	—0.74
2	0.5083	57.28	32.05	+2.93
3	0.2062	51.14	11.50	0.95
4	0.1011	44.68	5.127	0.610
5	0.0805	33.89	3.398	0.670
6	0.0512	28.81	2.042	0.395
7	0.0216	20.56	0.917	0.473
8	0.0110	17.35	0.594	0.403

TABLE 7.—GELATINE AND LACTIC ACID.

Series No.		Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab=f
XVII	1	0.1047	52.73	6.284	0.764
	2	0.0684	48.63	4.124	0.798
	3	0.0321	48.19	2.397	0.825
	4	0.0048	26.98	0.673	0.543

TABLE 8.— GELATINE (NEW SAMPLE) AND FORMIC ACID.

Series No.		Mgr-mols. of acid in 1 grm. of remaining solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. of acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab=f
B.	1	0.9918	47.90	48.01	0.48
	2	0.5196	49.74	26.16	0.31
	3	0.1910	53.95	11.33	0.97
	4	0.0786	55.92	5.236	0.838
	5	0.0511	55.47	3.669	0.834
	6	0.0196	47.31	1.640	0.711
	7	0.0146	41.40	1.064	0.464

TABLE 9.—GELATINE AND SULPHURIC ACID.

Series No.		½ mgr-mols. of acid in 1 grm. solution (Phenolphth.) a	Weight of solution absorbed by 1 grm. of dry gelatine b	½ mgr-mols. of acid absorbed by 1 grm. of dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. of dry gelatine c—ab=f
XVI	1	0.1055	20.17	3.178	1.050
	2	0.0685	20.85	2.469	1.041
	3	0.0303	25.27	1.855	1.089
	4	0.0024	31.65	0.944	0.868

TABLE 10.—SHEEP PELT DRIED AT 80° C. AND HYDROCHLORIC ACID.

Series No.	Original solution: Mgr-mols. HCl per grm.	Original solution: Mgr-mols. NaCl per grm.	Mgr-mols. HCl in solution a	Weight of solution absorbed by skin b	Mgr-mols. HCl absorbed by 1 grm. skin c	Acid "fixed" by 1 grm. skin c—ab=f
XXIX 1	0.1466	nil	0.1386	10.38	2.176	0.737
2	0.0488	nil	0.0466	10.76	1.236	0.735
3	0.0073	nil	0.0024	19.31	0.467	0.421
XXX 1	0.1807	3.00	0.1665	5.95	2.389	1.399
2	0.0907	3.01	0.0798	5.70	1.499	1.044
3	0.0378	3.02	0	4.71	0.364	0.364
XXXI 1	0.0692	4.17	0.0580	4.11	1.455	1.217
2	0.0826	1.66	0.0700	4.27	1.315	1.016
3	0.0981	0.48	0.0775	3.93	1.227	0.922

Attention must here be drawn to a research published by Stiasny on the absorption of water and acid by hide powder and ox-hide[1] by quite different methods to that adopted by the writer. From the data given it would be difficult or impossible to calculate the acid fixed, but the occurrence of a maximum of swelling in the weaker solutions is in both cases very clearly marked. The results with hide powder and ox-hide showed considerable divergence, which Stiasny attributes to difference in texture, but which perhaps may have been partly due to the time given having been insufficient to establish complete equilibrium.

One of the most striking effects of the "pickling process" which gave rise to the investigation is the extraordinary dehydration produced by the action of strong solutions of common salt on the acidified skin fiber, and also on the acidified gelatine; and acidified gelatine is also precipitated by it as a coherent mass from its warm solutions. No such effect is produced by common salt alone on neutral fiber or gelatine, the effect even of saturated solutions being somewhat to increase the swelling:—a gelatine absorbing about eight times its weight of water being capable of taking up about 11 of saturated common salt solution, and a larger quantity of one of medium dilution. The results of a

[1] Stiasny. Ueber negative Adsorption, und die Bestimmung der Schwellwirkung von Säuren auf Hautpulver und Blosse. *Gerber*, 1909, p. 183 et seq., and *Collegium*, 1909, p. 302 et seq.

series of experiments are given in Table 11. Some other salts, however, and notably ammonium sulphate and some other sulphates, are well known to exercise a powerful dehydrating effect on swollen gelatine or skin, and even to precipitate gelatine from strong warm solutions as a coherent mass. The discussion of these actions of neutral salts must be deferred till the effects of salts in acidified solutions has been more fully considered. It may be pointed out, however, that the effect is most noticeable in the case of sulphates of weak bases, such as ammonium and zinc.

It is unimportant whether the gelatine or skin-fiber is first swollen by acid and then submitted to the action of salt-solution, or the proceeding is reversed, since similar effects are produced by the addition of a suitable quantity of acid to the already salted gelatine, and an effective pickling may be produced by adding a calculated quantity of acid to skins placed in a strong brine, although commercially the method is more costly. The quantity of acid which is most effective is larger than that required to produce a maximum swelling, since the presence of salt enables the skin or gelatine to "fix" a larger quantity of acid than it can do in an equally dilute acid solution without salt. In presence of sufficient salt, however, the necessary quantity of acid may be, (and commercially usually is) largely exceeded without much interfering with the result, though large excess is undesirable, and, in dilute salt solutions diminishes the dehydration. Some instances of the action of acidified salt-solutions on skin are given in Table 10 (XXX and XXXI); and the results of much experimental work on gelatine in presence of hydrochloric acid and salt in different proportions in Tables 12 and 13.

TABLE XI.—GELATINE AND VARYING SALT SOLUTION.

	Series No.	Mgr mols. NaCl in solution	Weight of solution absorbed by 1 grm. dry gelatine	Mgr-mols NaCl in swollen jelly of 1 grm. dry gelatine	Salt in excess of that calculated in absorbed solution
I	1	3.633	11.90	47.21	3.98
	2	3.035	14.72	48.41	3.73
	3	2.383	17.08	41.22	0.52
	4	1.665	16.42	27.80	0.46
	5	0.876	15.11	13.66	0.42
	6	0	8.83	0	0

TABLE 12.—GELATINE, HCl AND NaCl. ACID APPROXIMATELY CONSTANT, SALT VARIED. THE ORIGINAL ACID WAS IN ALL CASES OF A CONCENTRATION OF 0.0921 MGR-MOLS. PER GRM. ON THE WATER EMPLOYED, AND THE VARIATIONS ARE CAUSED BY THE ADDITION OF SALT, AND THE FIXATION OF ACID BY THE GELATINE DURING THE EXPERIMENT.

Series No.		Mgr-mols. original HCl per grm. solution	Mgr-mols original NaCl per grm. solution	Mgr-mols. HCl in 1 grm. sol. after use (Phenolphth.) a	Weight of sol. absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in jelly of 1 grm. dry (methyl-or.) d	Diff. mols. HCl by methyl-or. and (phenolphth.) c—d	Diff. mols. HCl found and calculated from solution absorbed c—ab	Diff. mols. NaCl found and calculated from solution absorbed e
V	1	0.0694	4.172	0.0628	1.251	1.331	.....	.....	1.252	—0.488
	2	0.0723	3.624	0.0677	2.487	1.377	.....	.....	1.209	—0.362
	3	0.0757	3.027	0.0696	3.197	1.336	.....	.....	1.114	—0.561
	4	0.0790	2.376	0.0758	3.667	1.331	.....	.....	1.053	—0.298
	5	0.0829	1.661	0.0793	2.976	1.270	.....	.....	1.034	—1.127
	6	0.0871	0.873	0.0834	13.096	1.935	.....	.....	0.926	—1.104
VI	1	0.0667	4.676	0.0633	1.144	1.313	0.408	0.905	1.241	—1.258
	2	0.0694	4.172	0.0631	1.126	1.317	0.750	0.567	1.246	—0.607
	3	0.0723	3.624	0.0657	1.275	1.280	0.623	0.657	1.196	—0.325
	4	0.0755	3.027	0.0688	1.343	1.249	0.478	0.771	1.157	—0.472
	5	0.0790	2.376	0.0741	1.962	1.255	0.710	0.545	1.110	—0.344
	6	0.0829	1.661	0.0761	2.816	1.278	0.507	0.771	1.064	—0.670
	7	0.0871	0.873	0.0814	10.330	1.831	1.020	0.631	0.990	—0.218
	8	0.0894	0.445	0.0853	19.90	2.638	1.640	0.998	0.941	—0.314
	9	0.0921	.....	0.0893	31.56	3.525	2.807	0.718	0.707	.....

NOTE:—It would be desirable to repeat the determinations of this table with precautions to ensure that the acid was really constant *after equilibrium was established.* Comparison with Table 13 shows, however, that the comparatively small variations of acid have in this case but little influence on the results obtained.

TABLE 13.—GELATINE, HCl AND NaCl. ACID VARIED, SALT APPROXIMATELY CONSTANT. THE AMOUNT OF ACID IS DETERMINED AFTER EQUILIBRIUM IS ESTABLISHED, THAT OF SALT IS CALCULATED ON THE ORIGINAL SOLUTION, AS FIXATION IS NEGATIVE AND NEGLIGIBLE AS COMPARED TO THE TOTAL CONCENTRATION.

	Series No.	Mgr-mols HCl in 1 grm. solution after use (Phenolphth.) a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Phenolphth.) c	Mgr-mols. HCl in jelly of 1 grm. dry gelatine (Methyl-or.) d	Diff. mols. acid in jelly by Methyl-or. and phenolphth. c—d	Diff. mols. acid in jelly from that in solution absorbed c—ab	Salt "fixed" by 1 grm. dry gelatine
III	1	0.0832	1.57	1.239	0.229	1.108	1.108	+0.784
	2	0.0702	1.52	1.228	0.567	0.661	1.121	—0.064
	3	0.0601	1.3	1.257	0.554	0.703	1.175	+0.354
	4	0.0410	1.64	1.199	0.514	0.685	1.132	—.0329
	5	0.0251	2.05	1.138	0.438	0.700	1.087	—0.545
	6	0.0126	2.05	1.102	0.378	0.724	1.076	—0.762
		Salt in original solutions 3.02 mol. per gram.						
VII	1	0.1796	1.54	1.508	0.592	0.916	1.232	—0.912
	2	0.1492	1.58	1.434	0.548	0.886	1.198	—0.853
	3	0.1184	1.52	1.381	0.565	0.816	1.201	—0.885
	4	0.0872	1.60	1.303	0.665	0.638	1.163	—0.620
	5	0.0717	1.58	1.287	0.539	0.748	1.174	—0.495
	6	0.0564	1.58	1.248	0.414	0.861	1.159	—0.731
	7	0.0409	1.50	1.225	0.420	0.805	1.164	—0.690
	8	0.0262	1.50	1.179	0.288	0.891	1.140	—0.629
	9	0.0100	1.57	1.118	0.259	0.839	1.102	.....
	10	0.0021	1.62	1.095	0.209	0.886	1.091	—0.735
	11	0.0002	3.16	0.728	.....	0.727	0.727	—0.516
	12	.....	15.78	*0.109	.....	0.109	0.109	+0.180
		Salt in original solutions 302 mol. per gram.						
VIII	1	0.1817	13.62	3.495	2.673	0.822	1.020	.....
	2	0.1465	12.98	3.028	1.977	1.051	1.127	.....
	3	0.1154	12.57	2.553	1.558	0.995	1.102	.....
	4	0.0861	11.63	2.088	1.093	0.995	1.087	.....
	5	0.0722	10.93	1.842	0.855	0.987	1.052	.....
	6	0.0570	11.73	1.698	0.871	0.827	1.029	.....
	7	0.0347	11.52	1.426	0.508	0.918	1.026	.....
	8	0.0247	10.99	1.295	0.465	0.830	1.024	.....
	9	0.0096	10.73	1.142	0.221	0.921	1.039	.....
	10	0.0023	9.81	1.010	0.147	0.863	0.987	.....
	11	0.0002	10.44	0.684	.....	0.684	0.682	.....
	12	.....	11.90	0.103	.....	0.103	0.103	.....
		Salt in original solutions 0.76 mol. per gram.						

*This acidity is original acidity of gelatine, due principally to bisulphates.

Comparing the results with those of Tables 3-5 which give the results with hydrochloric acid alone, it will be noted that the total acid absorbed by 1 gram gelatine is lower, the contraction of volume caused by the salt expelling acid as well as water; but on the other hand the acid "fixed," as calculated by deducting from the total absorbed acid that contained in a volume of solution equal to that absorbed is in all cases higher than with hydrochloric acid alone. This does not necessarily imply that the acid actually attracted by the gelatine is greater when salt is present, but that the dissociation or hydrolyzation is less; or on the other hand, that the obviously doubtful assumption that the concentration in acid of the absorbed solution is equal to that of the external is incorrect. If, as is probable, the concentration of the absorbed solution is really less, the apparent "fixed" acid will increase in some inverse ratio to the volume of the solution absorbed.

On the other hand it must be noticed that the less ionized

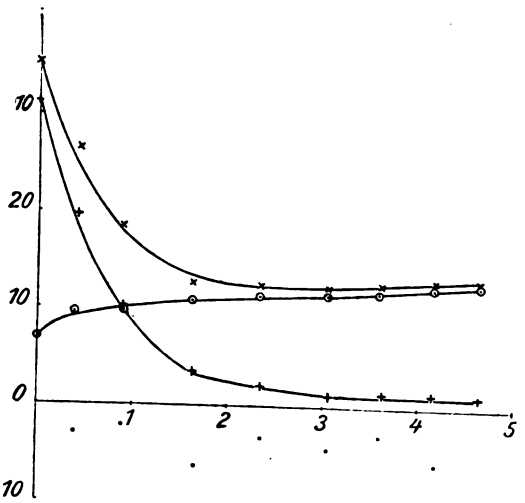


Fig. 3. (Table 12.)—Abscissas; Mgr. molecules NaCl in 1 gr. solution. Ordinates; x = Mgr-mol. HCl in 1 gr. dry gelatine; o = concentration of acid fixed by 1 gr. dry gelatine; + = wt. of solution absorbed by 1 gr. dry gelatine; o = "fixed" salt.

acid, as determined by its non-effect on the methyl-orange, is proportionately, and even actually less in the salted, than in the merely acid solutions. It is, however, by no means probable that methyl-orange is wholly insensitive to the acidity of the

acid-gelatine, and, unless this is the case, the effect of the latter will be increased by its greater concentration in the contracted jelly, just as methyl-orange is reddened by many organic acids in concentrated solution which scarcely affect it when dilute. Any direct action of the acid gelatine on methyl-orange will diminish its apparent "fixed acid" as determined by this means.

An interesting point in Tables 12 and 13 is that of the amount of salt "fixed," which in presence of hydrochloric acid appears to be always negative, the few apparent exceptions being obviously due to experimental errors, and accompanied by abnormal figures in one or other of the remaining determinations; while Table 11 shows that in absence of acid, a varying

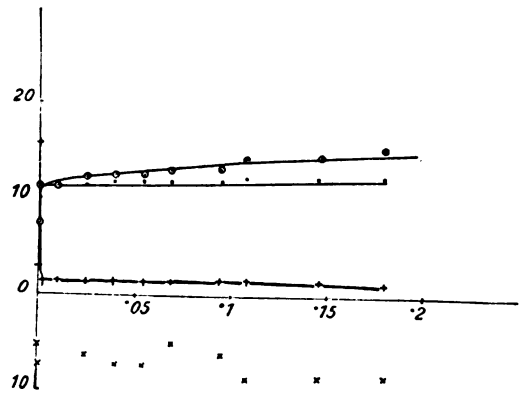


Fig. 4 (Table 13, series VII).—Abscissas; Mgr-mol. HCl in 1 gram solution. Ordinates; . =Mgr-mol. HCl in 1 gr dry gelatine; +=wt. of solution absorbed by 1 gr dry gelatine (b) o = "fixed" acid ; x = "fixed" salt.

positive amount is "fixed." The quantities were calculated by determining the total chlorine in the treated gelatine with argentic nitrate and potassium chromate, and subtracting from this the hydrochloric acid found acidimetrically, and the total chlorine calculated in the solution absorbed. From the large total amount of chlorides present, and the proportionately large effect of the absorbed solution, great quantitative accuracy cannot be claimed for these figures, but they strongly support the view that the chlorine absorbed as hydrochloric acid by the gelatine exerts a corresponding expulsive effect on the chlorine ions (both acid and salt) contained in the solution. It is noted in connection with the experimental work, that in several cases where large

quantities of salt were used, the sheets of gelatine, instead of appearing homogeneous and transparent, became white and opaque; and this must have been due either to the actual crystallization of salt in the gelatine, or to the formation of a cellular or at least heterogeneous structure enclosing solution of a different refractive index to that of the surrounding jelly. It is extremely probable that this circumstance may account for the irregularity of the figures with regard to fixation of salt.

From the curves given in Fig. 3 it will be seen that the swelling diminishes in a curve of hyperbolic character with increasing concentration of salt, becoming asymptotic to a value apparently somewhat above zero.

Apparently any acid and its corresponding neutral salt will produce a dehydrating effect on swollen gelatine, varying in intensity with the electrolytic dissociation-constant of the acid, and increasing with the concentration of the salt. The effect of sodium sulphate with sulphuric acid appears to be quite as great as that of sodium chloride and hydrochloric acid in equivalent concentrations, while that of the weak acids with their own neutral

TABLE 14.—SULPHURIC ACID AND SODIUM SULPHATE.

Series No.		½ mols. H_2SO_4 in residual solution (Phenolphth.) a	½ mols. Na_2SO_4 in original solution	Wt. of solution absorbed by 1 grm. dry gelatine b	½ mols. H_2SO_4 in 1 grm. dry gelatine after swelling (Phenolphth.) c	Excess over acid calculated in absorbed solution c−ab
XVIII	1	0.05342	0.8173	7.072	1.573	1.195
	2	0.05446	0.6963	9.840	1.629	1.093
	3	0.05668	0.5698	12.75	1.872	1.149
	4	0.05773	0.4374	14.42	1.901	1.068
	5	0.05883	0.2986	15.44	1.992	1.084
	6	0.06053	0.1530	35.18	3.033	0.903

salts is much less, though distinctly marked when compared to the swelling action of the acids alone, as will be obvious in comparing Tables 15 and 16 with 6 and 8. With the weaker acids, the excess of acid absorbed in excess of that due to absorbed solution ("apparent fixed acid") is much less and very irregular as compared to that observed with the stronger acids; and this is particularly the case with the feebly ionized acetic acid,

of which the ionization is still further reduced by the presence of its neutral salt.

TABLE 15.—GELATINE, FORMIC ACID AND SODIUM FORMATE. SODIUM FORMATE IN SOLUTION 1.33 MOLS.

Series	No.	Mgr-mols. acid in 1 grm. sol. a	Wt. of solution absorbed by 1 grm. b	Mols. acid in jelly of 1 grm. c	Excess over acid in absorbed sol. c—ab
D	1	0.9008	19.45	18.39	0.87
	2	0.4955	17.14	9.11	0.62
	3	0.2049	15.53	3.79	0.61
	4	0.1053	16.04	2.15	0.46
	5	0.0824	16.99	1.71	0.31
	6	0.0574	15.57	1.23	0.34
	7	0.0265	17.07	0.70	0.25
	8	0.0172	15.93	0.44	0.17

TABLE 16.—GELATINE, ACETIC ACID AND SODIUM ACETATE. SODIUM ACETATE IN SOLUTION, 1.33 MOLS.

		Mgr-mols. acid in 1 grm. sol. a	Wt. of solution absorbed by 1 grm. b	Mols. acid in jelly of 1 grm. c	Excess over acid in absorbed sol. c—ab
B	1	0.9656	20.83	20.64	0.50
	2	0.5018	17.64	9.74	0.89
	3	0.1991	15.89	3.32	0.16
	4	0.1007	14.38	1.56	0.11
	5	0.0788	14.20	1.e6	0.14
	6	0.0526	13.20	0.79	0.10
	7	0.0242	12.26	0.39	0.09
	8	0.0143	11.05	0.18	0.02

It is not necessary in order to produce contraction of swelling that the salt employed should have the same anion as the acid, and if the salt is one of a strong acid and in sufficient concentration, good contraction may be obtained even by acidification with very weak acids. Thus effective pickling may be obtained with formic or acetic acid in presence of common salt; and at the writer's suggestion formic acid has been to some extent used commercially for sheepskins, as the antiseptic effect is even greater than that of the customary sulphuric acid, while certain injurious effects of the latter on the final manufactured product are avoided. In the ordinary commercial process, as has been stated, sulphuric acid and common salt are employed; but except for questions of cost, hydrochloric acid and sodium sulphate would be equally effective, as shown in Table 17. Table

TABLE 17.—GELATINE, HYDROCHLORIC ACID, AND SODIUM SULPHATE.

Series No.		Mgr-mols. acid per grm. Original solution	½ mgr-mols. Na_2SO_4 per grm. Original solution	Mgr-mols. acid in solution after use (Phenolphth.) a	Wt. of sol. absorbed by 1 grm. dry gelatine b	Mgr-mols. acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab
XII	1	0.0574	0.8172	0.0560	7.41	1.492	1.067
	2	0.0587	0.6963	0.0524	8.79	1.457	0.941
	3	0.0601	0.5698	0.0533	8.07	1.513	1.028
	4	0.0615	0.4374	0.0558	9.24	1.603	1.035
	5	0.0630	0.2986	0.0555	10.03	1.682	1.050
	6	0.0645	0.1530	0.0565	11.85	1.766	0.937

Original concentration of acid in water only 0.0663 mols.

TABLE 18.—GELATINE, ACETIC ACID AND SALT.

Series No.		Mgr-mols. acid per grm. Original solution	Mgr mols. NaCl per grm. Original solution	Mgr-mols acid in solution after use (Phenolphth.) a	Wt. of sol. absorbed by 1 grm. dry gelatine b	Mgr mols acid absorbed by 1 grm. dry gelatine (Phenolphth.) c	Acid "fixed" by 1 grm. dry gelatine c—ab
IX	1	0.0696	4.373	0.0665	1.37	1.166	1.078
	2	0.0793	2.371	0.0739	2.65	1.217	1.021
	3	0.0874	0.871	0.0839	10.49	1.798	0.918

Original concentration of acid in water only 0.0926 mols.

TABLE 19.—GELATINE, HYDROCHLORIC ACID AND POTASSIUM CHLORIDE.

Series No.		Mgr-mols. acid per grm. Original solution	Mgr-mols. KCl per grm. Original solution	Mgr-mols. acid in solution after use (Phenolphth.) a	Wt. of solution absorbed by 1 grm. dry gelatine b	Mgr-mols. acid absorbed by 1 grm. dry gelatine c	Acid "fixed" by 1 grm. dry gelatine c—ab
XIII	1	0.0551	2.233	0.0524	2.130	1.186	1.069
	2	0.0567	1.914	0.0477	2.677	1.207	1.080
	3	0.0584	1.576	0.0539	3.732	1.263	1.063
	4	0.0601	1.218	0.0555	5.685	1.360	1.044
	5	0.0620	0.837	0.0572	11.19	1.664	1.024
	6	0.0640	0.432	0.0592	12.26	1.746	1.020

Original concentration of acid in water only 0.0663.

18 shows results with acetic acid and common salt. It will be observed that both the dehydration and the acid "fixed" are practically the same with acetic acid as they would have been if hydrochloric acid had been used.

Table 19 gives a series in which potassium chloride is substituted for sodium chloride with hydrochloric acid. The results are again practically identical with those of sodium chloride.

Summary.

Gelatine absorbs water with evolution of heat, and is capable of exerting large external pressures in the initial stages, but as the quantity of water becomes greater the avidity of the gelatine becomes less, and there is no further perceptible evolution of heat, while the mechanical force exerted is exceedingly slight and may be measured in a few dynes per sq. cm. The process is completely reversible, and water may easily be expelled from the fully swollen jelly by mechanical pressure, and completely removed by evaporation *in vacuo*, and to a large extent by dehydrating agents, though as dryness is approached the last portions of water are removed with great difficulty. The swelling does not proceed to infinity in cold water, but reaches a definite maximum, which is an equilibrium between the affinity for water and the elastic cohesive forces of the gelatine which are influenced not only by its chemical character but by its original volume at setting. In hot water complete solution takes place.

Gelatine is insoluble in, and water-swollen gelatine is impermeable to strong alcohol, which dehydrates and compresses it. If, however, alcohol is incorporated in the liquid jelly which is subsequently allowed to set, and immersed in water, the swelling is increased beyond the ordinary maximum.

Gelatine swells in very dilute acids to a much larger extent than in water. In weak acids this swelling increases with the concentration of acid till finally solution takes place, but with strong acids the swelling reaches a maximum at very low dilutions and subsequently diminishes in a curve of hyperbolic character till the jelly dissolves without further swelling, which limits the possible range of experiment. If, however, a neutral salt of the acid be added, the dehydration may be carried with

strong acids to a point at which the gelatine forms a solid and horny mass. With weak acids and their salts the effect is less marked but quite obvious. If, however, a weak acid is used with large excess of a salt of a strong acid, the gelatine behaves as if the strong acid only was present, while gelatine swollen with a strong acid and treated with the salt of a weak one naturally behaves as if the weak acid had been used.

In all cases the acid absorbed by the swelling gelatine is in excess of that due to the absorbed solution, and this excess is in any one series of experiments of an approximately constant amount over a wide range of concentration of the acid or acid and salt solution; while under no conditions does it pass a maximum of about 1.25 mgr-mols. of acid per gram of dry gelatine. In the case of strong acids which affect the color of methyl-orange even at very great dilutions, it is shown that a portion of the acid absorbed by gelatine, which varies with the conditions of the experiment but always falls within the limit above stated, has become so considerably less ionized than the free acid that it is incapable of affecting the color of methyl-orange, though it may still be estimated by phenolphthalein.

In the case of common salt it is shown that while in neutral solutions it increases the swelling of gelatine and an amount is absorbed in excess of that normally contained in the absorbed solution, in presence of even small quantities of hydrochloric acid, great dehydration is produced, and the fixation of salt is negative.

Theoretical.

As regards the explanation of the foregoing experimental results, anything which can yet be said, must, in view of the preliminary character of the investigation and the somewhat rough methods of experiments, be regarded as merely working hypothesis. As a preliminary to this, it is necessary to have some definite conception of the actual structure of a gelatine jelly, and the view which is here adopted is that of a network of gelatine molecules cohering to each other, but leaving interstices of molecular dimensions containing water or aqueous solutions, which being within the range of molecular attractions, are really semi-solid solutions in the gelatine, and have with it a common

internal pressure. The gelatine molecule, consisting as it does, of a complicated chain of amido-acids, is peculiarly fitted to produce such a structure. The range of molecular attraction does not apparently exceed 10 $\mu\mu$ (millionths of a millimeter) and may be much smaller; (cp. Freundlich Kapillarchemie, s 277); but as about 2 per cent. of gelatine is required to form a coherent jelly, there would be in each cubic space of $(10\ \mu\mu)^3$ a weight of gelatine over 13 million times the estimated weight of a hydrogen molecule, and therefore ample molecules for a net of molecular dimensions. The facts mentioned as regards the effect of concentration at the moment of setting on the subsequent swelling give considerable support to the idea of a molecular network formed at the time.

This view, though apparently very similar to the currently accepted one of van Bemmelen and Bütschli, is really very different, since these investigators assume a cellular structure of microscopic dimensions, and hence far beyond the range of molecular forces. That such cellular jellies or pseudo-jellies exist and can be produced is undeniable, but in the writer's opinion it is quite unproved that any such structure naturally exists in aqueous gelatine jellies, the microscopic observations all having been made on jellies hardened and shrunk with dehydrating agents, while no structure could be detected in the unhardened jelly, in which its dimensions if existant, must have been much larger. A dilute gelatine solution which has been sufficiently heated for complete solution shows only stray and probable accidental submicrons, and merely a slight Tyndall effect in the ultramicroscope, so that it is probably, for the most part, a true molecular solution in which the gelatine is uniformly distributed throughout the liquid. On cooling, no flocculation or visible contraction of the gelatine takes place, but the whole solidifies to a transparent and apparently homogeneous jelly, and it is hard to imagine how, under these conditions a cellular structure could be formed. In some other cases, as for instance in the flocculation of albumin solutions by heat, where the gel is obviously less hydrophile than the sol, the network, even if at first uniform and molecular, necessarily contracts, and a reticular structure must result; while when a solution separates into two partially immiscible liquids, an emulsion will be formed, which may be a pseudo-jelly; but

none of these causes appear to exist with gelatine, and the assumption of a cellular structure does not in any way assist, but considerably complicates the explanation of observed facts.

It is clear that if we accept the conception of a jelly as the solution of a liquid in an elastic solid, the whole question of swelling becomes one of osmotic pressures or perhaps more accurately, one of distribution between two immiscible solvents. In the latter case the common surface takes the place of a semipermeable membrane and as the solvents are no longer identical, the partition-constant (Teilungscoefficient), and sometimes also a different molecular complexity have to be considered. There is also an important difference between the two cases which may be overlooked. In ordinary osmosis the molecular attractions of the common solvent merely serve to overcome and balance those of the solute, and bring it into a region of equal and common internal pressure, where its kinetic energy can exert itself against a fixed semipermeable septum, so that in the terms of gas equation, V is constant and P varies. In the equilibrium of immiscible solvents on the other hand the kinetic energy of the solute is constant, and it is the varying internal attraction of the two solvents for its molecules which determines the partition-constant; and since the diffusion-surface is freely moveable, P is constant and V varies. This latter statement is somewhat modified in the case of jellies by the residual forces of solid cohesion which oppose change of volume. It can be shown, however. that in or near the region of maximum swelling these forces are extremely small. P. von Schroeder[1] showed that a jelly swollen in water lost a large amount of weight and volume (up to 73 per cent.) in an atmosphere of saturated water-vapor, but that this was completely prevented if the jelly were saturated with a N. 10^{-5} solution of an alkaline sulphate, and considerably lessened by one of N. 10^{-6}. It was subsequently shown by the present writer[2] that the energy involved in removing 1 gram water against the osmotic pressure of a N. 10^{-5} sulphate solution (about 350 erg.) was quite comparable to that done against surface tension in forming the surface of a sphere 1 gram weight; and that no doubt the shrinkage might be accounted for in that way. It

[1] *Collegium*, 1903, p. 204.
[2] Brit. Assoc. Rep., 1908, p. 216.

therefore follows that in most cases of considerable swelling the solid cohesion is almost negligible as compared to osmotic forces. On the other hand in the earlier stages of absorption of water by dry organic colloids, including gelatine, the forces involved are large, as is evidenced by the marked evolution of heat, the contraction of common volume, and the very considerable pressures obtained when the swelling is opposed by mechanical obstacles.

If the swelling of gelatine in pure water be admitted to be osmotic, still more evidently is this the case with regard to the dehydrating action of alcohol on the swollen jelly, since the latter, though freely permeable to water is practically impermeable to alcohol, and the jelly-mass acts as a simple osmotic cell. The curve of swelling in mixtures of water and alcohol (Table 2 is shown in Fig. 1) and is of a simple type corresponding closely to a rectangular hyperbola in the middle portion but diverging at both extremes, possibly because of the solid rigidity of the jelly. There is no reason to doubt complete reversibility. Alcohol shows considerable osmotic pressure in an osmometer with gelatine membrane, and it is shown that alcohol incorporated in jelly must produce a cellular structure, in which the jelly acts as a semipermeable membrane. It is possible that more complete investigation of the dehydrating effects of alcohol on jellies might afford some definite information on their cohesion and osmotic pressures, since the action is purely physical.

The explanation of acid swelling and the peculiar maximum of its curve, and of dehydration of acid gelatine by neutral salts is much more complex, and involves chemical as well as purely osmotic considerations. In what follows the most detailed consideration will be given to the action of hydrochloric acid and sodium chloride, as these have been most fully investigated, and there is no reason to think that the results differ in principle from those of other acids and their corresponding salts.

Gelatine-jelly is known to be very permeable to both acids and salts and to their ions, so that it is not easy to see how either can exert a direct osmotic pressure on the jelly-mass. It has, however, been shown that even very dilute hydrochoric acid is absorbed with some avidity by the jelly, which always contains acid in considerable excess of an equal volume of the surrounding solution with which it is in equilibrium: and this excess, rising

rapidly at first soon becomes an almost constant quantity (see curve of "fixed acid" in Fig. 2); strongly suggesting the idea of a definite though hydrolyzing chemical compound of the nature of a salt, in which the amphoteric gelatine acts as base. This idea is further supported by the fact that an approximately corresponding quantity of acid becomes neutral to methyl-orange, though it can still be hydrolyzed by sufficient excess of water, and estimated by titration with caustic alkali with phenolphthalein as indicator. If such a gelatine chloride exists, it is extremely probable that it will be much less permeable for hydrochloric acid and other chlorides than the neutral gelatine, or, if we regard the jelly as a solution, that the solubility of salts of a common anion in the acid jelly will be much less than in the neutral, while its affinity for water will be likely to be greater, owing perhaps to its greater ionization. The jelly of course must be in equilibrium with the surrounding solution in every respect, and firstly in regard to hydrolysis, in which it will obey the ordinary law of mass-action. As regards its volume the case is quite analogous to that of solutions of an acid and its salt separated by a movable septum permeable to the acid and to water, but not to the salt, which in the present instance is an indiffusible colloid jelly. The two solutions must be in complete equilibrium, and as the salt cannot diffuse, water and acid must pass through the septum till equilibrium is reached. Firstly then, the common anion must be at equal concentration in both solutions, and because of the salt-anions, the free acid must necessarily be less concentrated in the salt-solution than in that of the pure acid. Secondly the anion of the acid in salt-solution must be in equilibrium with that of the salt itself, and this can only occur by absorption or expulsion of water or acid till the ionic pressure of the salt is equal to that of the acid contained in its solution. Thus, the necessary data being given, the volume of the salt solution or jelly is definitely fixed; and dependent on the concentration of the acid ions, and the ionization and quantity of the salt. Again the quantity of unhydrolyzed and ionizable salt for a fixed quantity of base, depends on the hydrion concentration of the acid and the hydrolysis-constant of the salt; and thus different acids with different constants may produce very varied effects of swelling.

One consequence of what has just been said must be remarked. It is evident that the "fixed acid" calculated on the assumption that the absorbed solution is of equal acid concentration to the surrounding acid, does not represent the whole of the unhydrolyzed gelatine-salt, but is less than it by the amount of acid expelled by the salt from its solution. Whether the whole of this acid is expelled by the ionized salt, or a part also by the unionized, which demands water for its solution is not easy to determine, but probably unimportant for the general theory of the equilibrium.

It is of course impossible to treat the problem at present in any rigid mathematical way while so many of the factors are unknown, and especially that of the cohesive elasticity of the jelly, but it may be interesting to see how far the experimental results agree with theoretical assumptions.

We have assumed that the combination of gelatine with hydrochloric acid is of the nature of a salt of a weak base with a strong acid, of which the hydrolysis according to Mr. Ostwald is represented by the equation $\frac{hB}{b} = \frac{K_w}{K_g} = k$, when h is the hydrion concentration, b that of (colloid gelatine) ions and B of the hydrolyzed and anionized base (gelatine). K_w is the dissociation constant of water, K_g that of gelatine as a base. It may be taken without serious error that at the dilutions in question, HCl is fully ionized, and that therefore its concentration x in the solution is proportional to h the concentration of the hydrions. b is the concentration of the kation of the ionized but unhydrolyzed salt, and as the quantity of gelatine is constant in the experiment, B is obviously equal to $1-b$. The equation therefore takes the form $\frac{(1-b)x}{b} = k$, and resolving this as regards b, we have $b = \frac{x}{x+k}$ as the measure of the proportion of unhydrolyzed salt.[1] The same expression may also be obtained from the ordinary dilution equation $\frac{a^2}{(1-a)v} = k$, which, substituting the hydrolytic for the dissociation constant, also applies to mod-

[1] The hydrolyzed portion is obviously $\frac{k}{x+k}$.

erate hydrolysis. In this formula a is the hydrolyzed portion, which above has been called $1-b$; and $1-a$ is the unhydrolyzed salt b while the concentration of the hydrolyzed acid is the same as x, that of the external solution. Substituting these values and resolving as regards b, we again get $b = \frac{x}{x+k}$. It will be observed that v does not appear in this expression, since the concentration is determined by x, and therefore hydrolysis is not affected by the volume of the jelly. The value of b obviously rises rapidly at first and tends to unit value, and the rise is the more rapid and the later part of the curve the more horizontal the smaller the value of k. It must be observed that Ostwald's equation is merely an approximative one, and specially uncertain as complete hydrolysis is approached.

The unit value to which the expression tends is to that of a molecule or equivalent of the salt. In the actual experiments 1 gram of gelatine was used, and neither its molecular weight nor its valency is known, and it is quite possible that the latter may vary since as the acid becomes more concentrated it probably attacks additional amino-groups.[1] It is impossible to calculate equivalent weights from the direct experiments with hydrochloric acid, since much free acid solution is absorbed in swelling, and it has been shown above that this is not of the same concentration as the external solution. In very dilute external acid the error is not considerable, since the total acid of the solution absorbed is small compared to that fixed by the gelatine, but in this case the hydrolysis is also very large. It has been shown, however, that even with the highest concentrations of acid used, the swelling can be reduced to very small proportions by the addition of a sufficient excess of a salt with a common anion (*e.g.* sodium chloride), and as the anion does not increase but depresses the hydrolysis by lessening the ionization of the salt we may safely assume that the hydrolysis in this case is almost nil. Under

[1] It may be noted that both tables 3 and 4 show a sudden and rather considerable rise both in the total acid and in the "fixed" acid (as determined by calculation from the volume of the solution absorbed) at the concentrations above 0.2 N; and though this may be merely due to experimental error, it is more probable that it is an indication that at about this concentration a further amino-group of the gelatine is attacked, corresponding to its increased solubility in the acid.

these circumstances we find that the total acid absorbed by 1 gram of gelatine is about 1.3 mgr-mols. while that in the absorbed solution does not at most exceed 0.05 mgr-mols. so that we may roughly assume that under the conditions 1,000 mgr. of gelatine combine with 1.28 mgr-mols. of acid, or in other words that the equivalent (though not necessarily the true molecular) weight of the gelatine, considered as mono-valent, is about 780. It will therefore be necessary to multiply the values of x by 1.28 to obtain the actual acid combined with the gelatine-base.

We may now consider the further question of how the volume of swelling is connected with the absorption of acid. The experimental curve is a very peculiar one with a marked maximum, indicating that at first the swelling increases rapidly with increased concentration, but afterwards diminishes inversely in a slower ratio. According to the theory which has been suggested, the swelling is due to the superior solubility or attraction for water of the ionizing gelatine chloride as compared to the non-ionizing neutral gelatine, and it should therefore increase directly with the increase of the chloride. On the other hand it is repressed by the anion of the acid solution, which not merely causes the concentration of the jelly with expulsion of water till its total ionic pressure is equal to that of the acid, but also compels the expulsion of free acid from the jelly against the same pressure of x, so that the total anion-pressure of the jelly-mass may remain equal to x. The force required to compress the jelly therefore varies not merely as x but as x^2, and for a given increment of x the swelling should diminish as $1 - \bar{x}$. We should expect therefore that swelling would be represented by such an expression as $\beta \frac{x}{x+k} \div 1 - \bar{x}$, or $\beta \frac{1-\bar{x}}{x+k}$ where x and k have the same values as before, and β is an empirical constant connecting the volume of the jelly with its pressure. Such an expression will obviously give a marked maximum for some small value of x, and by differentiation it is shown that this maximum occurs when $x = k$. We have thus a means of arriving at a value for k, since the experimental maximum is clearly marked at about $x =$ N. 0.005, and the swelling curve on Fig. 2 is therefore calculated as $7.8 \frac{1-\bar{x}}{x+k}$. It is possible that the true value

of k is somewhat less than N. — 0.005, and that the higher maximum which this would cause is prevented by the cohesion of the jelly; and since the curve rises much more abruptly than it falls, the effect of this rounding off of its summit would be to shift the apparent maximum to a slightly higher concentration, but in any case if the hypothesis be correct it cannot be much lower than 0.005; and at least the order of the quantity remains unchanged.

Since $k = \frac{K_w}{K_g}$, and K_w is known, we can calculate an approximate value for K_g, the dissociation constant of neutral gelatine, as $\frac{0.6 + 10^{-14}}{0.5 + 10^{-2}}$, or of the order of 1×10^{-13}. It would be interesting to confirm this by more direct measurement.

Of the direct experimental results, only the value of the total absorbed acid remains to be calculated. This is evidently (from the mode of calculation of the "fixed acid"), the sum of the latter and of the volume of absorbed liquid in the jelly multiplied by the concentration of the external solution. As the former approximates closely to 0.8 mols. from the maximum of swelling onwards, and the latter to $x \frac{7.8\sqrt{x}}{x + k}$, the curve has been plotted on the sum of these, and sufficiently well expresses the experimental values, but offers no explanation of the amount and constancy of the fixed acid; a question which is discussed in the next paragraph. It is, however, interesting to note that the curve of absorbed acid is also well represented by $y = 87\, x^{0.41}$, the logarithmic plotting of the smoothed curve being only slightly convex to the origin, and showing that curves quite of the adsorption type may arise as the sum of purely chemical actions.

It has been assumed that the resistance of the jelly to compression by the acid of the outer solution is the product of the direct ionic pressure of the gelatine salt, and of that of the anion of the acid which is expelled along with the water, to maintain equilibrium, but which must carry with it its corresponding hydrion. The swelling pressure within the jelly is thus the sum of three partial pressures of which only one is that of the anion itself and the acid expelled is therefore only one third of

the total ionized gelatine salt. Since between $x = 0.5$ and $x = 0.3$ the quantity of gelatine chloride and its ionization remain sensibly total and constant, and what change takes place in the one is partially compensated by the corresponding change in the other, the "apparent fixed" and the expelled acid will also remain constant; the one being about 0.8 and the other about 0.4 mols. We have as yet no definite information as to the ionization of the gelatine salt, the repression of which is no doubt negligible within the limits named, but must become considerable in the presence of much sodium chloride or other salt with a common anion. In this case the acid fixed as unionized gelatine salt will increase, and that expelled will diminish, so that the curve of fixed acid must more and more closely approach that of the unionized gelatine salt, as under these circumstances it is experimentally shown to do.

A point much more difficult of explanation is the almost vertical rise of the fixed acid curve near the origin, and its slight maximum corresponding to that of the swelling curve. It is obvious that the really combined acid cannot exceed that of a correct hydrolysis curve, and no constants or modifications can be adopted for the latter to make its rise more rapid which do not at the same time throw the swelling curve derived from it entirely out of harmony with experiment. It is perhaps a somewhat forced, though not I think an altogether improbable explanation, that the uncombined gelatine at first adsorbs acid without actual combination, and that this adsorption is favored by the large volume of the jelly at the point of maximum swelling, where the small maximum also occurs on the fixed acid curve. This adsorption would of course tend to increase the apparent fixation of acid, and render it more uniform, and would disappear with the disappearance of free base, since it is improbable that the chloride would adsorb hydrochloric acid. Some alternative explanations may be suggested, but it is better to wait the results of further experiment.

It must, I think, be admitted that the complicated system of curves which has been deduced from the theory of actual chemical combination shows an agreement with experimental results which is more than accidental, and which in some sense really represents facts, whether these be strictly chemical or not. It

is not to be denied that an equally plausible hypothesis might conceivably be based on physical adsorption, but to be satisfactory it must show a correlation of experimental facts at least as complete as that which has been offered. It is to be admitted that much remains to be done in explaining the still outstanding deviations, in adducing further proof, and in replacing empirical constants by those based on definite knowledge, but the present paper at least provides a working hypothesis. The most marked deviation of fact from theory consists in the more rapid rise of the "fixed acid" to a small maximum above that allowed by the curve of unhydrolyzed salt, and disregarding probable imperfections in the dilution equation in such an extreme case, it is suggested that this may be explained by actual adsorption preliminary to chemical combination.

It is obvious that the theory affords a complete qualitative explanation of the dehydrating effect of common salt solutions and other chlorides on gelatine (including skin and connective tissue) swollen with hydrochloric acid, although our knowledge of the laws of concentrated solution is insufficient to enable us to apply the same equations quantitatively. The theory asserts that the falling of the swelling is due to the pressure of the chlorine ions, and it is indifferent whether these are furnished by the acid or some other chloride. That salt not only exerts a compressing pressure on the chloride jelly, but is expelled by the latter from the absorbed solution is proved by the last column in Tables 12 and 13 in which the fixation of salt is shown to be negative; though in presence of so much salt, the chlorine estimations cannot claim the same degree of accuracy as the acid ones. That salt exercises no compressing but rather a swelling influence on neutral gelatines is shown by Table 11, in which also the salt absorption is positive. The effect of salt in raising the apparent acid "fixed" is also easy of explanation, since the presence of the chlorine ion limits hydrolysis by repressing ionization, and increasing unionized chloride, and prevents expulsion of acid from the absorbed solution by being itself expelled in its place. A question arises, however, as to whether the compression of the jelly under these circumstances should be treated merely as a case of ionic equilibrium, or not rather as a "salting out" in which the avidity for water of the different con-

stituents is more important than their ionic pressure, and in which the unionized as well as the ionized sodium chloride plays its part. Throughout, it has been assumed in the equations that the whole of the gelatine chloride and not merely its ionized or unionized part is effective in the swelling; but obviously if the ionization is comparable to that of most salts, it must be practically total up to concentrations such as were used in the acid experiments.

It remains, however, to be considered whether the theory developed from the study of hydrochloric acid is one of general applicability to all acid swelling of gelatine or gelatinous tissues, or whether it is merely an exceptional case confined perhaps to a few of the stronger acids, since sulphuric acid and sulphates show completely parallel effects. (See Table 14.)

It has been often stated that since a swelling effect was common to all acids of sufficient hydrion concentration, the hydrion must be regarded as the active swelling agent; but this in the light of the present theory must be regarded as only indirectly the case, since the hydrion concentration is the measure of the avidity, and hence of the salt-forming avidity of the acid; and it is quite possible that, as in the case of ammonium salts and many other organic bases, not only the anion but the hydrion enters into the salt. In all cases the anion is the compressing and dehydrating agent; and in the absence of a neutral salt, a maximum with subsequent contraction is produced by the acid itself. This is, however, only obvious in the case of the stronger acids, since the weak acid, although it may produce a gelatine-salt, is so little ionized that its anion cannot reach a sufficient concentration to overcome the pressure of the more ionized gelatine-salt. Thus while sulphuric acid produces a marked maximum, that of formic acid though still obvious is much less distinct, and with acetic and lactic acids none is observable, and the swelling continues to increase with concentration, becoming in the end greater than that produced by the stronger acids, and going on without a break to the final solution of the gelatine. In these cases the apparent "fixed acid" is somewhat variable, sometimes higher and sometimes lower than that of strong acids according to whether the ionic concentration is sufficient to prevent hydrolysis or to attack additional amino-groups.

It may be objected that sodium or potassium chlorides will produce vigorous dehydration not only with hydrochloric acid, but with any other acid of sufficient hydrion concentration to produce swelling; but a little reflection makes it obvious that any such combination simply leads to a quadruple equilibrium in which each acid is balanced against its own neutral salt. Thus in the case of acetic acid and sodium chloride we have gel-ions acet-ions, and an enormous excess of sodium and chlorine ions, and if we imagine combination we must by the law of mass-action have much gelatine chloride balanced against sodium chloride and little gelatine acetate against sodium acetate. Hence the rule, since the salt is always largely in excess, that with the salt of a strong acid, the dehydrating effect is the same whether the acidification has been by a weak or a strong acid, and vice versa. Acetic or formic acid will produce as effective a pickling with common salt as sulphuric or hydrochloric.

As regards other acids and their salts it has been shown that in all cases depression of swelling is caused by a sufficient addition of the neutral salt, but this is most marked with the salts of the stronger acids, possibly because with weak acids the ionization of the salt added is insufficient to repress that of the gelatine compound itself.

I do not propose in this paper to discuss the complicated effect of the action of salts on the swelling of neutral gelatine which has been specially investigated by Pauli, Hofmeister, von Schroeder and others,[1] but it may be suggested that it is quite conceivable that in many cases a portion of the salt undergoes dissociation or hydrolysis, and that both acid and base combine with the gelatine, and that the compound so formed swells or is compressed by the remaining salt solution according to its concentration. Paessler[2] has shown that sodium acid sulphate is dissociated by hide-substance, only the neutral salt remaining in solution, and it is clearly proved in the case of chromic, ferric and aluminic salts that a similar action takes place in which both acid and base (or a basic salt) are absorbed. This absorption of

[1] Pauli (Paseheles) Pflug. Arch., 71. 336 u. 339 (1898).
Pauli u. Rona, Beitr. z. Chem. Physiol. u. Pathol., **2**, 25-26 (1902).
Hofmeister, Arch. für experim. Pathol. u. Pharmacol. **24**, 424, (1888).
von Schröder, *Collegium*, 1902, p. 306.

[2] Wissenschaftliche Beilage des Ledermarkt, 1901, ii, p. 106.

base may occur either by combination with opened-up COOH groups, or as complex salts such as are often formed by ammonia with other bases; and some of these may form complex ions which are unrepressed by those of the simple salt in solution.

The subject of alkaline swelling is also left untouched, but it is clear from some preliminary experiments, that in certain respects it differs radically from acid swelling. For instance swelling by sodium hydrate is not at all repressed by sodium chloride but is so by higher concentrations of the hydrate, showing that in this case hydroxyl ions and not the kation Na are the swelling and repressing agents. It is hoped to pursue the question of alkaline swelling.

It is obvious that the facts discussed in the paper have an important bearing on many physiological questions and in this connection a crude attempt made in the early stages of the inquiry to imitate muscular contraction may be worthy of mention. A slender spiral platinum electrode was embedded in a cylinder of jelly which was immersed in a salt solution containing a second electrode. When the gelatine electrode was the anode of a sufficient current to electrolyze the salt, the jelly contracted admirably, but its relaxation by a reverse current was somewhat unsatisfactory owing to the evolution of hydrogen which broke up the gelatine. No doubt with a suitable depolarizer better results might be attained, and it is quite possible that the condensation of the anion by a mere surface potential difference might be sufficient to produce the effect.

Pauli[1] has recently published a paper on albumen in which he supports very similar views to those just expressed, though laying more weight on the hydration of the colloid ion than has been done in the present work. In particular he strongly advocates the molecular as opposed to the cellular or network structure claimed by Bütschli. He also mentions the fact that acid jellies cannot be dehydrated by pure alcohol, which has been confirmed in the present investigation, though it has also been found that with acidified alcohol considerable contraction takes place.

[1] Zeitschrift für Ch. & Ind. der Kolloide 1910, S. 241.

ABSTRACTS.

The Microscopical Examination of Gambier.[1] By H. BRUMWELL.—The cultivation of the gambier plant and the manufacture of the extract from it are carried on mainly by Chinamen, and the product is frequently adulterated with such materials as clay, leaves, stalk, dung, etc. According to Professor Procter[2] *Nauclea* or *Uncaria Gambir,* a climbing shrub widely cultivated in Singapore, is the source of this extract. The plant grows rapidly, the cropping commences three years after planting and is continued two to four times annually with little regard to fitness of shrubs, the plant being cropped until it has hardly leaves left to support existence. This drastic treatment is sufficient to wear out a plantation in from ten to fifteen years.

Cropping is done with a knife called a *perang,* while a larger knife is used for cutting up the leaves and twigs, which are then placed in a boiler sunk in the ground, and boiled with water until the liquid, which is constantly stirred during the operation with a five-pronged stirrer, becomes syrupy. The leaves are then removed from the liquid and allowed to drain on a tray over the boiler. The coarser matter still remaining in the boiler is removed with an instrument similar to a racquet, and the finer by straining through a perforated cocoanut shell into small tubs, where it is allowed to cool with constant stirring with a wooden bar until the catechin crystallizes. When cold the pasty mass is turned out of the tub, cut into cubes with sides about 1 in. long with a hoop-iron knife and dried; this product is known as "cube-gambier." A common quality called "block gambier," instead of being cut into cubes, is run into large oblong blocks, which are wrapped in matting and exported in a pasty condition.

It will be seen that this article cannot be expected to be very pure, considering the crude method employed. Those who have seen the manufacture of gambier state that sand and dirt are actually shovelled into the material during the process.

The concentration of the liquid in open pans must lead to the loss of tannin and darkening of color by oxidation, and the presence of mineral matter in such large quantities must have a deleterious effect in the tannery, as the mineral matter invariably contains iron.

At a meeting of the International Association of Leather Trades Chemists, in London, in November, 1909, when the question of adulteration of gambier was discussed, it was pointed out that the present method of selling gambier was iniquitous, and that under the terms of sale it was impossible to get any satisfaction from the sellers if the delivery was bad.

Reference to the following tables will give an idea of the analyses of a few normal gambiers, as analyzed in the Leather Department, Leeds University, and which were thought not to be in any way adulterated.

[1] *J. S. C. I.,* 1911, April 29.

[2] Principles of Leather Manufacture, page 277.

	Cube Gambier			Block Gambier		
	"D" Per cent.	"CBL" Per cent.	"S" Per cent.	"P" Per cent.	"A" Per cent.	"B" Per cent.
Tanning matter. =	42.3	44.8	42.6	39.2	36.3	34.6
Soluble non-tans =	31.8	32.3	32.9	31.9	26.2	24.7
Insoluble ..... =	11.2	9.3	9.8	15.1	10.1	11.0
Water ..... =	14.7	13.6	14.7	13.8	27.4	29.7
Ash ..... =	5.4	4.2	3.7	4.3	4.4	4.5

Generally speaking the insoluble matter of gambier consists of material which is in no way available for the manufacture of leather, and not of "difficultly soluble" matter; if more scientific means were adopted in the production, the insoluble matter might easily be reduced to 3 or 4 per cent. at most, and even this might be available for tanners' purposes, as it would very likely consist of catechin, which is only slightly soluble in cold water, and would probably ultimately become converted into tannins by changes in the tan-yard.

A factory has been started to manufacture gambier extract in Indragiri (Dutch East Indies) on similar lines to those used for other extracts. The leaves are extracted with water, the solid matter is removed by suitable means, and the liquor concentrated in vacuum pans. The resulting extract which is in block form, is of excellent color, free from impurities, and contains about 40 per cent. of tannin.

The non-tans are high, which may be due either to the raw material or to the more complete extraction.

The insoluble matter of ordinary gambier, when examined under the microscope, was found to consist of small particles of leafy matter along with a large quantity of hairs. The hairs exist in the extract in larger proportion than on the leaves themselves, since being so fine they are not so easily removed by the crude method of filtering with the perforated cocoanut shell, as are the coarser pieces of leaf.

The cuticles of the leaf were separated by the method suggested by Dr. Hellon, of Whitehaven, which proved very satisfactory both for the leaves and the insoluble part of the gambier. The method is as follows:—A portion of leaf (about 0.1 grm.) is boiled for ½ minute with about 7 cc. of 5 per cent. sulphuric acid and the clear liquor poured away; the residue is then boiled for ½ minute with 7 cc. of 5 per cent. caustic soda solution and the liquid poured away; the residue is boiled for ½ minute with 7 cc. of nitric acid of sp. gr. 1.2, and the clear liquid poured away; the residue is boiled as before with another portion of nitric acid and during the boiling 0.01 gram of potassium chorate is added from time to time until the substance is absolutely white. The clear liquid is poured away, and the residue washed free from acid with warm water, transferred to the microscope slide, covered, and examined.

After the above treatment the cuticles were dyed in a dilute solution

[1] Abstract, this Journal 1909, page 25.

of Safranine. This method proves very satisfactory for almost all leaf cuticles and is far better in most cases than the nitric acid method, which is sometimes too severe.

The upper cuticle of the leaf is very similar in appearance to the upper cuticle of *Pistacia lentiscus* (frequently used as an adulterant of sumach) having very distinct cells fairly regularly disposed, and no hairs or stomata. The lower cuticle strongly resembles that of *Colpoon compressa* ("Cape Sumach"); the stomata are large, very distinct, in great profusion, and are devoid of hairs. In the samples of insoluble portions of gambier examined, no leaves were found which appeared to be other than those of genuine gambier.

Sago-flour is frequently added to gambier as an adulterant, and can be detected by adding a drop or two of iodine solution to a small quantity of the gambier on a microscopic slide, covering with a cover glass and examining under the microscope. In mixtures of gambier and sago-flour, mixed specially for testing this method, it has proved quite satisfactory, the starchy matter of the flour being colored deep blue and the cellulose deep brown. On the addition of a drop of sulphuric acid the starch granules swell up and finally burst, the cellulose becoming then quite blue.

Sumac. M. C. LAMB in LEATHER, IV, 111, 193, 225, 241.—Great Britain imports yearly upwards of 12,000 tons of sumac, valued at about £10 per ton. Most of this is from Sicily, and consists of the ground leaves of *Rhus coriaria*. The plant is cultivated, yielding a marketable crop the third year. As the age increases, the percentage of tannin in the leaves rises. An inferior variety is also cultivated, whose leaves are larger and the percentage of tannin lower, the color also being inferior.

The leaves and twigs are dried in the open air. Rainy weather causes loss due to darkened color and to fermentation which changes the tannin into gallic acid. The dried leaves are ground and sifted to remove twigs, etc. The finer portion is then ground a second and a third time, being sifted after each grinding to remove fibrous material. The ground material is then "ventilated," by being blown along a long narrow room by means of a fan. This room is several hundred feet long. Sand and other heavy particles, most of which are from the wear of the mills, drop near the fan.

Sumac is very liable to be adulterated, the most common substances used for the purpose being *Pistacia lentiscus, Tamarix Africana* and *Ailantus glandulosa*. In order to evade the strict Italian laws in regard to adulteration of sumac, many ingenious devices are resorted to. One of these is to ship the pure sumac and adulterants separately and have them mixed and re-bagged on ship-board.

The percentage of tannin in sumac varies from 22 to 30 per cent. All the adulterants are much lower. In the table a good sample of sumac is compared with average values for the three adulterants mentioned:

	Rhus conaria	Pistacia lentiscus	Tamarix Africana	Ailantus glandulosa
Tannins	26.4	12.8	9.1	11.2
Soluble non-tans	17.6	20.5	25.3	20.4
Insolubles	48.2	58.2	57.6	60.0
Moisture	7.8	8.5	8.0	8.4
Ash	8.8	6.8	10.5	....

The author concurs with S. R. Trotman in the suggestion that as a standard for mineral constituents of sumac the following figures be adopted:—Ash, 6.5 per cent., silica, 0.75 per cent., iron, 0.15 per cent. A total ash of over 8.5 per cent. may be regarded as indicating presence of Tamarix Africana or very bad ventilation.

The common adulterants of sumac may be discovered microscopically. Treatment with nitric acid almost completely destroys sumac leaves, while a certain part of the adulterants is not destroyed and may be filtered out and examined. The sumac leaf has very fine hairs which are absent from both Pistacia and Tamarix. One sample examined by the author was adulterated with spent sumac, dried and reground.

Sumac is one of the most valuable tanning materials for light leathers intended for book-binding, upholstering, etc. Considering the high proportion of available tannin, sumac is a relatively cheap material. The leather is soft and supple, and very light in color, so that it may be dyed in a great variety of shades. It is particularly valuable for book-binding because of its high resistance to gas fumes and other agencies liable to destroy bindings.

The tannin of pure sumac is mainly gallo-tannic acid, that of the adulterants being a catechol tannin. Sumac leather, unlike that made with catechol tannins, is not changed in color by the action of light.

The tannin of sumac is much less astringent than most tannins. so that a strong infusion may be employed even in the early stages of tanning without causing drawn or hardened grain. Sumac tanning is done at a comparatively high temperature, 25° to 30° C., (77° to 86° F.).

Sumac is best extracted at a temperature not exceeding 60° C. (140° F.). As much as one-fourth of the total tannin may be destroyed by extraction with boiling water. The infusion obtained at the higher temperature is also darker in color. The extraction is best done by placing the sumac in cold water, raising the temperature to 60° C. and maintaining that temperature for one hour.

Sumac infusion begins to ferment within two or three hours after it is made, the tannin being rapidly hydrolyzed into gallic acid.

Small black stains often occur on sumac leather, due to minute particles of iron or iron ore from the stones used in grinding the sumac. These may be avoided by letting the liquor settle before the skins are allowed to stand in them. Brown color in sumac leather may be caused by imperfect deliming. Yellow stains may be caused by too high a temperature in the tanning, causing the grease of the skins to combine with the coloring matter of the sumac.

Leather which has been tanned with other materials may be considerably lightened in color by retannage with sumac. This is done by drumming in a strong infusion of sumac, of a pasty consistency in consequence of solid matter in suspension. These solid particles are forced into the leather, making it firmer and thicker.

All vessels used in extraction or tannage should be steamed before being used again, to kill the germs which cause the gallic fermentation.

Souring of Tan Liquors. R. W. GRIFFITH in *Shoe and Leather Reporter,* March 16, 1911.—Liquors from myrobalans and valonia and from some barks sour naturally, while those made from woods do not to any extent. The souring is due to the fermentation of sugary matters called glucosides, giving a mixture of organic acids. The woods contain less sugar and therefore produce less acid. To increase the acidity of liquors the addition of glucose has been tried, and sometimes with success. An important difficulty is presented by the many undesirable fermentations liable to occur and hard to control. The total amount of acid in the liquors rarely exceeds 0.8 per cent. The bacteria which produce the acids cannot work in the presence of larger proportions of acid.

The direct addition of organic acids to the liquors is now practiced, the advantage of this method being that the souring is thus under complete control.

The hides are often put into the tail liquors in an alkaline condition, due to lime, and the acids must first neutralize the lime before the hide can absorb tannin. In this process the hide falls. The second function of the acids of the tail liquors is to restore the plumpness of the hides, and render them acid so that the tannin can be absorbed. In a yard where the tannin in the tail liquor is about 1 per cent., the acid should be not less than 0.35 per cent. In the head handler, with 3-4 per cent. tannin, the acidity should be about 0.6 per cent. In the layer liquors not much acidity is required.

Hides absorb more non-volatile than volatile acid. Roughly, the volatile acid in a liquor represents its neutralizing power and the non-volatile its plumping power. The absorption of non-volatile acids by the hide also determines to some extent the capacity of the hide for tannin, as it establishes a permanently acid condition in the hide.

The presence of a small quantity of salts in a liquor hinders the plumping effect of acids. (See this JOURNAL, 1908, p. 154.)

One-Bath Chrome Tannage. ALAN A. CLAFLIN, in *Shoe and Leather Reporter,* April 20, 1911.—The writer believes that the one-bath process will supersede the other for all purposes. He gives three reasons, 1st, because actual progress is being made in this direction, 2d, because the one-bath process is capable of more exact scientific adjustment than the other, 3d, because it is cheaper.

The one-bath method is the oldest form of chrome tanning, having been experimented with by Knapp nearly sixty years ago. In a one-bath liquor we have a plumping acid due to the hydrolysis of the chrome

salt, and two sorts of salts, the chrome salt and the sodium salt due to the neutralization of the acid formed by hydrolysis with sodium carbonate. The chromium salts have much less depleting effect than salts of sodium.

The tanning solution is acid to litmus. As the hide absorbs the tanning agent from the bath, whether this be chromium hydroxide or a basic salt of chromium, the equilibrium between the plumping acid and the depleting salt is upset, and must be restored by additions to the liquor. This restoration is not so important in the case of lighter leathers, because as the tanning progresses the skin becomes less susceptible to the plumping effect of acids and the depleting effect of salts.

With the heavier leathers it will be found that the acid is withdrawn (at least in all solutions that have been examined by the author) faster than the chromium salts are taken up.[1] In order to penetrate the thick hide there must be a certain excess of tanning agent. The author advises strengthening the one-bath liquor with concentrated solutions of chrome salts which are less basic than the original solution.[2]

Analysis of liquors before and after the skins are put in shows that the skins take up from the bath the chromium in the form of a basic salt rather than the hydroxide. On the other hand analysis of the leather does not show the presence of so much inorganic acid in combination with the chromium as to correspond with that taken up from the bath. It seems probable that a certain amount of acid is necessary to take the chromium into the skin, but this is removed in the course of subsequent operations.

How best to prepare a one-bath liquor is also of as much interest as how the liquor acts when it is prepared. The cheapest source of chromium under present market conditions is the bichromate of soda. This salt must be reduced before it can be used for the liquor. The cheapest reducing agent to use is theoretically glucose. To use glucose sufficient acid either muriatic or sulphuric is added to set free chromic acid according to the reaction.

$$Na_2Cr_2O_7 + H_2SO_4 + H_2O = Na_2SO_4 + 2H_2CrO_4$$

or

$$Na_2Cr_2O_7 + 2HCl + H_2O = 2NaCl + 2H_2CrO_4.$$

Then the glucose is added which reduces the chromic acid, chromium sulphate, water, and carbon dioxide being formed.

To translate this into pounds and allow for the percentages of the chemical compounds in the commercial products, *e.g.* commercial glucose contains 30 per cent. water, we find that 2.6 lbs. glucose will reduce theoretical 6 lbs. of bichromate of soda and with 8½ lbs. sulphuric acid form the normal chromium sulphate. The objection to the use of the

[1] The reverse of this statement is true, in some instances at least. ED.

[2] The exact reverse of this is recommended by some writers. See for instance this Journal for March 1911, p. 156.

glucose is that the reduction practically can never be made to work according to the theoretical reaction. Much of the glucose for instance is lost by volatilization in the form of aldehyde, and so an excess must be used, some of this excess will then also in all probability remain as unchanged glucose, and we have present in our one-bath liquor organic matter which is a complication and in my experience interferes to some extent with the efficiency of the tannage. Therefore for practical purposes it is probably better to use bisulphite of soda for the reducing agent.

For 6 lbs. of bichromate of soda 20 lbs. of bisulphite of soda and 5½ lbs. of sulphuric acid are required to produce the normal sulphate. To convert the normal chromium sulphate into the basic sulphate required for tanning purposes, sodium carbonate should be added according to the following equation:

$$Cr_2(SO_4)_3 + Na_2CO_3 + H_2O = Cr_2(SO_4)_2(OH)_2 + Na_2SO_4 + CO_2,$$

or in pounds, for the amount of normal sulphate produced from 6 lbs. of bichromate about 2 lbs. of sodium carbonate should be used. With the liquor once prepared the plumping and depleting properties may be regulated by the addition of common salt.

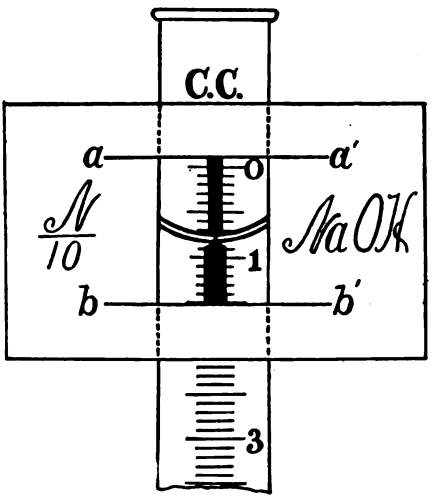
Crucible Support. W. M. THORNTON, JR., in *Journ. Ind. and Eng. Chem.*, May, 1911, p. 343.—The support consists of a slab of soapstone supported on iron legs with 3 inch holes conveniently spaced, adapted to the use of any standard triangles. The soapstone does not rust, and lids may be temporarily set on it, or crucibles left to cool. This apparatus has been in use in the laboratory of the Va. Geological Survey for 2 years with satisfaction.

Estimation of Soluble Mercuric Salts at Great Dilution. PROFS. H. R. PROCTER and A. SEYMOUR-JONES. J. S. C. I., April 15, 1911, p. 404.—In the presence of certain organic acids, such as formic or citric, mercuric sulphide is not precipitated on treatment of the mercuric chloride solution with H_2S, but remains in the colored colloidal form in solution. This color is definite for definite concentrations of the chloride and acid, if the liquid has been saturated with H_2S, and is directly proportional to the concentration of the original chloride solution. In making the comparisons a Schmidt and Haensch dipping colorimeter was used, (described in J. S. C. I., 1910, pp. 663-666, Reprint, this JOURNAL, August, 1910, p. 352).

A standard solution of one part $HgCl_2$ in 10,000 parts water and containing also 1 per cent. (by weight) of formic acid is saturated with H_2S and run into a 1 cm. cell, placed on the upper platform of the colorimeter. This gives the standard color, against which any solution of $HgCl_2$ weaker than 1:10,000 may be matched. The mercuric salt of unknown concentration is then made into a 1 per cent. formic acid solution and saturated with hydrogen sulphide gas. The colloidal sulphide solution is run into the dipping cylinder of the colorimeter, and

the dipping stage adjusted until the field of view in the telescope is of uniform color. The depth of the solution thus found is read off and its concentration calculated. As the depth of the standard is 10 mm., and its concentration 1 in 10,000, the concentration of the unknown may be easily found. With practice the difference between 76 and 77 parts per 100,000 may be distinguished.

A Simple Help for Reading the Ordinary Burette. Dr. Jaroslav Milbauer. *Chemiker-Zeitung,* 1911, p. 419, April 18.—In many laboratories, especially technical chemical laboratories, a very convenient form of burette, described by Schnellbach, is used. The Schnellbach burette has a white glass background, in the middle of which is a blue line, about 2 mm. wide. With clear liquids, not too dark colored, this line gives a sharp point, as reflected in the surface of the liquid. The level being thus sharply defined, readings may be taken with accuracy, ease and rapidity. For many years the writer has used the same principle in reading the ordinary burette. The apparatus herewith illustrated is



exceedingly simple, consisting preferably of a glazed visiting card, on which a blue or red line 2 mm. wide has been drawn between two slits *a a'* and *b b'*. The effect is quite analogous to the Schnellbach burette. The card must of course be slid up or down the burette as the level of the liquid is changed. The card also serves as a label. L. B.

Essential Qualities of Vegetable Tanning Materials. Dr. J. Paessler in *Shoe and Leather Reporter,* March 16, 1911.—The problem of the economic use of tanning materials is not quite the same in the case of leathers which are sold by measure as in that where they are sold by weight. The following points are to be considered:

[1] *Chem.-Ztg.,* 1885, p. 1482.

1—Cheapness; 2—Thorough extraction; 3—Liability to deteriorate in the tanning process; 4—Capacity to penetrate or be absorbed in large quantity. In making leathers to be sold by weight, all four points must be considered; in the other case, only the first three.

Prices of some tanning materials in the German market are as follows:

	Per cent. tannin shake method	Price of tannin m. per kilo.	Price of tannin cents per lb.
Oak bark	9.0	1.17	13.3
Oak wood extract	25.0	1.00	11.4
Valonia	27.0	0.93	10.6
Chestnut extract	28.0	0.86	9.8
Pine bark	10.0	0.65	7.4
Quebracho	19.0	0.63	7.2
Dividivi	38.0	0.63	7.2
Mimosa bark	33.0	0.61	7.0
Trillo	40.0	0.60	6.8
Myrobalans	30.0	0.50	5.7
Mangrove bark	38.0	0.39	4.4

The tannin in the extracts being more nearly all available, these prices do not give a fair comparison.

In considering the extraction of tanning materials care must be taken not to confound complete extraction with advantageous extraction. In many cases the more easily extracted and lighter colored tannin is much more valuable for the purpose intended.

The third point, that some liquors change with time, has often been overlooked. Some liquors remain clear, while others thicken badly, and still others separate considerably. Mangrove, mimosa and quebracho remain clear for as much as two months. An oak bark liquor becomes cloudy and one made from myrobalans becomes cloudy and separates considerably. Much of this is due to the tannin passing over into an insoluble form, thereby becoming unavailable. If, however, this change takes place after penetrating the skin, the result is beneficial. The percentages of tannin lost after 60 days for several materials are as follows, for a liquor of 14° Barkometer.

	Per cent. loss of tannin
Mangrove bark	0
Mimosa bark	2
Quebracho wood and extract	3-4
Gambier (cube)	0
Oak bark	5-7
Pine bark	10
Chestnut wood extract	11.5
Oak wood extract	12.5
Myrobalans	24
Valonia	29

The fourth point, weight giving properties, has been the subject of experiments at the Freiberg Institute. More tannin is absorbed in the presence of acid than in non-acid or feebly acid solutions. The best weight giving materials are quebracho wood, mimosa bark, oak wood extract, chestnut wood extract, oak bark, pine bark, mangrove bark and valonia, in the order named. Cold soluble quebracho extract gave a low weight.

The Estimation of the Saponification Value. L. W. WINKLER. *Zeitschr. f. angew. Chem.*, April 7, 1911, p. 636.—The author recommends the use of propyl alcohol instead of ethyl alcohol for the alcoholic potash solution, because on account of its higher boiling-point it makes possible the more rapid saponification of the material. Beeswax may be completely saponified in 10 minutes. No return condenser is necessary.

Ordinary commercial propyl alcohol is purified by distillation after standing a few days with 1 gram of KOH per liter in solution. In each liter of the redistilled liquid, 30 grams of the purest obtainable KOH is dissolved, and the solution filtered through a small cotton plug. This solution is approximately N/2. The KOH, crushed to a coarse powder, dissolves readily in propyl alcohol, the carbonate remaining undissolved so that it is removed by filtration. The flask being occasionally shaken, solution is complete in a few hours, but filtration is best postponed for two or three days. The solution thus prepared is colorless and after long standing becomes only slightly yellow.

To determine the saponification value, about 2 grams of the fat or wax is weighed into a flask of about 100 cc. capacity, and 25 cc. of the KOH solution run in. The flask is so covered with a small beaker (25 cc.) that the rim of the beaker does not touch the flask, and placed on the steam bath for 10-20 minutes. The heat is so adjusted that the contents of the flask may boil gently and evenly. Then about 0.01 gram of phenolphthalein is placed in the hot liquid and the excess of KOH titrated with N/2 HCl. In the case of materials difficult to saponify the time on the steam-bath is prolonged to 20-30 minutes. A blank determination should always be carried out. The author recommends for introducing the alcoholic potash a pipette furnished with a glass stop-cock and two marks, containing 25 cc. between them.

The author recommends for finding the acid value of oils and fats that 5.6 grams be placed in a glass-stoppered flask of 50 cc. capacity, 20 cc. of neutral alcohol added, with 0.01 gram phenolphthalein and then titrated with N/10 soda. For solid fats and waxes, a smaller quantity may be used, and dissolved in warm propyl alcohol.

A table of results is given, the saponification value of each substance having been taken after 10, 20 and 30 minutes heating. The three results are practically identical except in the case of wool-grease. In this case the value increased up to 30 minutes, but heating for 45 and 60 minutes showed no further increase. The author gives directions for the recovery of the propyl alcohol, stating that a moderate water content does no harm.

	Acid value	Saponification value
Almond oil	1.2	192.1
Olive oil	2.4	191.1
Sesame oil	6.1	191.0
Poppy oil	2.6	192.8
Rape oil	4.1	174.6
Castor oil	0.8	181.2
Linseed oil	3.1	192.7
Cocoa butter	3.4	194.5
Butter fat	1.2	223.6
Lard	0.0	196.5
Beef tallow	0.1	198.2
Whale oil	0.1	123.2
Wool grease	0.3	93.5
Bees-wax, 1	21.5	92.8
Bees-wax, 2	19.0	92.2
Bees-wax, 3	19.8	93.8
Japan wax	19.0	216.8

Tannins and the Tannery. Oak. U. J. THUAU. *Le Cuir,* 1911, Nos. 1 and 3.—Of all the tannins, those furnished by the oaks are most widely distributed. There are more than three hundred species of oaks. The wood contains tannin, and that of some species is used in making extracts. The bark of the oak is used directly in tanning and was for centuries the only tanning material used. Some species furnish fruits rich in tannin and much used, as valonia and knoppern. Gall nuts also grow on the oak. Finally the bark of the roots and the roots themselves of some species furnish very choice tannin. With the exception of valonia, the use of all forms of oak tanning materials is probably decreasing.

Oak wood is used to some extent in the manufacture of extract, and this industry is not increasing. Oak wood extract is very difficult to decolorize. It has low tannin content and high non-tans. Because of its high content of glucose it tends to ferment. A further reason for the small production of this material is that the yield of extract per cord of oak wood is small. Extract of oak wood, decolorized, is an excellent type of tan-stuff for sole leather because it furnishes a natural plumping effect. The tannin of chestnut wood extract is all of the pyrogallol class, while that from oak wood is a mixture of catechol and pyrogallol tannins. The presence of catechol tannins in the latter gives it great penetrating power.

Nine species of European oaks are mentioned. Of these the bark of *Quercus suber* has the highest percentage of tannin, (19 per cent.), but it is too red to be satisfactory.

The percentage of tannin in both wood and bark is less near the top of the tree than at the base. Old trees yield more tannin than younger ones, and the wood is of a deeper color. The deeper color of the heart wood also corresponds to a greater tannin content. Heart wood from

the base of an oak 2 feet in diameter gave 6.7 per cent. tannin, sap wood 1.2 per cent. Heart wood from the top of the same tree gave 4.8 per cent. and sap wood 0.9 per cent. From the largest branches, heart wood gave 6.1 per cent. and sap wood 2 per cent. The percentage also varies very much in different trees so that it is very difficult to obtain a dependable average. Heart wood from a tree more than 100 years old gave 9.8 per cent. tannin and 1.1 per cent. non-tannins.

The tannin from old oak wood is quite different from that of the bark. On heating extract of oak wood with bromine water, a characteristic green coloration is obtained at once, while bark extract gives the same coloration only after a considerable time. Means of analyses of oak wood extracts at 25° Beaumé:—

	Good extracts Per cent.	Extracts from young wood Per cent.
Tannin	26.5	16.1
Non-tans	13.0	20.6
Insolubles	0.5	0.9
Water	60.0	62.4
Sugar	3.1	....

Extracts from oak and chestnut woods resemble each other so much that it is difficult to distinguish them without analysis. Oak extract is generally clearer than chestnut, however. A good oak extract ought to dissolve very easily in cold water without much sediment. The yield of extract at 25° Beaumé is only 12 to 15 per cent. of the weight of the wood. Few samples of so-called oak-wood extract found in the market are pure, straight chestnut being often sold as oak.

Oak-wood extract made from liquor extracted without pressure and at a temperature not above 80° C. (176° F.) is one of the best for vat tannage giving a good yellow color and penetrating rapidly. This extract is particularly satisfactory for sole leather because of the firmness which it gives to the product. It is used to advantage mixed with oak bark liquor in the layers.

Beside the fault of lack of purity, oak wood extract has the disadvantage of decomposing easily. The table shows the changes undergone by a liquor made from oak-wood extract during a period of two months. The figures are grams in 200 cc.

	At start	After 6 days	After 18 days	After 1 month	After 2 months
Tannin	2.07	2.05	1.97	1.85	1.71
Non-tans	0.92	0.94	0.91	0.70	0.49
Total solubles	2.99	2.99	2.88	2.55	2.20
Insoluble	0.0	0.0	0.01	0.14	0.22
Total solids	2.99	2.99	2.89	2.69	2.42
Loss of tannin		0.7%	3.2%	7.4%	12.0%

Tannin and non-tans diminished together forming not only insolubles but also volatile matter which evaporated.

Oak bark is the best known tanning material. Three grades are distinguished, depending on the age of the tree. Oak bark, like the wood, is richer in tannin near the base of the tree than near the top. The tannin content varies from 8 per cent. to 15 per cent. averaging about 10 per cent., with a mean water content of 14 per cent. In order not to decompose the tannin during extraction it is best not to exceed a temperature of 80° C., (176° F.). If the extraction is done under pressure, much loss of tannin takes place. A sample which gave 11.1 per cent. tannin with boiling water, when extracted under a pressure of two atmospheres, raising the temperature to 122° C. (152° F.) gave only 8 per cent. At 4 atmospheres, (146° C., 295° F.) the amount was but 5.6 per cent., and at 6 atmospheres, (160° C., 420° F.), but 3.2 per cent.

For a long time it was believed that oak tannin was simple, and it was called quercitannic acid, and was classed as a catechol tannin. Stiasny's method of separating pyrogallic from catechol tannins by precipitation of the former with formaldehyde and hydrochloric acid, proves clearly that both kinds are present in oak bark. It would be interesting to determine the percentage of each, and what proportion of each is extracted at different temperatures. If colorless soluble tannin from oak bark be heated in a closed glass tube with water at 100° C., it changes into a red brown substance, difficultly soluble, and which is identical with the coloring matter found in oak bark. This change takes place with separation of water, and the product is a difficultly soluble phlobaphene.

Some recent experiments seem to show that at a low temperature, nearly all of the pyrogallic tannin of oak bark is capable of extraction but only a part of the catechol, the remaining parts of the catechol requiring a higher temperature. That portion requiring a temperature about 80° C. is dark colored, due to partial conversion of tannin into phlobaphenes.

The phlobaphenes of oak are very little soluble in water and deposit from it easily, but they are more soluble in solutions of oak tannins extracted below 50° C., (122° F.). It is advisable to let oak liquor stand to deposit the coloring matters or phlobaphenes, or even to filter it. It would be of advantage also not to mix the liquor extracted below 50° C. with that extracted from 50° to 80° C. The latter will on standing deposit a much larger quantity of coloring matter than the former, and the total quantity deposited will be greater than if they were mixed before standing, on account of the greater solubility of the coloring matters or phlobaphenes in the liquor extracted at a low temperature.

L. B.

Lactic Acid Anhydrides. DR. A. A. BESSON in *Chemiker Zeitung,* 1911, p. 26.—The author published in *Collegium* in Feb., 1910, an article on "'Lactic Acids and their Anhydrides." (Abstract, this JOURNAL, 1910,

page 231.) In this article he called attention to the fact that researches were in progress to determine the nature of the impurities which prevent correct results when the crude acid is heated with KOH. This research is still incomplete, and the present article is called out by Leon Monin's publication (Rev. gen. mat. color., 1910, vol. 14, p. 279) of a method of analysis. Monin claims that the commercial lactic acid cannot contain lactic anhydrides. His method is as follows:—Shake 2 grams commercial lactic acid with 30 cc. absolute neutral alcohol. Let stand, filter, wash with ether and evaporate in vacuum. Take up the residue with boiling water and titrate with soda and phenolphthalein.

Besson says that this method takes much time and does not give correct results. The author's method involves permitting the acid to stand some time with an excess of alkali without boiling, and then titrating the excess of alkali with standard acid. This method gives higher results than Monin's, particularly with concentrated solutions, and the author claims that this is due to the slow taking up of anhydrides by the alkali. A sample of lactic acid made by decomposing C. P. calcium lactate with H_2SO_4 which showed 18.01 per cent. free acid was treated by Besson's method and gave 18.01 per cent. combined acid. This same solution was concentrated in vacuum so as to show 78.45 per cent. free acid, when the combined acid shown by Besson's method rose to 84.89 per cent., indicating 6.39 per cent. present as anhydride. L. B.

The Testing of Tannin Extracts. A. GANSSER. *Collegium,* 1910, 101-6, 109-113.—The author describes further applications of his "animalized cotton" prepared by coating cotton with gelatine treated with formaldehyde. While not giving absolute values, this testing material is regarded as giving useful relative numbers for comparing extracts and it has the advantage over hide in being uniform.

Determination of Properties Giving Weight.—The percentages of increased weight of four different materials treated with various extracts were:

Extract	Silk	Hide powder	Grain split cowskin	Animalized cotton
(1) Quebracho, "Triumph"		35.0	41	16.2
(2) Quebracho, "Filling Ext." ..	25.0	37.1	45	11.5
(3) Quebracho, DDBM	27.2	28.5	34	15.3
(4) Chestnut, I	22.1	22.9	..	16.46
(5) Chestnut, F	22.1	38.5	..	19.05
(6) Mimosa, DC.		34.0	..	15.9

In using the cotton, 3 to 6 pieces are taken (2.5 grms. each) with 4 times that amount of liquor of 6° B. and tanned 12 hours, then dried directly, finishing at 80-90° in vacuo.

While the other materials gave variations of 10 per cent. in duplicate tests, the "animalized" cotton gave more concordant results :

Extract	Per cent. tannin	—Gain in weight, test—	
1.	35	24.1	25.4
2.	10-20	17.4	17.4
3.	37	19.6	21.4
4.	29	14.9	14.3
6.	37	21.7	22.3
7.	31	20.6	20.6

As the treated cotton is hygroscopic (8-10 per cent. gain in 12 hours) the air dried product is preferred to the desiccated preparation.

Determination of Properties Giving Strength.—Longitudinal test strips 50 × 16 cm. were tanned as before, then trimmed to 30 × 5 cm. and tested with a dynamometer, giving comparative breaking strengths. The original test material gave: plain cotton 15.51, "animalized" cotton 17.74. A blank test with pure water corresponding to the tanning conditions, gave 15.06 showing a loss of strength due to softening and solution. After tanning with various extracts and correcting for above loss, the following increases were found; chestnut (clarified) 1.28 chestnut, (blood decolorized) 3.28, American hemlock 1.66, European pine 2.09, sumac —0.65, myrobalans 0.88, quebracho 1.28, Kaki cutch 2.17, Indragiri gambier 2.0, quebracho sulphited (Lepetit) 2.8. Tests made upon mixtures gave results agreeing well with figures computed from above. It is thought that by further research, fairly reliable numbers may be obtained which will characterize the type of extract. Parallel trials with split hide gave much less uniform results.

Determination of Water Solubles in Leather. LOTHAR GODEL. *Collegium,* 1911, 113-4.—The author has observed that rasped leather gives higher solubles than the ordinary milled sample; with the latter, a tannage number of over 100 was sometimes obtained. He prefers to pulverize the leather with an ordinary coarse wood rasp and extract 12-15 grams in a cylindrical separatory funnel of 150-200 cc., which permits of occasional stirring; 4-5 hours are required.

Methodic Tannage of Goat and Sheep Skins in the Drum. *Le Marché des Cuirs,* 1911 [23] 74-5.—The tannage, with sumac for example, should be progressive, beginning with weak, finishing with strong liquors; the residual liquors are used progressively to exhaust their tannin. Chemical analysis of the liquors gives a better control than gravity determination and when made once for all, rules for practice are established. Four liquors are used for strengths ¼, ½, ¾ and 1, the hides remaining in each one day.

PATENTS.

Reconstructed Leather. U. S. Patent No. 989,788. MATTHEW MASON, New York, N. Y., assignor to the Arlington Leather Company.

The process involves mixing leather and balata gum and subjecting the mixture to pressure.

Evaporator. U. S. Patent 989,982. PAUL KESTNER, Lille, France.

Evaporator. U. S. Patent No. 989,996. JOHN PARKER, Philadelphia, Pa.

Evaporating Apparatus. U. S. Patent No. 990,878. JOHN E. KAUFFMAN, Kansas City, Kansas.

Feed-Regulating Device for Evaporators. U. S. Patent No. 991,342. RALPH MELLOR, Philadelphia, Pa.

Leather Working Machine. FRANKLIN JAY PERKINS, Woburn, Mass., assignor to the Turner Tanning Machine Co.

Vacuum Evaporator or Heater. U. S. Patent, reissue No. 13,425. JOSEPH E. DUNN, Philadelphia, Pa.

Process of Producing Carbon Tetrachlorid. U. S. Patent No. 992,551. WILLIAM F. DOERFLINGER, New York, N. Y.

Hide-working Machine. U. S. Patent No. 993,068. ALBERT A. HUTCHINSON, Winchester, Mass.

Composition for Waterproofing and Preserving Leather. U. S. Patent No. 993,315. CHARLES L. MILLER, Lynn, Mass.

The materials used are pine tar, linseed oil, Japan, and blue vitriol.

Method of Treating Leather. U. S. Patent No. 993,438. ELMER V. CUSHMAN and HARRY WRIGHT, Canton, Mass.

The materials used are linseed oil, bees-wax, indulin, stearic acid, and paraffin.

Process for the Manufacture of an Elastic Caoutchouc-like Substance from Animal Matter. U. S. Patent No. 993,626. WILLEM VAN DER HEYDEN, Amsterdam, Netherlands.

The process consists in boiling such materials as fish, mollusks and the mucous membranes of the intestines of mammals, filtering off the broth, evaporating it down, adding sulphur or sulphur and caoutchouc and vulcanizing it.

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THE TREATMENT OF TANNERY EFFLUENTS.

By J. A. S. Morrison.

With the growth of manufacturing industries in the early part of the Nineteenth Century came the attendant evils of river pollution. The most natural sites for new and progressing industries were on the banks of streams, for our forefathers were quick to recognize the advantages of situation. As can be imagined the increasing pollution consequent upon increasing prosperity of trade gradually attained such dimensions as seriously to affect the public health. The natural result was that communities quickly demanded means for the prevention of what was undoubtedly a public scandal. Repeated complaints and official inquiries led to the appointment of Royal Commissions and subsequent legislation. Following this and as a direct result of the efforts of large corporations, came the establishment of joint committees, entrusted with the powers of a sanitary authority, for the administration of acts for the prevention of rivers pollution, whilst the work of these Committees or Rivers Boards has been extensive and in some cases drastic, the evil seems to have been too deeply rooted at the commencement, and at the present day, in spite of magnificent work, the condition of English rivers passing through large manufacturing districts is extremely bad. No doubt the chaotic state of the laws on the subject has much to do with the slow improvement to be noticed. It can be quite understood that pressure upon manufacturers is followed by complaints on their part of harsh treatment, for their works in the majority of cases have been developed to such an extent that want of space for purification works is only too evident. Various other claims are put forward on their behalf, the strongest of which is possibly that they, being large rate payers, are entitled to have their effluents admitted to the public sewers. Here is shown the ridiculousness of the existing law in that local authorities are bound to give access to the sewers, unless the sewers are only sufficient in size to meet the existing requirements of the community, or unless the admission of the refuse would interfere with the sewers or the treatment of the sewage. The proviso nullifies the act and thus renders its unworkable, for authorities have only to show that their works are

just sufficient for local conditions and their responsibility ceases. Many local authorities, however, are prepared to admit manufacturing refuse to the sewers, provided that regulations drawn up by themselves are complied with. It must, I think, be admitted that manufacturers are entitled to some little consideration in this matter, for after all, upon them falls a considerable share of the burden of taxation, and some few sanitary authorities have already recognized this by obtaining special acts of Parliament. Foreshadowed legislation will probably at an early date make provision for the universal admission of trade effluents to the sewers, on one of two lines, either preliminary treatment, or payment of fees according to the nature of the effluent and the increased cost of treatment at the sewage works of the authority. This willingness on the part of large authorities to admit trade effluents to the sewers has been found to be very helpful to tanners in the larger sanitary districts. Repeated pressure on the part of Rivers Boards was causing undoubted unpleasantness and uneasiness. Many tanners had not the land for such development as was necessary for their business, and even where this difficulty could be surmounted, the provision of the necessary capital—exceptionally large owing to the strong character of the effluent—tended to cripple an industry which is very fluctuating. Now the way seems clear for brighter understanding It will be seen that on this subject tanneries may be divided into two classes, those having access to the sewers and those which must treat their effluent to render it fit to discharge to a stream.

Before considering any special treatment it may be well to consider the general chemical aspect of river pollution. The power of a river to keep itself pure may be directly related to its power of dissolving oxygen. Thus a river receiving but a small amount of polluting effluent may easily oxidize such polluting matter and recover its original vitality in the course of its flow, especially if in that course are to be found bridges and weirs, passage through and over which considerably helps aeration. Thus a well known English holiday resort actually pumps its drinking water from the river into which, but a few minutes previously, has been discharged the effluent from the sewage works. Thanks to efficient aeration no ill effects have been noted. On the other hand sluggish rivers receiving many effluents never

recover themselves and thus are said to be polluted. It will be seen that pollution is one of degree, peculiar to local conditions, and consequent upon this that no standardization of effluents is rational or desirable. This is a consideration which it is essential to remember, and which causes great dissatisfaction between contending authorities and mill owners. The main object of treatment of crude effluents may thus be said to be the removal of those constituents which have an adverse influence upon the stream receiving them, in that they prevent the stream recovering its partial or absolute purity. It may at once be said that the most important impurities which it is necessary to remove are the solid matters carried in suspension. Brief consideration of their nature will at once convince one of the necessity for this step. The deposition on the bed and banks of a river of large amounts of solids, each particle of which is covered with organic matter in a high state of putrefaction, must have an undesirable effect. Gradually one sees the formation of grey vegetable growths which are soon covered over with slimy masses and the river then assumes that unpleasant state from which it is so difficult to change it. Having prevented pollution from these bodies, it is still necessary to attack dissolved solids which may by their presence prevent the self restoration of the river to its natural state.

It may be advisable to consider the tests for the putrescibility of an effluent. At the present time no method is known by which this is directly determinable, consequently the number of indirect tests is very great. Possibly the most valuable is the determination of the oxygen absorbing power of the effluent. In contact with an acid solution of potassium permanganate effluents will absorb varying amounts of oxygen in proportion to the organic matter present. If, then, we can reduce this absorption to its reasonably lowest limits, we can assume a great degree of purification. It is quite impossible to tell from this determination alone whether an effluent is putrescible or not, for it is quite conceivable that of two effluents, one may have a larger oxygen absorption than the other, and still be not so disastrous in its effect. Still, this determination is possibly the most helpful that we have. Another test which is relied upon—possibly to too great an extent—is the determination of albuminoid nitrogen. This was

devised by Wanklyn in 1867 and depends upon the fact that organic nitrogenous bodies are partially oxidized when distilled with alkaline permanganate, liberation of ammonia resulting. This determined, gives an indication of the liability of the sample to undergo putrefactive decomposition. It will be seen that, if treatment results in a diminution of this figure, we may assume purification roughly proportional to the diminution. Of many other methods possibly one of the most helpful is that devised by Scudder, in which the effluent is mixed with tap water fully saturated with oxygen. The diminution of this dissolved oxygen is determined after certain periods and from the rate at which this proceeds one judges the possibility of putrefaction. Of course, these and other methods are really relative, for no strictly quantitative deductions can be drawn from the results.

We have thus far briefly discussed the general aspect of the problems of pollution and its prevention and it is necessary to specially consider its bearing upon our industry. It must be admitted that the treatment of tannery effluents has not progressed to the extent which one might reasonably expect, and in the main this is due to the chaotic state of laws previously described. It is only natural that manufacturers have delayed consideration of the question until the last moment in order that they may take advantage of legislation long overdue. For this reason, apart from description of preliminary treatment in cases where access to large sewage works has been obtained, it will only be possible to suggest lines of full treatment based on achievements in some few cases of exceptional difficulty, or in experimental plant.

Of the waste liquors in a tannery, the soaks, spent liquors and old limes are the really objectionable ones. The other liquors, various wash waters and waste dye liquors from the currying shops and chrome yards, are much more easy of treatment and happily do not influence the treatment to the same extent as those first mentioned. The volume of these liquors run to waste in any tannery is of course a quantity peculiar to that tannery. A tannery having a capacity of 1,500 market hides per week will probably run to waste 25,000 gallons of old tan liquors and 10,000 gallons of old limes; puers and wash waters will account for 75,000 gallons, whilst soaks add 40,000 gallons, making a total of about 150,000 gallons. Of course, these amounts vary

week by week and must only be regarded as approximate. It is still more difficult to estimate the volume of liquors run from a currying shop, but their effect on the total effluent is in no wise proportional to their volume, as they contain matters which are but moderately polluting.

It is well known that lime liquors and tan liquors are mutually precipitable, and for this reason it is advisable and necessary to have separate drainage for lime liquors. Much bother is experienced where the one drain conveys both liquors to the purification plant, for the precipitation which is so helpful in treatment is obtained before the bulk of the liquors are mixed. In tanneries known to the writer sludging of the drains occurs and, if these be not often cleaned out, back washes occur in running off old limes and one actually gets lime-tannin precipitation and staining in lime pits. The results can readily be imagined.

It is generally necessary to pump the liquors from the drains to precipitation tanks. Here one sees the advisability of separate drainage, for the tanner is greatly helped by the coprecipitation of the various liquors. What generally happens is, that with this lime tannin precipitate a great part of suspended animal matter, fibers, hair, dung, etc., is enclosed and carried down. Here then comes the chemist's first concern and that is the regulation and equalization of these liquors in order that the maximum precipitation may be obtained. To this end it is necessary to decide whether quiescent settlement or continuous flow settlement shall be adopted. In the former method a series of tanks is filled in rotation and each tank is allowed to stand full for a certain time before the top layer is discharged. Two tanks might be sufficient, each having a capacity equal to half a day's flow of waste liquor. In the latter method the waste liquor is allowed to flow continuously through one or several tanks arranged in series. Naturally with this method, in order to ensure slow flow of the liquor, one has to provide tanks of as large a capacity as convenient. If quiescent settlement be adopted the design of the tanks does not call for much skill. Large square wooden tanks, conveniently placed above the ground are necessary. They are fitted, at a suitable height, with a pipe and tap through which the supernatant liquor can be run off to the gutter leading to sewer or filter. In the bottom of the tank is filled a similar pipe and

tap. Through this the sludge is run off at intervals. On the top of the tanks is placed a gutter, fitted with valves, so that any or all of the tanks may be filled with the waste liquor pumped from the works drains. In practice one then fills each tank in turn. As each tank is filled one gets good mixing of the various liquors and the resultant coprecipitation takes place. It may be, by reason of continued excess of one liquor, that full precipitation is not always attained, and in this case, the addition of precipitants is necessary. By far the best precipitant in our case is sulphate of aluminium. One generally finds that the waste liquors, owing to excess of lime, are alkaline, and this then causes precipitation of aluminium hydrate. This precipitation generally occurs on and around particles of organic matter and causes their deposition. In other extreme cases it may be necessary to use lime as precipitant in conjunction with the aluminium sulphate. Other precipitants on the market in England contain iron salts. This prohibits their use in the treatment of tannery effluents—owing to the dark coloration formed with tannins. These are matters for laboratory investigation. It will be found, however, after a few days control, that the amount of precipitant required for each tank will be a fairly constant quantity, and close chemical control will not always be necessary. After precipitation, settlement is allowed to take place, and at the end of a few hours, this having been effected the top liquor may be run off by the tap provided. It is not necessary to run off the sludge after each settlement for it is generally recognized that remaining sludge helps further precipitation after subsequent filling of the tank. Considerations of space may not allow provision for quiescent settlement, and continuous flow settlement may then be adopted. In this case three or four tanks of as large a capacity as possible are provided. The total capacity obviously depends upon the volume of liquor to be treated, but the tanks should be capable of holding at least half a day's flow of liquor. They are fitted with taps similar to those already described when dealing with tanks for quiescent settlement. With this method the internal arrangement of the tanks calls for consideration. To ensure efficient sludge settlement, boards are fixed so that the liquor flows alternately downwards and upwards from one end of the tank to the other. Especially is this necessary

when hot dye liquors are intermittently pumped into the tanks, for otherwise these hot liquors would float across the top of the full tank and run away without mixing or treatment. Each tank, similarly constructed, is joined to the next one, and the liquor, with a slight head, thus flows from the inlet of the first to the outlet of the last one. Across the top of the tanks is placed a feed gutter fitted with valves so that any tank may be made the first of the series. The precipitation difficulties are greater when this continuous flow system is adopted, because it is not easy to effectively equalize and mix the various liquors. By laboratory investigation the most suitable amounts of precipitant to add per gallon of waste liquor will be determined. This addition, in the majority of plants, is carried out by running the liquor over a water wheel on the periphery of which are small buckets which pass through milk of lime on the one side and a solution of the aluminium sulphate on the other, and with each revolution deliver definite amounts of these precipitants into the liquor. In practice the liquor is pumped from the works drains over the wheel into the end tank, and having run its course through the tanks it is led away through the gutter to the series or to filters. Precipitation commences in the first tank, and if efficient design has been attained is almost complete when the liquor passes out of the second tank. The accumulation of sludge at the bottom of the baffle boards somewhat helps to retain the finer particles present in the flowing liquor, but by this process larger quantities of sludge are produced than by quiescent settlement. The sludge accumulated will have to be run off at intervals and needs careful attention. Each of these systems has its advantages and drawbacks. Quiescent settlement will need greater attention and therefore the labor cost will be greater than if continuous settlement be adopted. On the other hand, more exact and efficient treatment will be obtained by quiescent settlement; this means a saving in the cost of precipitants. Another point to consider is that quiescent settlement will give the smaller yield of sludge; this is a most important cost saving when one considers the difficulty of disposal. The amount of suspended solids to be removed by settlement varies with the flow of one or other waste liquor.

An average sample of untreated effluent from a tannery at Burnley gave on different days the following figures:—

	Parts per 100,000.		
	Total	Organic and volatile	Ash
Sample A, solids in suspension	324.0	308.0	16.0
" " " " solution.....	256.0	206.0	50.0
" B, solids in suspension.....	80.0	43.2	36.8
" " " " solution	84.0	26.8	57.2

Naylor gives the following figures in his book "Trades Waste."

	Parts per 100,000.		
	Total	Organic and volatile	Ash
Solids in suspension sample C.....	125.0	11.0	114.0
" " " " D.....	128.0	100.0	28.0
" " " " E.....	106.0	87.0	19.0
" " " " F	82.0	53.0	29.0
Solids in solution sample C.....	298.0	127.0	171.0
" " " " D.....	506.0	168.0	338.0
" " " " E.....	166.0	98.0	68.0
" " " " F	279.0	171.0	108.0

These figures prove what already has been written,—that each effluent demands treatment peculiar to itself, and that no generalization can be made.

We may now be said to have reached the first point of purification mentioned in the general discussion above. The greater part of the suspended solids have been removed, and with them much of the matter in solution which may be polluting, or which may prevent subsequent purification. One must not lose sight of the fact that the more complete the removal of soluble tannins at this stage the easier the attainment of success in treatment, for the well known oxygen absorbing power of alkaline tannates has a serious effect in after stages. This too is the stage where responsibility ceases for those tanners who are fortunate in having access to the public sewers, the effluent in this case generally being run off through sieves to the drain. This final sieving is a requirement of most public authorities.

The sludge has still to be dealt with but consideration of its treatment may be postponed.

From this point treatment of the effluent becomes difficult, and it will be the duty of the writer to point out the trend of modern developments, and to suggest what, to him seem the most hope-

ful lines of investigation. Up to the present day the tanner has possibly considered his obligations to be fully met by running his effluent over coke and ashes and thence to the stream. This latter treatment as generally carried out has little purifying action. More efficient purification may, however, be attained by constructing and operating filters in a manner which has proved so effective in the case of sewage purification works.

Early English investigation in the treatment of sewage showed the necessity for purification beyond the stage of precipitation, and to Frankland must be given the credit of pioneer work. The Royal Commission of 1868 in its third report issued in 1876 adopted the view that land treatment was the best and most natural method of sewage purification. Frankland, as a member of this Commission, recognized the difficulties attendant upon the acquirement of sufficient land for this treatment, and instigated experiments with a view to increasing the amount of sewage which could be treated upon a definite area of land. He found that choking of land did not occur if the sewage was applied in small doses. His method was to dose the land with the sewage at definite intervals, carefully regulating the volume applied to limits which he found to be most suitable for the particular soil in use. Thus, for a town of 10,000 inhabitants be considered that five acres of land filters should suffice if the land were divided into four equal plots and the sewage applied to one plot after the other, each for six hours. These conclusions were the result of his laboratory experiments, in which, by the use of glass cylinders filled with soil through which was inserted a glass tube to ensure aeration, he obtained effluents, non-putrescible and containing nitrates. His methods may well be regarded as the basis of modern biological methods of sewage treatment, but the credit for practical extension of the principles laid down by him must be given to the Massachusetts State Board of Health. Experiments were carried out by the Board's officers with many filters composel of various materials. Their method was to fill tanks with the material under investigation, and the filter thus formed was then treated with sewage at definite intervals, periods of rest being allowed between successive applications. Some gravel filters provided with artificial aeration received screened sewage at the

rate of 350,000 gallons per acre per day and gave purification of 80 per cent. as measured by the diminution of the oxygen absorbed. Experiments in England led to the development of contact beds in which the sewage stood for some hours, and after the sewage was run off, the bed rested for a similar interval to recover its powers of purification. Corbett in Salford recognized the principle, laid down by Frankland and the Massachusetts Board, that the liquid should always be allowed to freely flow away. To ensure even distribution and aeration he discharged the sewage on to beds of coarse material by means of spray jets from which the sewage was forced by pressure. To further attain efficiency he adopted open ventilated flows under the filter. One great difficulty at this time was the proper distribution of the sewage over the material forming the filter. It was found that with the use of coarse material, the sewage simply passed through the bed unpurified. Massachusetts experimenters tried to overcome this by the use of syphons which discharged the sewage on to the filter at regular intervals. Corbett's spray jets were devised to attain the same end, but later experiments have shown that by the use of graded materials, a fine layer at the top and coarser ones toward the bottom, this difficulty is overcome.

It would be beyond the scope of this article to fully discuss the theories of the actions which go on in this method of sewage purification. Frankland assumed that the dissolved organic matters were oxidized by the air contained in the pores of the soil whilst the sewage was percolating through the soil. Work by different investigators on nitrification in soil by micro-organisms led the Massachusetts experimenters to explain the purification by the assumption that bacteria in the sewage and in the filter effected mineralization during actual flow of the sewage through the filter. Dunbar attacks this and other theories, and at the same time puts forward the theory of absorption. He assumes that dissolved organic matters are first separated from the sewage during its passage through the filter, and are retained in the filter, to be decomposed and oxidized by micro-organisms during succeeding periods of rest. He shows that dissolved organic matters pass through the finest filtering materials without diminution in quantity, and he therefore dismisses the possibility of

mechanical filtration. Similarly he dismisses the general possibility of chemical combination between the organic matters in solution and the filter material, and finally, he advances his absorption theory. In support, he shows that whilst a filter receiving sewage greater in volume than its water retaining capacity delivers an effluent containing slightly less organic matter than the original sewage, yet if the volume applied be less than the water retaining capacity, the putrescible matters are to a small extent removed. Repeated dosing shows increased retention of putrescible matters until purification to the extent of 60 per cent. is attained. Thus organic matter is quickly retained although it was present in solution. He theorizes that the particles of sand and other matters forming the filter gradually become coated with a film of gelatinous substance of increasing thickness. This gelatinous coating, on examination, is found to contain bacteria and low forms of life as well as amorphous substances varying with the nature of the sewage and filter. This film becomes thicker and thicker; diminishing the volume of the pores but increasing the water retaining capacity of the filter. When the effluent contains nitrates the filter is assumed to be mature, the last stage of mineralization and oxidation having been reached. It is assumed that the film has a honey comb structure, and having an internal as well as an external surface can absorb gases and also many organic substances of high molecular weight. Assuming absorption as explained by Dunbar, it is easy to see that the more thorough the contact between the sewage and the material forming the filter, the more thorough the purification. Corbett's sprays then seem to help matters to a considerable extent, for as the sewage falls in single drops, each drop spreads over the surface of the material and gradually drops from one piece to another, everything tending to help absorption of the dissolved organic matter. This also shows the weak points of contact beds into which the sewage is quickly delivered. The extensive film on the material being washed off owing to strength of current, efficient contact cannot take place nor can aeration be effected to the required extent. It must be remembered that it is this contact and aeration which is so necessary in order to ensure activity of bacteria and the attendant oxidation. Percolating filters need not be constructed of fine

material if efficient distribution be attained, and consequently they are less costly in upkeep. Contact beds tend to clog up, but with a carefully graded percolating filter having fine material at the top little trouble is experienced.

The development of bacterial treatment of sewage having been briefly sketched, the real question now before us is the application of such methods to the treatment of partially purified waste liquors. Theoretically it would seem, that providing the filter be properly matured with the most suitable organism, it should be possible to purify any special trade waste, that is, in the absence of matters which will inhibit bacterial action. Dunbar has proved that, with sewage, inhibition does occur if antiseptics be present in the sewage, the action of the filter gradually diminishing until no purification takes place. So far as we are concerned with tannery effluents, practically the only antiseptic which, may have this action is sulphide of arsenic. Experiments about to be described will show that this has been successfully combated.

In England, little bacterial purification of tannery effluents has been attempted, and in the few instances where success has been attained, no results have been published. One has therefore to look to the United States for pioneer work which is undoubtedly important. The Massachusetts Board of Health has, in its report for 1909, some interesting results which must be of interest to all concerned in the problem. The Board's special powers of investigation on the large scale are noteworthy and clearly show the need for development in a similar direction in the case of the English Rivers Boards. The Royal Commission on sewage disposal, appointed in 1898, has recommended the formation of a Central Authority endowed with such powers of investigation, and to the writer it has always appeared that help of this character must, in the end, lead to the quicker and more efficient cleansing of our streams.

Of the experiments described in the report of H. W. Clark, chemist to the Massachusetts Board, the following are possibly the most interesting:

Tannery A.—This tannery was engaged in tanning and currying sheep skins. It discharged an effluent varying in daily volume between 20,000 to 50,000 gallons. This effluent was offen-

sive in character and highly colored, but did not contain matters which would prevent bacterial action. Nitrification was therefore easily effected. The first attempts to treat this effluent on a sand filter, two feet in depth, were not very satisfactory. Although the effluent, applied at the rate of 25,000 gallons per acre per day, had its oxygen absorbed figure reduced from 61.25 to 7.92 parts per 100,000, the filter soon became clogged, owing to suspended matter in the effluent. In face of this difficulty precipitation and sedimentation was tried. It was found that mixture with the old limes, followed by settlement, effected removal of 60 per cent. of the organic matter in solution. The settled liquor was still very impure, and was then applied, at the rate of 30,000 gallons per acre per day, to a filter containing fine sand to the depth of four feet. It being winter when the experiment was started there was little nitrification at first, but this increased as the weather became warmer, and for two and a half years an effluent was obtained which was clear and colorless, contained large amounts of nitrates, and had a low oxygen absorbed figure. It is interesting to note the analyses of the precipitated liquors run onto the filter, and of the effluent from the filter. We find considerable diminution in the ammonia content, whilst the nitrates present increase from 0.17 to 9.96 parts per 100,000. At the same time the albuminoid nitrogen diminishes from 2.39 to 0.23 parts, and the oxygen absorbed diminishes from 46.66 to 1.79 parts per 100,000. Further experiments at this tannery were with a coke strainer containing 2 feet in depth of coke, the upper portion being coke breeze and the lower portion coarser coke. This strainer was operated at the rate of 250,000 gallons per acre per day, and was successful in removing about 80 per cent. of the organic matters present, still giving an effluent which was polluting and which required to be treated on a sand filter. The purification effected by this coke strainer may be noted from the following results. The albuminoid nitrogen was diminished from 4.45 to 0.35 parts per 100,000, and the oxygen absorbed diminished from 95.20 to 3.96 parts per 100,000. Nitrates were produced to the extent of 0.56 parts per 100,000.

Tannery B.—This tannery was treating cured skins and for this reason naphthalene was found in the waste liquors. Arsenic limes were used in depilation and consequently arsenic was

found in the waste liquors to a considerable extent. Precipitation by means of the old limes was first effected, settlement followed, and then the liquor was treated on filters. No. 1 a sand filter, 4.5 feet in depth, produced a good effluent, but the extent of nitrification was considerably affected by variations in the amount of arsenic present in the liquors—the amounts being so high that, in general, bacterial growth was checked. The presence of arsenic, as above stated, caused some trouble, and it was necessary to find some means of removal. Precipitation by means of the waste limes caused precipitation of a considerable proportion of the arsenic. It was found that whilst the liquors delivered to the precipitation tanks contained an average amount of 8.54 parts As_2O_3 per 100,000, the liquors fed onto filters only contained an average of 1.67 parts As_2O_3 per 100,000. Although this purification is considerable, it is insufficient when we consider that bacterial purification is to follow. The Board's chemist found that by passing through a strainer of coke breeze almost entire elimination of arsenic occurred, an average of 0.08 parts As_2O_3 per 100,000 being found. He attributes this to the presence of iron in the coke. It is interesting to note that examination of the coke bed showed that the greater part of the arsenic was retained on the upper few inches of the strainer. Evidently as the result of these investigations, a coke filter was constructed containing 2 feet in depth of coke breeze. The settled liquors were applied to this filter at the rate of 100,000 gallons per acre per day, and the effluent from this was then applied at the same rate to a sand filter 4.5 feet in depth. Whilst the settled liquor contained matters giving 4.70 parts of albuminoid nitrogen per 100,000, the coke bed reduced this to 0.77 parts, and the sand filter further reduced the figure to 0.11 parts. Similarly the oxygen absorbed figure was reduced from 40.50 to 10.57 parts per 100,000 by the coke bed treatment, and to 3.52 parts by the sand filter. Nitrates were produced in considerable amounts, the coke bed effluent giving 0.12 parts per 100,000; this figure was increased by the sand filter to 1.97 parts. This plant worked well for some considerable time, producing an effluent which was uniformly good.

Other experiments of a similar nature were carried out at other tanneries but sufficient has been quoted in this article to demon-

strate the extreme importance of the work of the Board's Chemist. He has conclusively shown that it is possible to well purify tannery effluents by means of precipitation, straining through coke breeze, or in extreme cases through coke and iron filings, and then by final filtrations through sand or similar filters.

In the Journal of the Society of Chemical Industry for February 28, 1911, Dr. Fowler of Manchester publishes some interesting experiments on the treatment of effluents from ammonia recovery plants. Great difficulty has hitherto been experienced in the treatment of this class of effluent, the presence of phenol and thiocyanates being most injurious to fish life. At the same time these bodies tend to prevent self recovery of the stream. Fowler has shown that solutions of phenol and thiocyanate can be purified by means of bacterial filters; in the case of phenol by the action of a single species of organism, and in the case of thiocyanate, by the combined action of several organisms. What is more important is that he finds this oxidation to go on without denitrification, and therefore we still have the possibility of further purification after entry to streams. Employing works effluents, he finds, that by distribution over a filter 5 feet deep, composed of clinker, carefully graded from ¼ in. to 6 inches, he can obtain a purification of 98 per cent. as measured by the oxygen absorbed figure. This, of course, does not directly concern us as leather trades chemists, but it shows the possibilities of the method which is slowly being extended in application. Similarly, in the laboratory of the West Riding of Yorkshire Rivers Board, it has been found possible to purify, by bacterial filters, effluents from wool scouring mills. These effluents had previously caused excessive trouble, precipitation methods alone being found to be almost totally inadequate in practice.

With the foregoing results before us, it should not be difficult to devise a scheme for the successful treatment of tanning effluents. It is, however, quite beyond the powers of the writer to give detailed specifications. Each works will vary in its effluent so as to render this impossible.

In the first place, discrimination should be shown in the collection of the various waste liquors. It should be the object of the chemist to prevent precipitation in gulleys and drains, for besides saving considerable labor cost in cleaning, one helps pre-

scribed. It must obviously depend upon the nature of the stream into which it is to be discharged. One might, however, suggest the following limits as being desirable, and generally speaking, quite fair.

	Parts per 100,000
Oxygen absorbed in 4 hours at 80° F	below 2.0
Solids in suspension	below 10.0

One cannot suggest standards for the albuminoid nitrogen or for the nitrate figures. Reduction of the former generally ensures increased nitrification and lessened oxygen absorption. Both must therefore be considered in conjunction with the oxygen absorbed figure.

One matter referred to above is the question of sludge disposal. The sludge obtained from settling tanks has undoubtedly a good manurial value and is consequently of value to farmers. As run off from the tanks its water content may generally be as high as 80 per cent., and the difficulty of transport in this state, coupled with its excessive cost, renders drying necessary. No tannery in England produces sufficient sludge to warrant laying down of sludge pressing plant, and tanners have had to adopt other means of treatment. Manure merchants are generally willing and anxious to undertake the removal of the sludge. They recognize its value, especially in combination with other waste products. Their method of treatment is to run off the sludge onto heaps of stable manure. Intimate mixing is then carried out by repeated forking and turning over. In this way a really good saleable manure is obtained which can easily be disposed of. This is an arrangement generally carried out by the majority of tanners and seems to be satisfactory to all concerned. In American tanneries where much larger quantities of sludge must be dealt with it may be profitable to install sludge presses. The cake then obtained will undoubtedly have a good manurial value and should be easy of disposal. Such presses are in general use in sewage works and need no description in this article.

In a subsequent paper the writer hopes to give a resumé of standard methods of analysis as carried out in the laboratory of the West Riding of Yorkshire Rivers Board. This may, he hopes, be helpful in the attainment of that efficient control which is so necessary and desirable.

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