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EDITORIALS

THE SCOPE OF PHARMACEUTICAL CHEMISTRY.

The term Pharmaceutical Chemistry conveys no very definite idea to many who are engaged in other branches of the science; and with these indeed, may be included many who are connected with this branch of chemistry. For this condition, the pharmaceutical chemists themselves are responsible. Men engaged in the various divisions of pharmaceutical work, forgetting how dependent they are upon the other classes of workers in this field, have failed to keep in touch with one another. With this condition existing among the pharmaceutical chemists it is not difficult to understand why other chemists often have vague ideas as to what pharmaceutical chemistry comprises.

The term should be applied to the chemistry directly involved in the preparation and dispensing of medicines, in other words, that connected with the practice of pharmacy in any of its branches. The retail pharmacist often makes chemical and microscopical examinations of urine, or even maintains a general commercial laboratory; and the chemist in a manufacturing house may be called upon to examine flue gases, coal, paints and other materials used in construction work, but none of these can be included in the branch of chemistry under consideration.

There are four well defined divisions of pharmacy in which chemistry plays an important part—Retail Drug Business, Pharmaceutical Education, Pharmaceutical Manufacturing, and Drug Inspection. These divisions originated in the order named and each is directly dependent upon those preceding it.

The retail drug store is the unit upon which the whole structure of pharmacy rests and from which the other divisions were evolved. A considerable knowledge of chemistry is required by the successful prescriptionist to whom many difficult problems come. The retail pharmacist also manufactures a certain number of his preparations, and his manufacturing operations should differ only in magnitude from those of the manufacturing pharmacist which we shall consider later. The retail pharmacist should also be competent to inspect his purchases of drugs and chemicals and this requires careful analytical work. Hence, the purchase of a medicine at the drug store or the compounding of a prescription should not be considered as a commercial transaction, but as a professional service and should be paid for accordingly. While conditions in pharmacy are not ideal, rapid advancement is being made and the attitude of the public toward the pharmacist, influencing as it does the financial returns of the business, will be an important factor in pharmaceutical progress.

In the early days of scientific pharmacy the education of the apprentice was an important duty of the proprietor, but as pharmacy developed, schools were organized for the purpose of training men to act as retail pharmacists. Further progress, however, brought a demand for men trained to fill positions as chemists for manufacturing houses, boards of pharmacy, drug commissioners, etc. The schools have not met this demand and in most cases men must be selected who have a pharmaceutical education with very little chemical training or a good training in chemistry and no knowledge at all of pharmacy. The knowledge of chemistry or pharmacy which is lacking must then be obtained and, as the latter is more easily acquired, such positions are usually filled by men who have little or no knowledge of pharmacy. This condition is very unsatisfactory as the chemist may be handicapped for years by his ignorance of pharmaceutical conditions and facts which have never happened to come to his attention. It is true that attempts have been made by some of the colleges, to provide courses for chemists who wish to take up pharmaceutical work, but most of them have failed to provide training of the proper sort. Four-year pharmacy courses are often built up by taking a two-year course as a basis and attaching here and there a more or less unrelated subject until the time is reasonably well filled. Another idea is to devote a third year, after the regular two-year pharmacy course, to *food* and drug analysis. Bacteriology, botany, mineralogy, toxicology, urine analysis, water analysis, fire assaying and other interesting subjects are available for the construction of such courses; and there seems to be little realization of the fact that four years is a very short time in which to train men for pharmaceutical work, even if the curriculum is well chosen. The ideal training would include a knowledge of the retail drug business although this is not absolutely essential; the essential features are instruction in pharmacy and as broad a training in chemistry as possible. Of course, it is understood that mathematics, physics, languages and other subjects must be included in a course of this kind. Graduate courses of study should be established so that pharmaceutical chemists could pursue their studies under competent instructors.

We believe that the cause of this unsatisfactory condition in pharmaceutical education is found in the fact, already noted, that the men in any one of the divisions of pharmaceutical work have not sufficiently interested themselves in the work of the other divisions; and thus the educational men have had little opportunity to learn what is required in the other lines of work.

The chemical work of the manufacturing pharmacist is varied in character; and in order to gain a clearer idea of its nature it may be well to consider it in several steps. The inspection of crude materials is obviously a most important factor in the production of a good product. This inspection consists in the positive identification of everything purchased, exclusive of those things which are identified by a botanical examination; and as thorough a study as possible of the purity and strength of the material. Drugs of vegetable or animal origin containing known active principles must be assayed in order to determine their value. The determination of the nature and amount of impurities in organic and inorganic chemicals, oils, resins, gums, balsams, etc., taxes the resources of any chemist, and the pharmaceutical chemist is often driven to the expedient of rejecting clearly unsatisfactory materials on account of the presence of unidentified impurities. In choosing materials it is understood that certain amounts of harmless impurities must be permitted in all medicinal substances otherwise their cost would be prohibitive.

Having determined that the crude materials are satisfactory, the manufacturing processes must be controlled by the examination of preparations in different stages of manufacture in order to give directions for finishing products of proper strength and composition.

The finished products must then be examined to determine their compliance with standards of strength and purity, and also by aging experiments to determine something of their keeping qualities.

It is said that it is impossible to remain stationary; if this is true no manufacturer can stop when he has accomplished what has been outlined above; he must strive to advance. Many of the analytical methods used in this work leave much to be desired and a constant effort must be made to improve them. Manufacturing processes must be improved in order to produce better products and, to make them more economically, new processes and new products must also be devised.

With the enactment of food and drug laws the inspection of drug products became a very important division of pharmaceutical work. Extremely valuable results have already been achieved by workers in this field and by conservative work much more will be accomplished. The sensational methods and arbitrary rulings which have, in a few instances, been resorted to, are, however, to be greatly deplored.

Having discussed our subject in a general way it may be of interest to give some definite idea of the number of substances with which the pharmaceutical chemist has to deal. A certain manufacturing house lists about four thousand products, in the preparation of which about seven hundred different materials, which must be examined chemically, are used.

Pharmaceutical chemistry presents an inviting field of work to the young chemist. Comparatively little is known concerning the composition of many of the hundreds of vegetable drugs in use. Even in case of some of the most important drugs our knowledge is very defective. Ergot may be cited as an example, the most important contributions to our knowledge of its composition having been made within the last few years, although its study has been undertaken by many eminent chemists during a period extending over many years. The composition of the vegetable drugs alone offers an interesting and important field of work for the pharmaceutical chemist for generations to come. The effect of cultivation upon the chemical composition of medicinal plants has been almost entirely neglected, although the remarkable increase in the quinine content of cinchona bark through cultivation has long been known. The relation of chemical constitution to physiological action, and the study of the enzymes and hormones which may be used medicinally are merely suggestive of the broad fields which await the pharmaceutical chemist of the future.

While a review of the progress of pharmacy would not be appropriate here it may not be out of place to call attention to the several lines of coöperative analytical work which are being carried on. The keeping quality of medicinal preparations has already been referred to and this subject has had the serious consideration of manufacturers for a number of years. Several of the largest manufacturers have collaborated on this work and have published the results already obtained in the form of a brochure on the "Stability of the Drug Extracts." The work has shown that preparations of this class are as a rule remarkably stable.

The pharmaceutical division of this society has a Committee on Quantitative Methods whose function is the study and improvement of analytical methods used in pharmaceutical work.

The U. S. Pharmacopoeia and the National Formulary, which are our official standards for medicinal substances, are now being revised, and in these great undertakings a large number of workers in all branches of pharmacy are collaborating. As these works do not include all articles which are commonly used in medicine, the American Pharmaceutical Association has a standing committee for the establishment of unofficial standards in which all classes of pharmaceutical workers are represented.

As the pharmaceutical chemists are thus striving to advance this branch of chemistry, it is to be hoped that they will not neglect any opportunity for furthering closer relations with one another and with chemists in other lines of work.

F. R. ELDRED.

ORIGINAL PAPERS

STRUCTURE OF GALVANIZED IRON.

BY WALTER ARTHUR AND WILLIAM H. WALKER.

Received December 11, 1911.

Galvanized iron, by which term in this article we shall include all zinc protected iron, consists not of a sheet of iron covered with a layer or skin of pure zinc, as one might expect, but, on the contrary, of a complicated system of iron-zinc compounds, starting with pure zinc on the outside and passing through these alloys to the iron base within. We shall consider the structure of zinc protected iron under the three heads:

1. Hot galvanized—material made by passing the iron through a bath of melted zinc.

2. Sherardized—the article heated in the presence of finely divided zinc and zinc oxide.

3. Wet or Electrogalvanized—a layer of either zinc or a zinc alloy deposited electrolytically on the iron article from an aqueous bath.

By examining the zinc-iron alloy diagram constructed by v. Vegesack,[1] which is reproduced in part as Fig. 1, we see that by raising the temperature iron will dissolve in melted zinc to at least 24 per cent. Beyond this point it is impossible to go, owing to the volatility of the zinc. Hence the composition of the crystals separating along the dotted line DX is not accurately known, and will, for want of a better name, be called "binding alloy." From the molten mass at this point, crystals of this "binding alloy," $FeZn_3$, $FeZn_7$ (or a more or less saturated solution of zinc in $FeZn_7$), separate on cooling, the nature of the primary alloy depending on the concentration. The point *n* on the diagram represents the maximum solubility of zinc $FeZn_7$, and it is probably this saturated solid solution which is noticeable in certain sections of galvanized iron. A fraction of one per cent. (0.5–0.7 per cent.) of iron remains dissolved in the zinc after solidification.

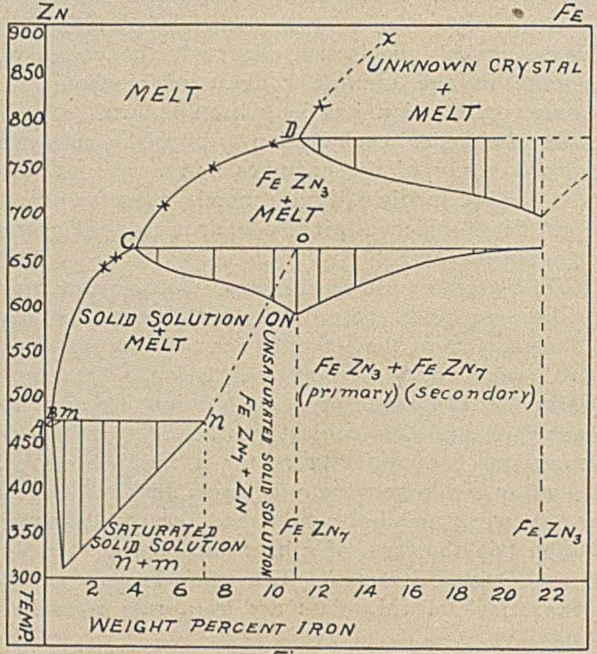

FIG. 1.

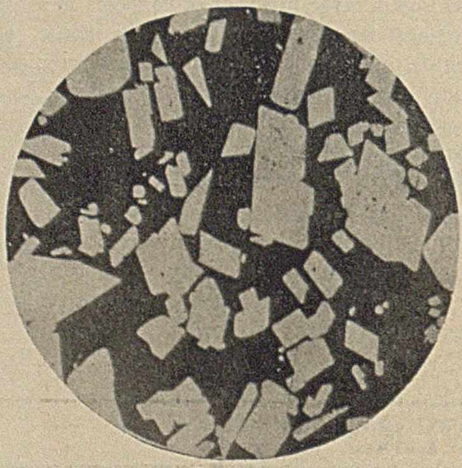

PLATE 1.

Hot Galvanizing.—Consider first the ordinary method of galvanizing with reference to the equilibria indicated above. A piece of iron dipped into melted zinc at once begins to dissolve, the amount of solution depending on the length of time the iron is in the bath. As the solubility of iron in zinc is very low at this temperature the zinc bath soon becomes saturated, and a separation of the solid solution represented by the point *n* occurs. This crystalline compound is the "hard dross" of the galvanizer's bath and is shown in the photograph, Plate 1. There is also a tendency for equilibrium to establish itself on the surface of the iron, and as at this point of contact between molten zinc and solid iron all possible concentration may be considered to exist, the specific properties of the individual crystals determine the character and amount of each constituent. The actual behavior under varying conditions is best shown by microphotographs of the galvanized plates viewed in cross sections.

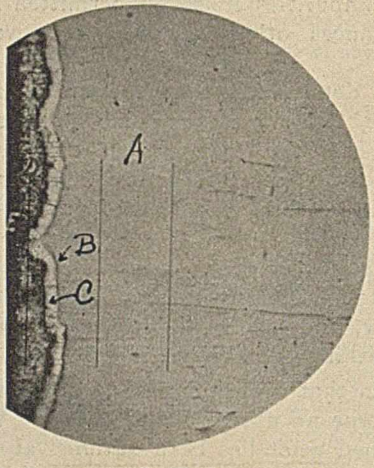

PLATE 2.

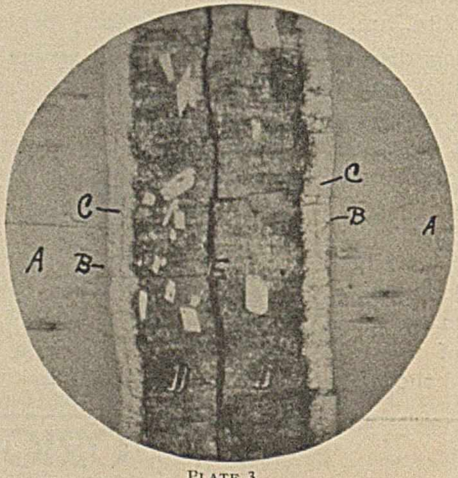

PLATE 3.

The preparation and polishing of plates in cross

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[1] v. Vegesack, *Zeit. anorg. Chem.*, **52**, 30 (1907).

sections presented some difficulties, the chief of which lies in the tendency of the zinc to "flow" in polishing, and the ease with which it gives rounded or "burred" edges when cut at right angles. To prevent "burring" several strips of the iron were immersed in sodium silicate solution until the surfaces were thoroughly covered, clamped tightly together in a small hand vise and dried for about two hours at 100° C. The hardened sodium silicate served to fill out the interstices resulting from the unevenness of the galvanized iron surfaces, thus preventing the burring of the edges at such points and the filling of such spaces by zinc and iron particles in cutting and polishing. After the sodium silicate had thoroughly hardened, the edges of the pieces were all cut to the same plane by means of a fine file, the final strokes being made in alternate directions so as to prevent any flowing of the zinc. The file was followed by fine emery paper, and this by still finer emery paper until the edges presented an unscratched surface to the unaided eye. The final

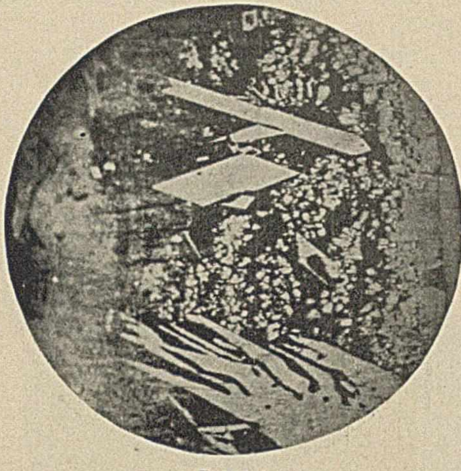
Plate 4.

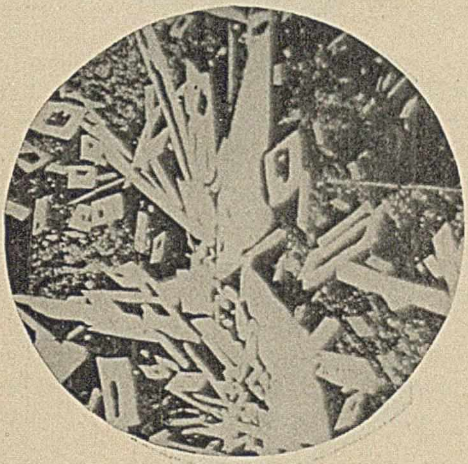
Plate 5.

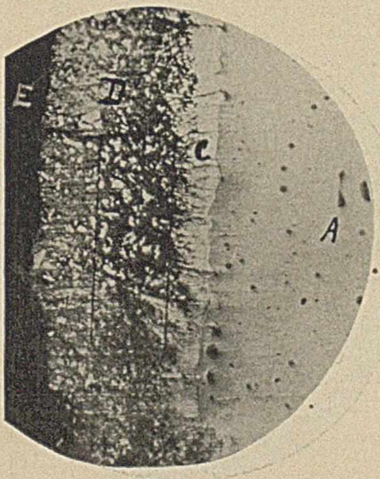

Plate 6.

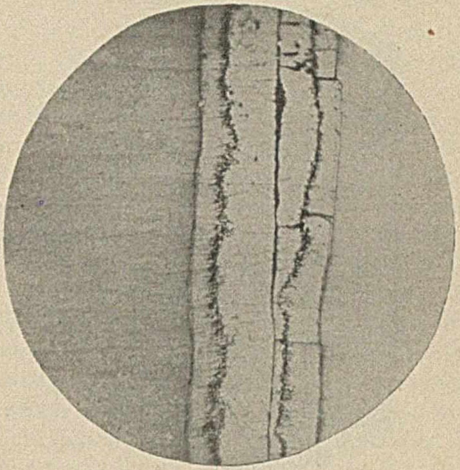
Plate 7.

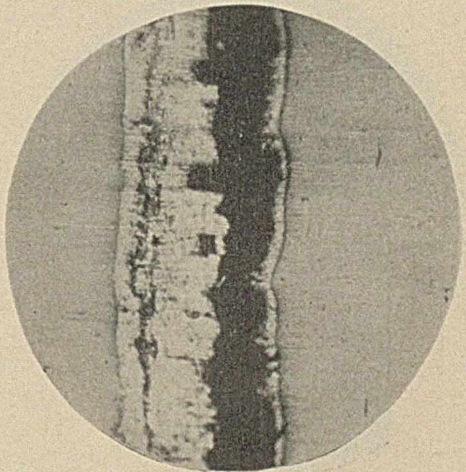
Plate 8.

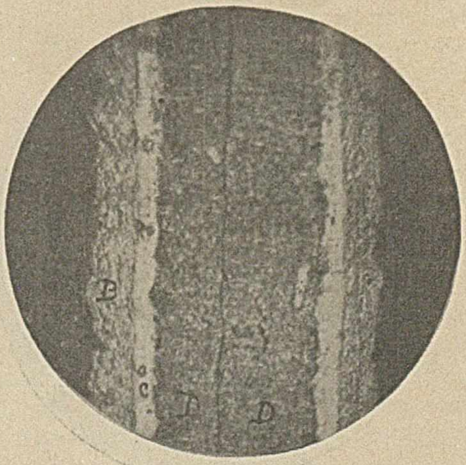

Plate 9.

polishing was done on soft cotton flannel, mounted on a piece of rubber, and covered with jeweler's rouge. In order to secure the best results, the final strokes were made very slowly and with a light pressure and always in alternate directions: 0.5 per cent. nitric acid in 95 per cent. alcohol was used as an etching reagent. By means of a micrometer eye piece the thickness of the various layers found in the etched specimens was measured. Each division of the scale shown in certain of the photographs represents 0.072 mm. on the specimen. Plate 2 shows a section of ordinary hot galvanized iron in which A is the iron, B a very thin layer of the "binding alloy" of undetermined composition, C the compound FeZn$_3$, D the zinc layer which is filled with tiny crystals of FeZn$_7$ not visible in the photograph, and finally the sodium silicate. Plate 3 shows a section of heavily galvanized iron in which, because of a longer period of immersion in the zinc bath, much larger crystals of FeZn$_7$ have formed. The large increase in the amount

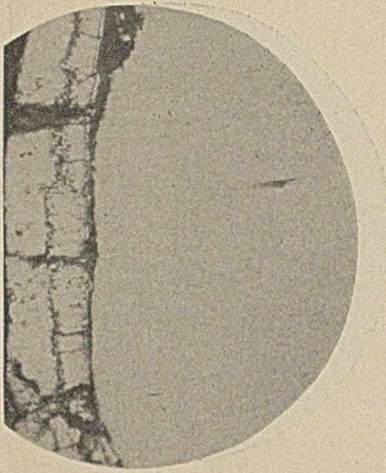
Plate 10.

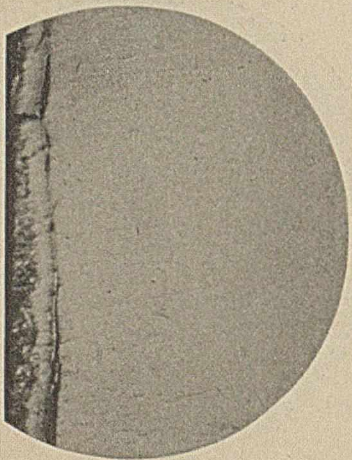
Plate 11.

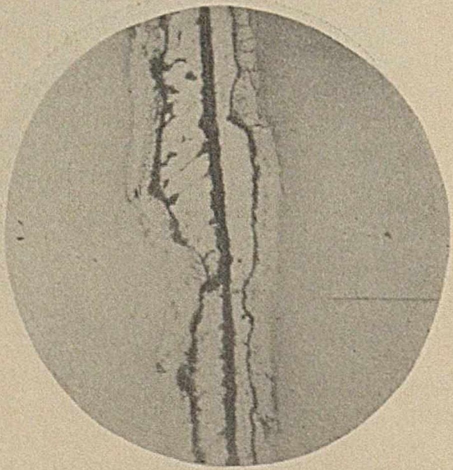
Plate 12.

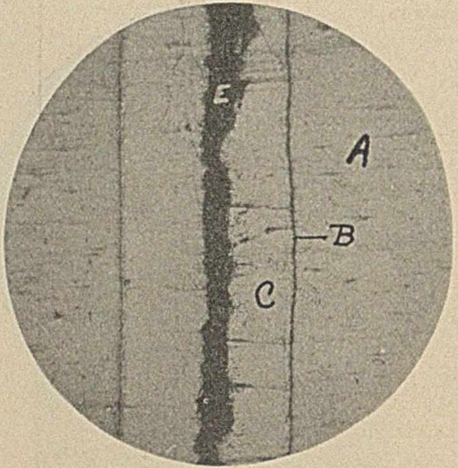

Plate 13.

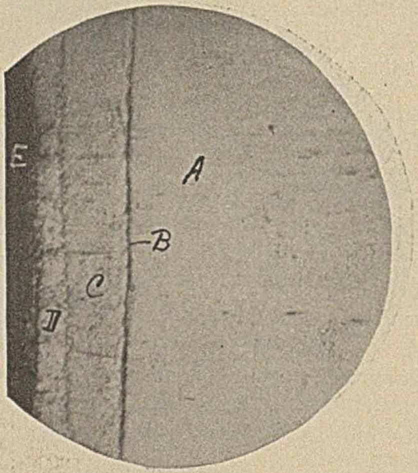

Plate 14.

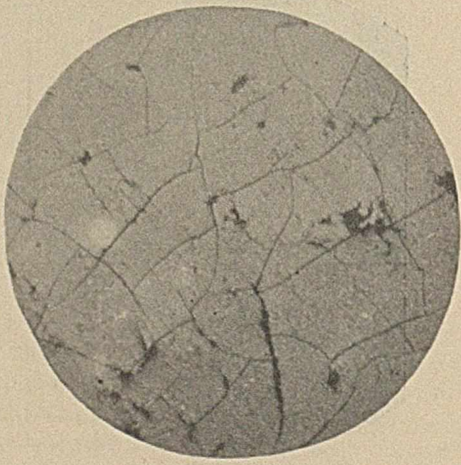
Plate 15.

of the compound $FeZn_7$ due to abnormally long immersion in the zinc bath is shown in Plates 4 and 5.

That the tiny crystals of $FeZn_7$ are always present in the outer zinc layer can be determined in another way. If an ordinary galvanized plate is cautiously treated with caustic soda it is possible to dissolve the zinc without affecting the compound. On a surface prepared in this way the tiny needle-like crystals of the compound become visible against the darker polygons of zinc.

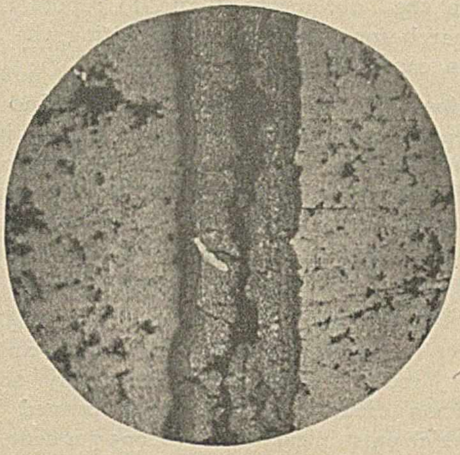

PLATE 16.

Plate 6 is a cross section of a piece of galvanized pipe used and left by the French at Panama. It is remarkable that after an exposure of some thirty years there should still remain so unusual a coating of zinc. The layer of alloy $FeZn_3$ is also very heavy and the zinc is full of small crystals of $FeZn_7$, both facts indicating that the pipe was immersed for a considerable length of time in the galvanizing bath, and that the bath was fully saturated with $FeZn_7$.

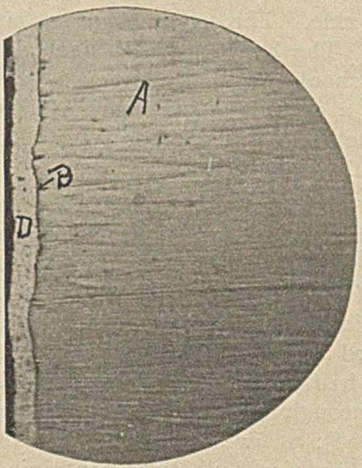

PLATE 17.

Plate 7 is two pieces of ordinary galvanized iron, one very irregular in thickness, which have been so etched as to bring out more strongly the binding alloy B.

We have already corrected[1] a statement erroneously made by one of us[2] that these alloys were electronegative to iron. While not so electropositive as zinc, they are *not* electronegative, and hence afford a distinct protection to the iron base. Plate 8 represents two parts of a galvanized sheet which had been exposed to the weather for a number of years. The left side is from a spot which showed no corrosion, and exhibits a continuous layer of zinc on the alloy $FeZn_3$. The right side was selected from a spot very close to where corrosion of the iron had already commenced. Only the alloy is left and this is broken through at one or two points. Plate 9 shows two sections of heavily galvanized iron which had been allowed to rust in a damp place, but which have not been artificially etched. A is the rusted iron surface. B is a strip of iron surface next to the alloy which has been protected from corrosion by the electropositive character of the alloy. C is the alloy and D the zinc.

A property of galvanized iron with which all users are familiar is its tendency to crack and peal off when sharply bent. Investigation of cross sections made of specimens which had been bent showed that the parting of the galvanized coating from the iron takes place at the surface of the "binding alloy." This is as would be expected, inasmuch as the high iron alloys are very brittle. Such a break is shown in Plates 10 and 11.

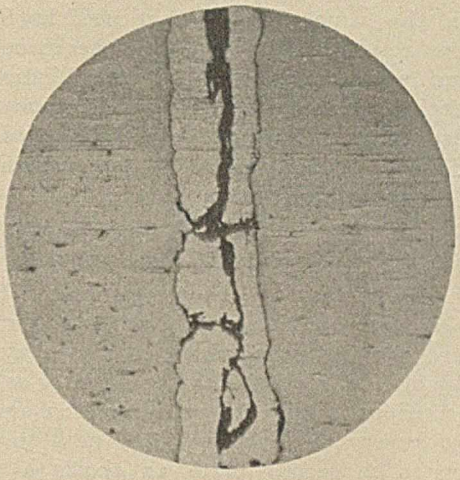

PLATE 18.

Another property of galvanized iron is that of blistering with subsequent "flaking off" when heated, such, for example, as is seen on the flue of a house furnace. It was at first thought that the phenomenon was due to oxidation, but experiments carried on in an atmosphere of hydrogen and also carbon monoxide showed that this flaking occurred when the galvanized article reached a temperature of 360° C., or thereabouts. A polished section shows that in this case the parting takes place between the zinc and the alloy $FeZn_3$. Plate 12 shows such a structure. The black space between the alloy and the zinc is sodium silicate which has flowed in between the two layers.

Sherardized Iron.—The material known as sherardized iron is not a definite structure, but differs

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[1] Patrick and Walker: THIS JOURNAL, **3**, No. 4 (1911).

[2] Walker: *Proc. Am. Electrochem. Soc.*

according to the temperature, time and composition of the zinc-powder mass employed. When the zinc powder is diluted with inert material, such as silica, and the time relatively short, the coating will consist of a very thin layer of the alloy $FeZn_3$, together with a more or less distinct layer of binding alloy of unknown composition. If the time is increased, and the powder richer in metallic zinc, a heavy coating is obtained as shown in Plate 13. If continued long enough, a layer of zinc forms on the surface of the alloy as shown in Plate 14. In all sherardized coatings are to be seen many cracks running through the alloy. This is particularly shown in the upper part of Plate 13. By polishing a section at right angles to the cross section, Plate 15 is produced. This shows the alloy to be broken into numberless fissures much resembling mud cracks. It is probable that greater study of etching methods would bring out still other alloys in this complicated structure. Thus Plate 16 shows two sherardized sections which have been etched by slow rusting in the air. They are from the same sheet as that used in Plate 13, and show a second alloy between the main coating alloy and what we have called the binding alloy. The blotched portions are the iron surfaces spotted with rust flecks. Owing to the brittleness of the main alloy a regular outline at the sodium silicate surface is difficult to obtain.

Electrogalvanized Iron.—The metal deposited by an electric current depends upon the impressed voltage and the composition of the electrolyte or bath. A coating of very pure zinc may be produced, or an alloy of widely varying proportions of iron may be obtained by adding iron salts to the bath, or as is sometimes erroneously done, by using an iron anode. In any case a very thin binding alloy next to the iron is always to be seen. Plate 17 shows a piece of ordinary wet galvanized iron in which the coating D is pure zinc. E is the sodium silicate layer, and B the binding alloy. Plate 18 shows two pieces of such iron which have been bent before mounting. The coating is seen to have parted from the iron base along the line formed by it and the alloy.

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

THE ESTIMATION OF OXYGEN AND OCCLUDED GASES IN COPPER AND A CORRECTION TO THE ELECTROLYTIC ASSAY IN THE COMPLETE ANALYSIS OF COPPER.

BY GEORGE L. HEATH.

Received January 2, 1912.

The only strictly quantitative chemical reaction for the estimation of the oxygen in commercial copper was first proposed by Dr. W. Hampe,[1] of Germany. He subjected the finely divided metal to a gentle heat for a few minutes in a current of pure carbon dioxide, called the loss (a few mg.) moisture and ignored it: the oxygen was then determined by the loss of weight, or water produced, on heating in a current of hydrogen at red heat. His method was improved[2] by simplifying the cleaning of the metal and by absorbing the traces of evolved sulphur in an ammoniacal solution of cadmium chloride.

To secure the complete evolution of all gases from the metal, it is necessary to take a precaution not mentioned in any published description of the method. It is the purpose of this paper to correct the serious error in the old method[1] and to report the result of a search for a means of estimating the occluded gases in cast refined copper.

The loss on heating copper filings, or fine drillings, in hydrogen, until there is no further change in weight, is not entirely[2] due to oxygen from cuprous oxide and sulphurous acid, but also includes the gases derived by the metal from the fuel and the refining in the furnace, and in addition, any trace of moisture, mechanically held, and finally is subject to the error to be explained.

I have found that, within the limits of an ordinary analysis, red-hot copper has practically no affinity for carbon dioxide. It has been proved that the gases which exist in cast metal (0.005 per cent. or more) can be driven out of the same by replacing every trace of air in the glass tube with perfectly pure, dry carbon dioxide, and then heating the copper in contact with the gas for 20–30 minutes. The loss in weight is due to evolution of the occluded H, with traces of CO, CO_2, N, and possibly argon.

The loss of weight found by heating subsequently in hydrogen *does not express the true oxygen* of the cuprous oxide present in the cast metal, for the metal retains, after long exposure to a current of hydrogen, nearly twice as much hydrogen in an occluded state, or solid solution, as was present in the absorbed gas of the cast metal; the original occluded hydrogen gas was driven out by the preliminary heating in carbon dioxide. This serious error has hitherto escaped attention. The hydrogen held back after heating in hydrogen should be finally expelled from the reduced copper by a current of pure carbon dioxide, exposing the hot metal to this gas for twenty minutes before cooling and weighing in air.

Carbon Dioxide.—Carbonic acid free from every trace of oxygen and other impurities cannot be produced as easily from marble, or calcite, as by the method of Bradley and Hale.[3] They use a paste of sodium bicarbonate and water in a 700 cc. flask surmounted with a separator tube. The generator is started half an hour before use and the gas allowed to flow through the purifying and drying tubes (to be described), as far as a three-way valve placed just before the ignition bulb tube containing the copper.[3] If the gas is generated from marble, or calcite, it is even more necessary to absorb the trace of oxygen constantly given off from the mineral after the air is all driven out of the apparatus. If a trace remains, it will tint the red-hot metal at the point where it enters the bulb.

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[1] *Z. f. Berg Hütten- and Salinen Wesen*, **1873**. Fresenius *Zeit.*, **1874**.

[2] Archbutt: *Analyst*, **25**, 253. Hoffmann: *Trans. A. I. M. E.*, **34**, 671. Heath: *Jour. Am. Chem. Soc.*, **27**, 313.

[1] Described by the author in *Jour. Am. Chem. Soc.*, **27**, 313.

[2] *J. Elect. Chem.*, **16**, 707. *Chem. Abstracts*, **1911**, p. 3384.

[3] *J. Am. Chem. Soc.*, **30**, 1090 (1908.)

The carbon dioxide is purified and dried as follows: (A) Casamajor generator with elevated pressure bottle, and small bottle on the table, containing the marble on a bed of large lead shot; the upper bottle is filled with hydrochloric acid (1 part to 2 of water). (A_1) Bulb of saturated, neutral $KMnO_4$. (B) Glass-stoppered U-tube sealed at the bottom with a solution of silver sulphate. (C) Bowen's (potash) bulb filled with strong sulphuric acid, after which may be placed a short tube of anhydrous calcium chloride. (D) A tube of dry chromous chloride.[1] (E) Tube of stick-phosphorus. (F) Two tubes of phosphorus pentoxide. (G) Short tube of dry calcium chloride. The expensive chromous chloride can be regenerated by passing a current of pure hydrogen through the tube at a gentle heat as long as any hydrochloric acid or moisture is given off.

By pulling out the second stopper in the tube B, the gas may be allowed to discharge into the air until the air is swept out of the generator, or it may be discharged under pressure from under a seal of 30 mm. of mercury, if generated from sodium bicarbonate by the method of Bradley and Hale.[2] The gas should always be passed through the bulbs as far as a three-way valve placed in front of the ignition tube until a test on hot copper shows that the gas is pure, giving no discoloration whatever at the point nearest the generator.

Hydrogen Gas.—The part of the generator holding the pure granulated zinc should be rather small, in order that the air may more easily be swept out. The action should be started and the gas passed over the copper for 15 minutes before lighting the burners. The purifying train[3] is as follows: A small washing bottle of 10 per cent. KOH, saturated with $KMnO_4$. Bowen's bulb, conc. sulphuric acid, (C) palladium asbestos tube, heated by alcohol lamp, after air is expelled. (D) An Allihn 250 cc. washing bottle containing 100 cc. of water, 100 grams of KOH (alcohol free) and 5 to 10 grams of pyrogallic acid. (E) Two tubes of dry calcium chloride and the three-way valve in succession (C and D, alternative, tube of stick P, and two tubes of phosphorus pentoxide).

Preparation of the Copper Sample for Ignition.—If a lot of copper is very porous, or of unknown origin, it may be advisable to dry it at 100° C. in an atmosphere of pure carbon dioxide or nitrogen (instead of heating in ignition tube to a heat which would expel some of the gases—an operation recommended by Hampe originally). If the speed and size of drill are regulated to produce fine drillings without any heating and oxidation, or contamination from grease, it will not be necessary to clean the drillings with ether. The adoption of the Copper Specifications of the American Society for Testing Materials will secure a fair sample of any casting, although equally good results are assured by boring half way through from both top and bottom, and also from the sides. With very pure material, an inch in depth is sufficient, the oxide having been previously removed by starting the hole through the surface skin with a larger drill.

As a prominent chemist has just noted: "It is impossible to remove all the soapy lubricant, or organic matter, from wires by washing with alcohol or ether directly." In such cases, it is suggested that the wire be cut in three-inch pieces and digested for a few minutes with alcohol KOH, 1 per cent. strength, as warm as possible without producing oxidation, then wash in water, alcohol, and ether successively. If a slight abrasion of the "skin" is not objectionable, the wire could be scoured, wet, with sharp silica (ground to pass a 40-mesh sieve), then washed with alcohol, etc. Extraction with petroleum ether (88° to 85° Bé.) in a Soxhlet tube will sometimes remove the offending material.

The ignition is performed in a hard-glass tube about 30 cm. long and 6 mm. internal diameter, which has one long bulb, or two round ones, at the center. It is cleaned, ignited, weighed, and the 50 gram sample fed into the tube very quickly in the following manner: Slide a tight fitting rod into one end as far as the nearest bulb, and attach to the other end, by short tubing, a short-stemmed funnel, whose diameter equals that of the tube. By using a long platinum wire, and tapping the tube, the drilling can be packed in the bulbs, after which the tube is wiped with a dry warm cloth and allowed to stand 10 minutes on the balance before weighing. When connected with the apparatus, the ignition tube rests on a lamp ring of 10 cm. diameter, and is protected from overheating by wrapping it with a fresh piece of thin asbestos paper, held in place by a short piece of stiff bent platinum wire.

IGNITION OF COPPER.

For Absorbed Gases.—A short drying tube and jet tube can be attached to the rear end of the ignition tube through a glass three-way valve and the carbon dioxide passed through the tube system for 30 minutes to sweep all the air out of generator and tubes. The fan burner, or triple Bunsen burner, is then lighted, the copper kept at a full red heat for 20 minutes, the tube cooled with an air blast and the CO_2 replaced by air which will require 10 minutes. The tube is then wiped clean and allowed to stand on the scales 10 minutes before weighing. The loss is due to gases from the cast metal.

For Total Oxygen and Sulphur.—Pass in hydrogen for 15 minutes, then keep at a red heat (not high enough to distil the metal into the glass) for 1 hour if the sample is filings, or 2 hours for coarse drillings. The necessary time should be ascertained in each laboratory by repeating an ignition on drillings of their standard fineness, until the weight is constant. The three-way valve at the rear of the ignition tube should be turned during this heat so that the gases pass through a small U-tube, or bottle, containing 10 cc. of a solution of ammoniacal cadmium chloride (20 grams per liter). Start the current of CO_2 through its own set

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[1] Recommended by J. O. Handy.

[2] *J. Am. Chem. Soc.*, **30**, 1090 (1908).

[3] Handy proposes the following alternative: (1) KOH, (2) conc. H_2SO_4, (3) $CaCl_2$, (4) heated palladium asbestos tube, (5) dry P_2O_5 opened up with glass wool.

of purifying tubes 20–30 minutes before the copper is all reduced, so that every trace of air shall be swept out of the tubes as far as the three-way valve in front of the copper. When the hydrogen has been passed long enough to complete the reduction of all oxides in the metal, turn off the hydrogen and pass in pure CO_2 for at least 20 minutes. Then cool the tube with an air blast until the copper is but slightly warm, replace the CO_2 with air and weigh with the same precautions as before.

Sulphur.—About 70 cc. of water are placed in a No. 1 beaker, the cadmium solution and sulphide washed into it with the aid of dilute hydrochloric acid (1 : 1) and the sulphur is titrated[1] at once with standard iodine (2 grams of I per liter). 1 cc. of this solution = 0.00025 gram of S.

Experimental proof of the completeness of the reduction of the copper by ignition in hydrogen and carbonic acid may be obtained by a careful electrolytic assay of the reduced drillings. The sum of the per cent. added to that of the other impurities as found by complete analysis will total 100 per cent. without any oxygen, if the work and sampling are correct. In order to attain such a result it will be found necessary to take the sample for oxygen determination from the very same bottle of drillings employed for the complete analysis, that is for the electrolytic assay of the original cast copper. In sampling a casting, the per cent. of oxygen varies directly with the per cent. of copper and silver and is variable enough in different samples drilled in the same casting to prevent the results adding up exactly 100 per cent. on complete analysis unless one sample is used for all tests.

	Sample No. 1.		No. 2.			No. 3.	No. 4.
	a.	b.	a.	b.	c.	"Low set".	Arsenical.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
OCCLUDED GASES AND COMBINED OXYGEN IN REFINED COPPER.							
Absorbed gases—by heating in CO_2	0.0064	0.0064	0.0074	0.0070	0.0070	0.0058	0.0077
Apparent loss—heating to constant weight in H gas and cooling in H gas			0.0523	0.0659	0.0579		0.0610
Additional loss by heating next in CO_2			0.0156	0.0132	0.0139		0.0018
Total Oxygen—by heating in H gas followed by CO_2 gas	0.0238	0.0254	0.0679	0.0741	0.0718	0.1664	0.0628
SUMMARY OF COMPLETE ANALYSIS.							
Oxygen and occluded gas averages		0.0310			0.0784	0.1722	0.0705
Foreign metals in copper		0.0081			0.0066	0.0080	0.0146
Arsenic							0.0674
Copper and silver		99.9560			99.9210	99.8120	99.8420
Total		99.9951			100.0060	99.9922	99.9945
PROOF OF METHOD FOR OXYGEN, ETC., BY ANALYSIS OF CU FROM IGNITION TUBE.							
Sulphur evolved and titrated		0.0006			0.0003		0.0011
Electrolysis (Cu and Ag)		99.9920			99.9930		99.9070
Foreign metals in Cu		0.0081			0.0066		0.0820
Total		100.0007			99.9998		99.9901

There is slightly less occluded gas in low-set, or oxidized, cast copper than in copper which is well refined to standard grade. Highly refined metal which shows "true" over-poling (due not to sulphur, but to poling too high in the furnace) would certainly show a large increase in occluded gases, near the upper surface of the castings of chilled metal.

Since the occluded gases in cast copper are so small in weight, a sample of 100 grams in a bulb of the style recommended by Dr. H. O. Hofmann would give a better result than the quantity I have specified.

CORRECTION TO ELECTROLYTIC ASSAY IN COMPLETE ANALYSIS OF COPPER.

The exact electrolytic assay of refined copper as described elsewhere by the author[1] gives results sufficiently accurate for valuation of the metal, but the deposition on the cathode is not absolutely complete, when a test of 1 cc. of electrolyte with hydrogen sulphide remains colorless.

As noted by W. C. Ferguson in a recent paper, we have also observed that about 0.005 per cent. to 0.008 per cent. remains in solution.

When an accurate complete analysis of the metal is desired, the author is accustomed to treat the electrolytes from the 5- or 10-gram battery assays with hydrogen sulphide gas. The sulphides are collected on a filter, roasted directly in a porcelain crucible, treated with a few drops of nitric and sulphuric acids, diluted with a little water, and the copper deposited on a small weighed platinum strip, and added to the principal cathode copper. Electrolytic deposits on platinum, as obtained by strictly following the method just quoted, have been found to be free from any appreciable quantity of absorbed hydrogen.

The methods already described might be used for gases in steel,[2] by substituting nitrogen for carbon dioxide. Only of late has the effect of oxygen in steel received the attention it deserves.

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[1] We use a specially prepared starch indicator which gives a very clear blue, with none of that disagreeable muddy red, given by ordinary starch (*Am. Chem. Abstracts*, **4**, 2617). The starch is allowed to stand over night, covered with cold water, containing 0.001 per cent. of hydrochloric acid. The next morning the acid is carefully washed out and the starch dried for two hours in an air oven at 100° C. Five grams of this prepared material is boiled with 500 cc. of water, filtered, or decanted from the sludge, and 15 drops of oil of cassia added before bottling, to render the solution permanent: 3 cc. of starch indicator are used in each test; a deduction is made for the iodine required to produce the end point, as determined by a blank titration.

[1] THIS JOURNAL, **3**, Feb., 1911.

[2] *Ibid.*, **3**, June, 1911, p. 372.

SOME OBSERVATIONS ON THE DISINTEGRATION OF CINDER CONCRETE.

By George Borrowman.

Received Feb. 8, 1912.

Cinders, as an aggregate in concrete, are used rather commonly where a light, cheap mixture is desirable; also in fire-proof construction and perhaps in the latter capacity this kind of concrete finds its most important application.

Its efficiency, however, has been the subject of considerable discussion. Various tests have been made, the results of which tend to show the superiority of this material over all other fire-resisting substances. There are also several patented floors involving cinder concrete which have been used successfully. Nevertheless, it has failed in some instances when employed for ordinary purposes, cracking and disintegration taking place. These discordant results are due, no doubt, as Freitag suggests in his "Fire-proofing of Steel Buildings," to the use of cinders of varying quality, but to the writer's knowledge the matter has not been further investigated. A particular case of disintegration, accompanied by a powdery efflorescence on the surface of the concrete, was observed by Dr. S. Avery, now Chancellor, but formerly head of the department of chemistry in this University, who prompted some study of the phenomena and also made various helpful suggestions during the experiments.

Blocks of concrete containing cement, sand and quarter-inch cinders were first prepared, the proportions by weight being 1 : 2 : 3, respectively. The cinders were from steam coal and slack and were carefully screened. The cement and sand were of good quality, the latter being sieved through twenty-mesh onto thirty.

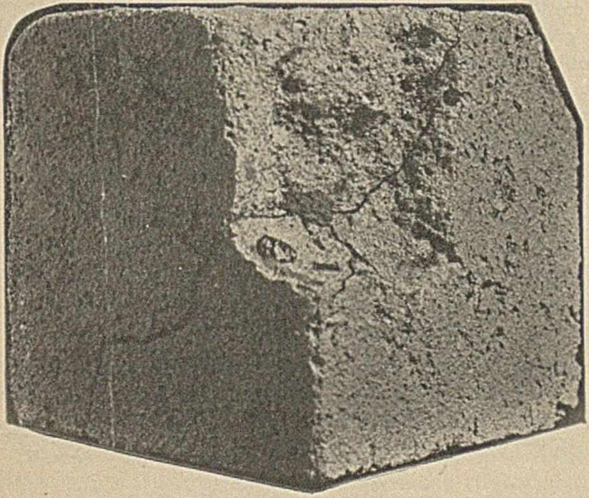

Fig. 1.

Another lot was then made up using cinders from one-half to one inch in size, the proportions being 1 : 1 : 1. In each case just enough water was used to insure thorough incorporation without running. All the blocks were placed on a glass plate to prevent loss of moisture and covered with a damp cloth for two weeks.

At the end of this period, the specimens having the proportions 1 : 2 : 3 showed no change but were somewhat porous and friable, owing to the relatively large bulk of cinders. A little later, however, fine cracks developed, with general disintegration. The others (1 : 1 : 1), though compact and hard, also showed signs of cracking and in a short time the breaks became very pronounced. In each case they radiated from certain points.

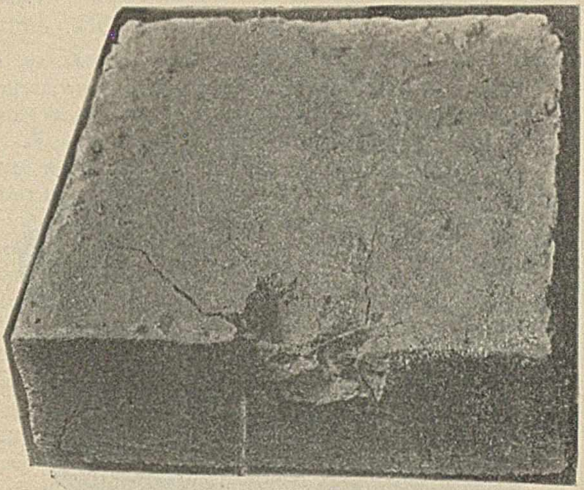

Fig. 2.

These latter specimens were broken open to facilitate examination and in some cases the breaks originated from cinders that showed oxidation of much iron. The accompanying cuts show plainly these nodules and the mode of cracking. The surfaces of the concrete bounding the cracks crumbled easily, indicating more or less general weakening.

The appearance of these oxidized cinders suggested the presence, originally, of much ferrous iron, probably as sulphide. The analysis of the cinder stock showed considerable sulphur as sulphide and sulphate; also iron, though the proportion of ferrous iron could not be determined in material of this sort, with accuracy:

Analysis of Cinders.

	Per cent.
SiO_2	37.86
Total Fe as Fe_2O_3	21.16
Al_2O_3	17.40
CaO	10.96
MgO	0.83
S	0.60
SO_3	5.82
Undetermined (C, etc.)	5.37
	100.00

It seemed probable, then, from the foregoing data, that oxidation of iron and sulphur produced internal stress and consequent cracking, aided, no doubt, by the general weakness produced by the diffusion of soluble sulphates. This theory was further strengthened by finding that the efflorescence, found on the surface of the disintegrating concrete before mentioned, was ferrous sulphate.

On this assumption attempts were made to bring about similar results by substituting for cinders artificial iron sulphide, prepared in several ways.

These experiments, however, were not successful. On breaking open the blocks, the sulphide was found to be unchanged, surrounded by hard, compact cement. Soluble sulphates being absent in the mixture, the blocks had, of course, greater initial strength than those containing cinders and would have withstood considerable stress had there been any. The lack of oxidation, though, in these tests, indicated that in the case of the cinders the necessary oxygen must have come from the cinders themselves, since they were equally well protected from the air.

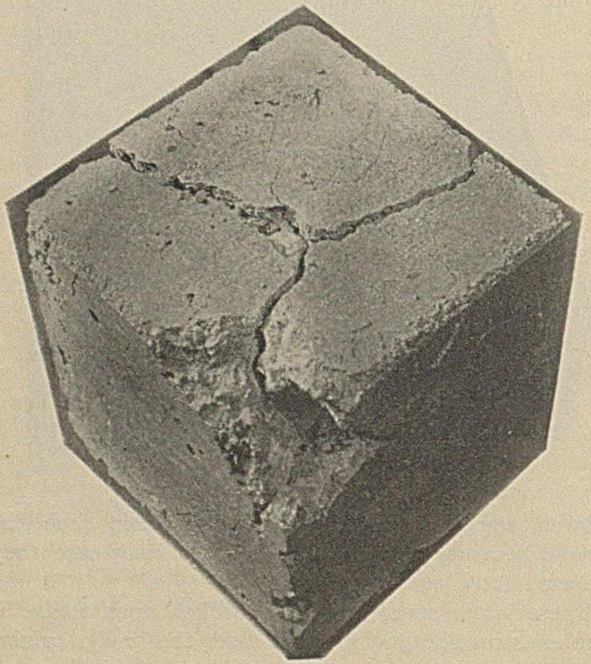
Fig. 3.

This conclusion drew attention to the fact that about one-third of the cinder stock consisted of a very porous coke. As is well known, this substance will persistently occlude large amounts of oxygen. According to Starr and Lewis, air-dried coke contains absorbed gases in the proportion of about seven-tenths of a cubic centimeter per gram of coke, two to six per cent. of the gases being oxygen. The oxidation in the concrete was most pronounced in the coke. Moreover, some pieces of the latter were picked from the cinder stock and tested for sulphide sulphur, about one per cent. being found. The nodule from which the cracks radiate in Fig. 1 proved to be a piece of coke so thoroughly oxidized as to look like a mass of ferric oxide. This was tested and found to contain but a trace of sulphur.

As a final experiment, some of the original stock of cinders were kept exposed to air and moisture until, on washing, they showed the presence of no soluble sulphate. They were then made into a block of concrete similar to those prepared before (1 : 1 : 1). Under parallel conditions no disturbance took place, the material retaining perfect stability.

From these tests we may conclude that cinders with much sulphide and sulphate sulphur are likely to give unsatisfactory results, especially if there is much coke or porous material present; also that such material may be improved if allowed to weather, with occasional washing, until the ferrous iron and sulphur have been oxidized and leached out.

University of Nebraska,
Lincoln.

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.[1]

THE MANUFACTURE OF CHLOROFORM FROM BLEACHING POWDER AND ETHYL ALCOHOL.

By F. W. Frerichs.

Received January 5, 1912.

(Concluded from the May No.)

Experiments Series F, comprising six experiments and representing six days' work in the plant, were made to determine whether that part of ethyl alcohol which is destroyed in the reaction can be substituted by methyl alcohol.

Apparatus Fig. 2 (page 350) was used, with 1500 cc. retort.

The experiments were made in the same manner as the experiments of Series E, only the larger part of the ethyl alcohol was substituted by methyl alcohol.

1. Materials used: 100 grams bleach, 35 per cent.; enough water to make 500 cc.; 20 cc. ethyl alcohol, 94 per cent.; 500 cc. methyl alcohol, 90 per cent. free of acetone; mixed at 20° C. and distilled. Products obtained: 1.2 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate A).

2. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 3.7 grams washed chloroform, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate B).

3. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 5.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate C.).

4. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate C mixed at 20° C. and distilled. Products obtained: 7.2 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate D).

5. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate D; mixed at 20° C. and distilled. Products obtained: 7.6 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate E).

6. Materials used: 100 grams bleach, 35 per cent.; enough water to make 300 cc.; 20 cc. ethyl alcohol, 94 per cent.; 700 cc. distillate E; mixed at 20° C. and distilled. Products obtained: 7.8 grams chloroform washed, s. g. 1.48; 700 cc. diluted mixed alcohols (distillate F).

Table VII.—Comparison of Experiments Series D and F.

Number of experiment.	Bleach, 35 per cent., used. Grams.	Chloroform washed, s. g. 1.48, obtained in	
		Series D.	Series F.
1	100	1.2	1.2
2	100	3.6	3.7
3	100	5.4	5.2
4	100	7.5	7.2
5	100	6.7	7.6
6	100	9.0	7.8

Conclusions from Series F.—Comparing experiments Series D and F, it is proven that the presence of large amounts of methyl alcohol (free of acetone),

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[1] Address read at the Annual Meeting of the American Institute of Chemical Engineers, in Washington, D. C., December, 1911.

in presence of a small amount of ethyl alcohol, does not increase the yield of chloroform from bleach.

Experiment Series G, comprising nine experiments, were made for the purpose of studying the decomposition of chloral hydrate with water and hydrated lime.

It is supposed that the decomposition runs by the following equation:

$$2CCl_3CH(OH)_2 + Ca(OH)_2 = 2HCCl_3 + (HCO_2)_2Ca + 2H_2O$$

The chloral hydrate crystals and hydrated lime used for the following experiments were free from hydrochloric acid. Apparatus Fig. 2 was used with a 1500 cc. retort. In each of the following experiments 30 grams chloral hydrate were used which theoretically would require 6.71 grams $Ca(OH)_2$ for decomposition and would make 21.6 grams of chloroform. Hydrated lime was taken in excess of theory. This was done because the reaction was studied as part of the chloroform formation occurring in the action of bleaching powder upon alcohol, in which case hydrated lime was always present in excess. To secure quick mixing the chloral hydrate was used in form of solution having 30 grams chloral hydrate to 100 cc. The distillation was carried out as in the former experiments.

1. Materials used: 15 grams $Ca(OH)_2$; 1000 cc. water; 30 grams chloral hydrate dissolved in 70 cc. water; mixed at 18° C. and distilled. Products obtained: 15 grams chloroform and 40 cc. water.

The 40 cc. water were separated from the chloroform and returned to the retort together with additional 15 grams hydrated lime, and the distillation was repeated but no additional chloroform was obtained. The contents of the retort were analyzed for chlorine by filling up to 1500 cc., filtering off 50 cc. solution, neutralizing these 50 cc. exactly with nitric acid and titrating with standard silver solution, using potassium chromate as indicator. As much chlorine was found as is contained in 1.86 grams of chloroform.

The 1450 cc. of material not used for this analysis was acidulated with nitric acid to dissolve all of the hydrated lime, and in an aliquot part of the solution chlorine was determined by the gravimetric method of precipitating with silver nitrate and weighing as silver chloride. The result was the same as the value found by titration.

In order to find out whether the proportion of hydrated lime would influence the yield of chloroform, the same experiment was repeated with the same quantities of materials and under the same conditions with the only exception that the quantity of hydrated lime was varied. In all instances the materials were mixed at ordinary temperature and slowly heated until 50 cc. had been distilled over. The chloroform was then separated from the water, the latter being returned to the retort. In a second distillation, in no case was any additional chloroform obtained. The results were as follows, *viz.:*

2. Materials used: 25 grams hydrated lime; 1000 cc. water; 30 grams chloral hydrate, dissolved in 70 cc. water; mixed at 18° C. and distilled. Product obtained: 15.1 grams chloroform.

The contents of the retort were analyzed for chlorine in the same manner as described in Series G1, and chlorine was found equivalent to 1.53 grams chloroform.

The experiments with these proportions and the same temperature were repeated a second and a third time, with the following results:

2a. 15.75 grams chloroform were obtained and nitrate of silver would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.80 grams chloroform.

2b. 15.7 grams chloroform were obtained and nitrate of silver would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.78 grams chloroform.

Average of Series G2, 2a, and 2b. 15.5 grams chloroform and chloride of calcium, equivalent to 1.7 grams chloroform, were obtained, out of a possible total of 21.6 grams. The difference of 4.4 grams of chloroform, or its equivalent, was decomposed into other organic chlorine compounds.

3. Materials used: 50 grams hydrated lime; 1000 cc. water; 30 grams chloral hydrate dissolved in 70 cc. water; mixed at 18° C. and distilled. Products obtained: 15.3 grams chloroform and silver nitrate would precipitate in the acidulated contents of the retort an amount of chlorine equivalent to 1.46 grams chloroform.

Conclusion from Series G1, 2a, 2b, and 3.—A large excess of hydrated lime has no influence upon the yield of chloroform from chloral hydrate. In using 15, 25, and 50 grams of lime, respectively, upon 30 grams of chloral hydrate, 15, 15.5 and 15.3 grams chloroform were obtained in the respective experiments, and chlorine in inorganic compounds equivalent to 1.86, 1.70 and 1.46 grams chloroform could be precipitated from the residual material in the retort by silver nitrate. The respective values of chloroform added would give 16.86, 17.2, and 16.76 grams accounted for, as against 21.6 grams required by theory. This would tend to prove that under the conditions of the experiments a large proportion of the chloral hydrate is decomposed into organic chlorine compounds, not chloroform, which would account for part of the loss in the manufacture of chloroform from bleach and alcohol.

This series of experiments was continued by varying the temperature at which the materials were mixed and reacted upon. All the following experiments were executed in the same manner as Nos. 1, 2 and 3, with the only exception of the temperatures observed. In each case, the first 50 cc. water distilling over with the chloroform were returned to the retort and upon repeated distillation no additional chloroform was obtained.

Apparatus Fig. 2 used with 1500 cc. retort (long stem funnel in retort).

4. Materials used: 25 grams hydrated lime; 1000 cc. water; heated to 80° C.; 30 grams chloral hydrate; 70 cc. water; 18° C. warm poured by a long stem funnel into the milk of lime contained in the retort and distilled. Products obtained: 16.5 grams chloroform and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.52 grams of chloroform.

5. Materials used: 25 grams hydrate of lime; 1000 cc. water; heated to boiling point; 30 grams chloral hydrate; 70

cc. water; 18° C. warm poured by a long stem funnel into the boiling milk of lime contained in the retort and distilled. Products obtained: 18.4 grams chloroform and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.11 grams of chloroform.

5*a*. Experiment No. 5 was repeated in exactly the same manner.

18.4 grams chloroform were obtained and silver nitrate would precipitate from the neutralized contents of the retort an amount of chlorine equivalent to 1.39 grams chloroform.

As an average of 5 and 5*a*, 18.4 grams chloroform and chloride of calcium equivalent to 1.25 grams chloroform were obtained, out of a possible 21.6 grams.

The difference of 1.95 grams of chloroform or its equivalent was decomposed into other organic chlorine compounds.

Conclusions from Series G2, 2a, 2b, 4, 5 and 5a.—The temperature at which the materials are brought together is of marked influence upon the yield of chloroform from chloral hydrate and hydrated lime. The yield is greatest if the materials are mixed at the boiling point of their solutions.

The yield was, in three experiments, 15.1, 15.75, and 15.7 grams out of a possible 21.6 grams of chloroform, if the ingredients were mixed at ordinary temperature.

The yield was in one experiment 16.5 grams, out of a possible 21.6 grams of chloroform, if the ingredients were mixed at 80° C.

The yield was in two experiments 18.4 and 18.4 grams, out of a possible 21.6 grams of chloroform, if the ingredients were mixed at the boiling point of their solutions.

The destruction of organic chlorine compounds by action of hydrated lime was equivalent to the complete destruction of chloroform ranging from 1.11 grams to 1.86 grams, out of a possible 21.6 grams.

In all instances, some organic chlorine compounds, not chloroform, were produced, the amounts of which ranged from an equivalent of 1.95 grams to 4.4 grams chloroform, out of a possible total of 21.6 grams.

More organic chlorine compounds, not chloroform, were formed if the solutions were mixed cold than if they were mixed hot.

More chloroform was destroyed if the solutions were mixed cold than if they were mixed hot.

Experiments Series H, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated with the variation that 20 grams hydrated lime were added to the charge in the retort in each experiment.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments was 6.5, 8.6, 10.3, and 11.1 grams, respectively.

Experiments Series H*a*, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated with the variation that the 15.5 per cent. of free calcium hydrate, which was present in the bleach, was neutralized by 10 per cent. hydrochloric acid before addition of the alcohol. Temperature in mixing 20° C.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments, was 6.8, 9.1, 9.8, and 10.5 grams, respectively.

Experiments Series H*b*, comprising four experiments and representing four days' work in the plant, were made to ascertain the influence of calcium hydrate upon the formation of chloroform.

The experiments, Series E*a*, were repeated, with the variation that the 15.5 per cent. of free calcium hydroxide, which was present in the bleach, was neutralized by 10 per cent. hydrochloric acid before addition of the alcohol. Temperature in mixing 20° C.

Subsequently, the temperature was slowly raised until the chloroform reaction was induced (about 80° C.), which could be observed by the mixture becoming milky from separated hydrated lime. The contents of the retort were then neutralized again by adding 10 per cent. hydrochloric acid. The amount of hydrochloric acid used for the second neutralization corresponded to 6.5 grams $Ca(OH)_2$ as an average of four experiments: 2.4 grams $Ca(OH)_2$ were used up for the decomposition of organic chlorine compounds.

Finally, the chloroform and alcohol were distilled off in the same manner as described in the experiments, Series E.

The yield in washed chloroform, sp. gr. 1.48, in four consecutive experiments, was 67, 8.8, 9.9 and 10.8 grams, respectively.

TABLE VIII.—COMPARING RESULTS OF EXPERIMENTS SERIES H, H*a*, H*b* WITH E*a*.

Operation. No.	Series E*a*. 100 grams bleach, 35 per cent.; 200 cc. alcohol, 94 per cent.; water to make 100 cc. Temperature 20° C. made chloroform. Grams.	Series H. 100 grams bleach, 35 per cent.; 200 cc. alcohol, 94 per cent.; water to make 1000 cc.; 20 grams $Ca(OH)_2$. Temperature 20° C. made chloroform. Grams.	Series H*a*. 100 grams bleach, 35 per cent.; 300 cc. H_2O neutralized with HCl, 10 per cent.; 200 cc. alcohol, 94 per cent.; water to make 1000 cc. Temperature 20° C. made chloroform. Grams.	Series H*b*. 100 grams bleach, 35 per cent.; 300 cc. H_2O neutralized with HCl, 10 per cent.; 200 cc. alcohol, 94 per cent.: water to make 1000 cc. Temp. 20° C. heated and neutralized again with 10 per cent. HCl made chloroform. Grams.
1	6.75	6.5	6.8	6.7
2	8.4	8.6	9.1	8.8
3	10.5	10.3	9.8	9.7
4	110.9	11.1	10.5	10.8

Conclusions from Series Ea, H, Ha and Hb.—Larger or smaller quantities of hydrated lime present during the reaction have no marked influence upon the formation of chloroform from bleach and alcohol, but part of the calcium hydrate generated by the chloroform reaction combines *in statu nascendi* with chlorine coming from organic chlorine compounds. As an average from Series H*b*, 8.9 grams $(CaOH)_2$ were formed by the chloroform reaction, 2.4 grams of which combined again with chlorine taken from organic compounds, to make calcium chloride.

Experiments Series I, comprising three experiments and representing three days' work in the plant, were made for the purpose of determining the temperature at which the chloroform reaction takes place, and to ascertain the amount of

$Ca(OH)_2$ formed in the chloroform reaction. Apparatus Fig. 2 was used, with 2500 cc. retort.

A filtered solution of bleach in water, containing 35 grams of active chlorine and 2.3 grams $Ca(OH)_2$ in one liter, was used in the following experiments. One liter of this solution would correspond to 100 grams bleach, 35 per cent., containing 2.3 per cent. $Ca(OH)_2$, but no $CaCO_3$.

1. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 200 cc. alcohol, 94 per cent.; mixed at 20° C. and distilled. Products obtained: 8.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate A).

The chloroform reaction commenced at 60 to 65° C. and could easily be observed by the clear solution becoming milky, caused by separation of $Ca(OH)_2$.

The residue remaining in the retort after the distillation contained 8.14 grams $Ca(OH)_2$ by titration, a small part of which was combined with CO_2.

2. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 700 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 10.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate B).

The chloroform reaction commenced at 60° to 62° C.

The residue remaining in the retort after distillation contained 7.96 grams $Ca(OH)_2$, some of which was combined with CO_2.

3. Materials used: 1000 cc. solution of bleach = 35 grams Cl; 700 cc. distillate B; mixed at 20° C. and distilled. Products obtained: 10.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate C).

The chloroform reaction commenced at 60° to 65° C. and the residue remaining in the retort after distillation contained 7.95 grams $Ca(OH)_2$, combined with a small amount of CO_2.

Experiments Series J, comprising four experiments and representing four days' work in the plant, were made to ascertain the temperature at which the chloroform reaction takes place at various concentrations of alcohol.

The reaction could be observed by the clear solution becoming milky, caused by separation of $Ca(OH)_2$, and the completeness of the reaction could be measured by titrating the contents of the retort for $Ca(OH)_2$ with normal hydrochloric acid on the basis of the experiments in Series K.

Apparatus Fig. 2 used with 2500 cc. retort.

1. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 200 cc. alcohol, 94 per cent.; mixed at 20° C. and slowly heated. Products obtained: 8.2 grams washed chloroform.

The chloroform reaction commenced at 60° to 65° C. and was finished after boiling, the contents of the retort measuring 8.14 grams $Ca(OH)_2$.

2. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 1000 cc. alcohol, 94 per cent.; mixed at 20° C. it turned turbid very slowly. Titrated for $Ca(OH)_2$ after standing 24 hours at 20° C., it contained 6.97 grams $Ca(OH)_2$.

3. Materials used: 1000 cc. solution of bleach = 35 grams Cl and 2.3 grams $Ca(OH)_2$; 1200 cc. alcohol, 94 per cent.; mixed at 20° C.; reacted at once, without being heated, and after one hour the contents of the retort measured 6.99 grams $Ca(OH)_2$.

Conclusions from Series I and J.—The temperature at which the chloroform reaction takes place and the time which it requires depends upon the concentration of the alcohol in the charge.

Approximately 20 per cent. alcohol will react with bleach at 60° to 65° C.

Approximately 50 per cent. alcohol reacts with bleach at 20° C. within twenty-four hours.

Approximately 55 per cent. alcohol reacts with bleach at 20° C. instantly, without application of external heat.

Experiments Series K, comprising fourteen experiments and representing fourteen days' work in the plant, were made for the purpose of determining the amount of chloroform and $Ca(OH)_2$ formed by repeated reaction of 750 cc. of a filtered solution of chlorinated lime, containing 35 grams Cl and 1.7 grams $Ca(OH)_2$ on 200 cc. alcohol, 94 per cent.

No alcohol was added except in the first operation. Apparatus Fig. 2 was used with 2500 cc. retort.

The series is a repetition of Series E*a*, carried on to fourteen operations, the difference being that filtered solution of chlorinated lime was used instead of the solid salt, on account of which fact the $Ca(OH)_2$ which was formed by the chloroform reaction could be measured.

1. Materials used: 750 cc. solution bleach = 35 grams Cl, and 1.7 grams $Ca(OH)_2$; 200 cc. ethyl alcohol, 94 per cent.; 500 cc. water; mixed at 20° C. and distilled. Products obtained: 7.5 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distllate A). The contents of the retort measured 7.4 grams $Ca(OH)_2$ by titration.

2. Materials used: 750 cc. solution bleach = 35 grams Cl and 1.7 grams $Ca(OH)_2$; 700 cc. distllate A; mixed at 20° C. and distilled. Products obtained: 8.2 grams washed chloroform, s. g. 1.48; 700 cc. diluted alcohol (distillate B). 7.1 grams $Ca(OH)_2$ in contents of retort.

This was repeated to fourteen operations and the results are entered in the following table:

TABLE IX.—EXPERIMENTS SERIES K.

Operations. No.	Chloroform washed, s. g. 1.48 obtained. Grams.	$Ca(OH)_2$ in residue in retort. Grams.	$Ca(OH)_2$ in 750 cc. solution chlorinated lime. Grams.	$Ca(OH)_2$ formed by chloroform reactions. Grams.
1	7.5	7.4	1.7	5.7
2	8.2	7.1	1.7	5.4
3	9.0	7.5	1.7	5.8
4	9.8	7.9	1.7	6.2
5	10.2	7.2	1.7	5.5
6	9.4	7.7	1.7	6.0
7	9.8	7.2	1.7	5.5
8	8.6	7.3	1.7	5.6
9	8.2	6.6	1.7	4.9
10	8.6	7.2	1.7	5.5
11	8.2	7.5	1.7	5.8
12	6.7	6.6	1.7	4.9
13	8.0	7.5	1.7	5.8
14	6.0	7.7	1.7	6.0

Conclusion from Series K.—The amounts of chloroform and calcium hydrate formed in the chloroform reaction are in direct proportion.

Experiments Series L, comprising twenty-six experiments and representing twenty-six days' work in the plant.

The experiments of Series K were continued with the exception that determinations of lime were omitted after the fourteenth operation, to determine how much chloroform could be obtained from 200 cc. alcohol used in the first operation. The amounts of chloroform obtained in the subsequent operations are entered into the following table:

TABLE X.—EXPERIMENTS SERIES L.

Series L. No.	Bleach, 35 per cent., used = 35 gr. Cl + 1.7 gr. $Ca(OH)_2$ in 750 cc. filtered solution. Grams.	Alcohol, 94 per cent., present. cc.	Chloroform, s. g. 1.48, obtained. Grams.	Alcohol, 94 per cent., used for chloroform reaction. cc.	Alcohol, 94 per cent., in after-distillate. cc.
1	100	200.0	7.5	9.4	190.6
2	100	190.6	8.2	10.3	180.3
3	100	180.3	9.0	11.3	169.0
4	100	169.0	9.8	12.2	156.8
5	100	156.8	10.2	12.7	144.1
6	100	144.1	9.4	11.8	132.3
7	100	132.3	9.8	12.2	120.1
8	100	120.1	8.6	10.8	109.3
9	100	109.3	8.2	10.2	99.1
10	100	99.1	8.6	10.8	88.3
11	100	88.3	8.2	10.2	78.1
12	100	78.1	6.7	8.4	69.7
13	100	69.7	8.0	10.0	59.7
14	100	59.7	6.0	7.5	52.2
15	100	52 2	5.3	6.6	45.6
16	100	45.6	3.8	4.8	40.8
17	100	40.8	4.5	5.6	35.2
18	100	35.2	5.6	7.0	28.2
19	100	28.2	6.0	7.5	20.7
20	100	20.7	5.3	6.6	14.1
21	100	14.1	3.8	4.8	9.3
22	100	9.3	3.4	4.3	5.0
23	100	5.0	1.9	2.4	2.6
24	100	2.6	0.8	1.0	1.6
25	100	1.6	1.1	1.4	0.2
26	100	0.2	0.0	0.2	...
			159.7	200.0	

1.25 cc. alcohol, 94 per cent., made 1 gram chloroform.

Conclusion from Series L.—The amount of alcohol, 94 per cent., used for the chloroform reaction at a concentration of 10 per cent. or more is less than 1250 cc. of 94 per cent. alcohol to 1 kilogram of washed chloroform, or less than 15 gallons alcohol, 94 per cent., for 100 lbs. of chloroform.

Experiments Series M, comprising ten experiments, representing a run of ten days in the plant and designed for the purpose of determining the amount of alcohol, 94 per cent., used up in successive operations, the concentration of alcohol in the first operation being approximately 10 per cent.

Apparatus Fig. 2 was used, with 2500 cc. retort.

In each operation 750 cc. diluted alcohol were distilled which was used in the subsequent operation, together with 1.25 cc. alcohol, 94 per cent., and for every gram of washed chloroform obtained in the previous operation.

1. Materials used: 750 cc. solution bleach = 35 grams Cl; 150 cc. alcohol, 94 per cent.; 600 cc. of water; mixed at 20° C. and distilled. Products obtained: 7.8 grams washed chloroform, 1.48 s. g.; 750 cc. diluted alcohol (distillate A).

2. Materials used: 750 cc. solution bleach = 35 grams Cl; 10 cc. alcohol, 94 per cent.; 750 cc. distillate A; mixed at 20° C. and distilled. Products obtained: 9.0 grams washed chloroform, 1.48 s. g.; 750 cc. diluted alcohol, 94 per cent. (distillate B).

This was repeated to ten operations and the results are entered in Table XI.

The 750 cc. diluted alcohol coming from the tenth operation were diluted with an equal volume of water and redistilled with 20 grams hydrated lime, whereby 3.7 grams chloroform were obtained, together with diluted alcohol, containing 161 cc. alcohol, 94 per cent.

TABLE XI.

	Materials used.				Products.	
Operation. No.	Bleach, 35 per cent., used in filtered solution. Grams.	Bleach, 35 per cent., used in filtered solution. cc.	Alcohol, 94 per cent., used. cc.	Diluted alcohol from previous operation. cc.	Chloroform, s. g. 1.48, obtained. Grams.	Diluted alcohol distilled off after chloroform cc.
1	100	1350	150	...	7.8	750
2	100	750	10	750	9.0	750
3	100	750	11	750	9.7	750
4	100	750	12	750	9.4	750
5	100	750	12	750	9.0	750
6	100	750	11	750	9.8	750
7	100	750	12	750	9.6	750
8	100	750	12	750	10.1	750
9	100	750	13	750	9.3	750
10	100	750	12	750	9.8	750
	1000	...	255	...	93.5	...

Conclusion.—1000 grams of bleach, 35 per cent., and 94 cc. of alcohol, 94 per cent., had, therefore, made 97.2 grams of washed chloroform, 1.48 sp. gr. The amount of alcohol, 94 per cent., used for the chloroform reaction, at a continuous concentration of 10 per cent., is approximately 968 cc. for 1000 grams washed chloroform, sp. gr. 1.48, or not quite 1 cc. alcohol, 94 per cent., for 1 gram of chloroform.

Experiments Series N, comprising ten experiments and representing a run of ten days in the plant. This series is a repetition of Series M, except that the materials were mixed near boiling point. (Compare Experiments Series G.)

Apparatus Fig. 1 was used, with 2500 cc. retort, carrying a long stem funnel, reaching toward the bottom of the retort.

The diluted alcohol was charged into the retort and heated to boiling, whereupon the solution of bleaching powder was poured, in small portions, through the long stem funnel into the alcohol, which was boiling in the retort.

The quantities of materials used were the same as in Series M, except the fresh alcohol, 94 per cent., was added at the rate of 1 cc. alcohol, 94 per cent., for every gram chloroform obtained in the previous operation. (See conclusion above.)

The results of ten operations are entered in the following table:

TABLE XII.

	Materials used.				Products.	
Operation. No.	Bleach, 35 per cent., used in filtered solution. Grams.	Bleach, 35 per cent., used in filtered solution. cc.	Alcohol, 94 per cent., used. cc.	Diluted alcohol from previous operation. cc.	Chloroform, s. g. 1.48, obtained. Grams.	Diluted alcohol distilled off after chloroform. cc.
1	100	1350	150	...	7.2	750
2	100	750	7	750	9.8	750
3	100	750	10	750	10.4	750
4	100	750	10	750	10.8	750
5	100	750	11	750	10.9	750
6	100	750	11	750	10.2	750
7	100	750	10	750	11.0	750
8	100	750	11	750	10.8	750
9	100	750	11	750	11.0	750
10	100	750	11	750	10.6	750
	1000	...	242	...	102.7	...

The 750 cc. of diluted alcohol coming from the tenth operation were treated in the same manner as described in Series M, whereby 3.2 cc. chloroform, sp. gr. 1.48, and 146 cc. alcohol, 94 per cent., were obtained.

Conclusion.—1000 grams bleach, 35 per cent., and 96 cc. alcohol, 94 per cent., had, therefore, made 105.9

grams of washed chloroform, sp. gr. 1.48, which would make 103.4 grams pure chloroform after washing with sulphuric acid 66° and redistilling. The amount of alcohol, 94 per cent., used for the chloroform reaction, at a continuous concentration of 10 per cent., is approximately 922 cc. alcohol, 94 per cent., for 1 kg. of washed chloroform, sp. gr. 1.48.

This work done, the most favorable conditions were figured from the conclusions Nos. 1 to 40, drawn from 126 experiments, which represent 126 days' work in the plant. They were found to be as follows, *viz.:*

1. The concentration of alcohol in the charge was to be about 10 per cent.

2. There was to be not less than 100 cc. alcohol, 94 per cent., present for every 100 grams of bleach, 35 per cent.

3. The alcohol and the solution of bleaching powder was to be brought together at boiling point, or as near to it as possible.

If these conditions could be given in the plant, 100 lbs. pure chloroform could be expected from 967 lbs. bleach, 35 per cent., and 11.5 gallons alcohol, 94 per cent. (see experiments Series N), in place of from 1510 lbs. bleach, $33^{1}/_{3}$ per cent., and 11.73 gallons alcohol, 94 per cent., which were obtained as an average in the manufacture of 100,257 lbs. chloroform in actual practice (see Table I). While the consumption of alcohol was about the same as in the old process, the saving in bleaching powder was approximately 34 per cent.

In order to comply with these requirements one old apparatus, represented in Fig. 1 (p. 346), was changed as indicated in Fig. 3, by closing up the manhole in the still and riveting to the top of the still a funnel in the center of which a four-inch pipe reached down toward the bottom of the still. In place of a square box which, in the old process, had served for dissolving the bleaching powder, a round agitating apparatus, *A*, was installed, in which the bleaching powder was more readily dissolved in the necessary amount of water. The receiver *D*, taking the chloroform and diluted alcohol, which ran from the cooler, was changed to the form indicated in the drawing and a receiving tank, *E*, capable of holding 400 gallons of diluted alcohol, was set in the ground under the receiver, for the purpose of storing the diluted alcohol distilled in one operation. The bottom of the receiving tank was connected by a 1-in. pipe with the upper part of still *B*, and, by air pressure, the contents of the receiver could be blown out into the still as soon as the latter was ready for a new operation.

The apparatus was operated in the following manner:

120 gallons alcohol, 94 per cent., were charged into still *B*, Fig. 3, and sufficient water added to make the alcohol about 20 per cent. This would fill the still about 2 ft. One cask bleaching powder, holding about 1000 lbs., was charged into agitator *A*, containing sufficient water to fill the agitating vessel to within 6 inches from the top. Then the diluted alcohol was heated by direct steam to boiling, and the solution of bleaching powder was introduced into *B*, in small quantities, through the funnel tube.

The reaction would take place at once and the chloroform would distil freely, together with some alcohol. When all the bleaching powder was introduced, the chloroform, and subsequently the alcohol, were distilled off, about 400 gallons of diluted alcohol being obtained in each operation.

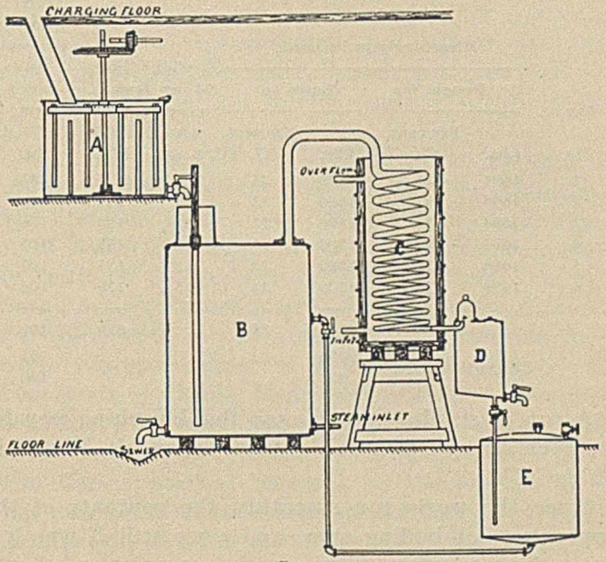

Fig. 3.

The diluted alcohol thus obtained was used for the subsequent charge and sufficient fresh alcohol, 94 per cent., was added to make up for the alcohol which had been converted into chloroform in the previous operation. With this alcohol and another 1000 lbs. bleaching powder, dissolved in sufficient water to fill the agitating tank *A* to within 6 inches from the top, the operation was repeated once a day and chloroform was thus obtained in a continuous run.

A run of six days was made with this improved apparatus, with the following results, *viz.:*

Table XIII.

Day.	Bleaching powder used.				Alcohol, 94 per cent., used.	Chloroform, s. g. 1.48, obtained.	1000 lbs. bleach, 35 per cent., made chloroform, s. g. 1.48.
	Bought for		Equal to				
No.	Lbs.	Per cent. Cl.	Lbs.	Per cent. Cl.	U. S. gal.	Lbs.	Lbs.
1	1129	31	1000	35	120	81	81
2	1129	31	1000	35	10	100	100
3	1129	31	1000	35	10	102	102
4	1129	31	1000	35	10	108	108
5	1129	31	1000	35	10	106	106
6	1129	31	1000	35	10	105	105
Proportion.......			4000	35	...	421	105
			952	35	...	...	100

Not counting the first two days, in which the previous charges have an influence upon the yield, an average of 105 lbs. washed chloroform, sp. gr. 1.48, were obtained from 1000 lbs. bleach, 35 per cent.

An attempt was made to increase the capacity of the plant by charging 1500 lbs. of bleach, 35 per cent., into agitator *A* for each charge, adding sufficient water to make the same volume of solution as in the previous run, and using this more concentrated solution of bleach in the same manner as the weaker solution in the previous work.

TABLE XIV.

Day.	Bleaching powder used. Bought for		Equal to		Alcohol, 94 per cent., used.	Chloroform, s. g. 1.48, obtained.	1000 lbs. bleach, 35 per cent., made chloroform, s. g. 1.48.
No.	Lbs.	Per cent. Cl.	Lbs.	Per cent. Cl.	U. S. gal.	Lbs.	Lbs.
1	1694	31	1500	35	120	125	83
2	1694	31	1500	35	15	147	98
3	1694	31	1500	35	15	159	106
4	1694	31	1500	35	15	158	105
5	1694	31	1500	35	15	153	102
6	1694	31	1500	35	15	159	106
			6000	35	...	629	105
Proportions......			1000	..	...	...	105
			952	..	...	...	100

A run of six days, with 1500 lbs. bleaching powder for each charge, was made with the result given in Table XIV.

Since the works ran smoothly, the contents of the apparatus not boiling over, and since still *B* was less than three-quarters filled at the completion of the charge, the larger charge was thought possible in the regular run, whereby the capacity of the plant was increased by 50 per cent.

In making this run it was observed that the first thousand pounds bleach made more chloroform proportionately than the following 500 lbs. In Experiments Nos. 3 to 6, 113, 116, 113, 116 lbs. washed chloroform, respectively, were obtained from the first thousand pounds bleach, 35 per cent., while 47, 40, 40, 45 lbs., respectively, were obtained from the following 500 pounds.

From this observation it might be concluded that greater concentration of alcohol would produce a still greater yield. But the advantage did not seem sufficiently large to justify the increased consumption of steam and the decrease of the capacity of the plant, and for this reason experiments in this direction were not carried on.

Following these runs, all six apparatus were changed in the same manner and they were operated parallel with bleaching powder, 31 per cent. to 37 per cent., for several years. From time to time, operations were discontinued to make calculations, or for other reasons, and the following are the results obtained from several lots. In every instance, the diluted alcohol obtained in the last operation was redistilled with calcium hydrate, and the amount of alcohol obtained was deducted from the amount of alcohol used in the aggregate operations, the difference being the alcohol, 94 per cent., used up for chloroform.

Record of a thirty-three days' run, with 35 per cent. bleach, showed the daily variations. On every day, except the thirtieth day, six apparatus were used, while on the thirtieth day only five were in commission, one being in repair. One and one-half casks bleach, 35 per cent., weighing about 1500 lbs., were used for a charge in each apparatus in every day's run except on the first day, when only one cask per apparatus was charged.

The diluted alcohol, coming from the last operation, contained 640 gallons alcohol, 94 per cent., and from the 31,419 lbs. washed chloroform, 30,675 lbs. pure chloroform were obtained. The net result of the run was, therefore, that 299,525 lbs. bleach, 35 per cent., and 3441 gallons alcohol, 94 per cent., made 30,675 lbs. pure chloroform, which is equivalent to 102.4 lbs. pure chloroform from 1000 lbs. bleach, 35 per cent., and 11.49 gallons alcohol, 94 per cent., or 100 lbs. pure chloroform required 977 lbs. bleach, 35 per cent., and 11.22 gallons alcohol, 94 per cent.

TABLE XV.

Day. No.	Bleach 35, per cent., used. Lbs.	Alcohol, 94 per cent., used. U. S. gal.	Chloroform, s. g. 1.48, obtained. Lbs.	1000 lbs. bleach, 35 per cent., made chloroform. Lbs.
1	6,322	559	510	81
2	9,055	90	940	103
3	9,160	120	959	104
4	9,011	120	931	103
5	9,196	90	968	105
6	9,125	120	942	103
7	9,075	120	949	104
8	9,503	90	1,039	109
9	9,268	90	967	104
10	9,206	90	930	101
11	9,100	90	943	104
12	9,221	120	924	100
13	9,172	120	954	104
14	9,157	120	987	108
15	9,274	120	1,001	108
16	9,240	120	927	101
17	9,254	120	967	104
18	9,352	90	942	100
19	9,160	120	969	105
20	9,263	120	1,001	108
21	9,146	90	977	106
22	9,107	120	1,016	101
23	9,311	90	984	105
24	9,327	120	985	103
23	9,106	120	1,029	103
26	9,154	90	970	106
27	9,207	120	968	105
28	9,140	120	957	105
29	9,072	100	949	105
30	7,576	120	838	100
31	9,632	90	1,013	105
32	9,047	120	993	100
33	9,556	152	990	103
	299,525	4,081	31,419	105

Record of 8 lots chloroform, made from bleach containing 31 to 37 per cent. chlorine and alcohol, showing variations by different strengths of bleach:

TABLE XVI.

Lot.	Bleaching powder used. Bought for		Equal to		Alcohol, 94 per cent., used.	Chloroform obtained. Crude, s. g. 1.48.	Pure.
No.	Lbs.	Per cent. Cl.	Lbs.	Per cent. Cl.	U. S. gal.	Lbs.	Lbs.
1	353,375	32	323,085	35	3,710	30,155	29,446
2	53,968	32	49,342	35	536	4,244	4,046
3	185,414	35	185,414	35	1,930	16,065	15,982
4	299,525	35	299,525	35	3,441	31,419	30,675
5	168,178	31	148,958	35	1,732	15,373	14,925
6	83,218	37	87,973	35	880	8,279	8,182
7	577,871	35	577,871	35	6,646	62,595	61,124
8	799,387	35	799,387	35	9,013	77,916	77,551
			2,471,555	35	27,888	246,046	241,931
Proportions....			1,000	35	11.28	99.5	97.9
			1,022		11.53		100.0

Comparing this with the results obtained by the old process and recorded in Table I, a saving of 0.20 gallon alcohol, 94 per cent., and 415 lbs. bleaching powder, 35 per cent., was effected for every 100 lbs. of chloroform made by the new process.

The saving in alcohol was insignificant, but there was no saving expected, the experiments indicating the consumption of 11.5 gallons alcohol for every 100 lbs. of chloroform, while 11.53 gallons were used in actual work. The gain in bleaching powder, however, was 29 per cent., quite near to the 34 per cent. saving, which were indicated by the most favorable experiments in Series N. The consumption of steam was larger than in the old process, since about 400 gallons diluted alcohol were to be distilled off in each operation, in order to recover all the alcohol. About 3 tons steam were required for each apparatus in a day's work. However, 1500 lbs. bleach could be worked daily in each of the six stills, in place of 1000 lbs., and 147 lbs. pure chloroform were manufactured per day in each still, in place of 70 lbs., which could be made by the old process, an increase in capacity of the plant of over 100 per cent.

The amount of steam used by the new process was 2 tons for 100 lbs. chloroform, against 1.1 tons in the process, for the same amount.

The same number of laborers ran the improved plant, after mechanical washers had been installed, the same laborers making more than twice the former product.

There are localities in the western states where corn, limestone and salt are cheap, where coal and power are abundant. There may be a market for caustic soda but none for bleach, which cannot be disposed of on account of the freight rates. By making chloroform, many pounds of material can be condensed into one and can be shipped to the centers of population.

COMPARISON OF SOME METHODS FOR THE ESTIMATION OF SULFUR IN VULCANIZED RUBBER WITH ESPECIAL REFERENCE TO ELECTROLYTIC OXIDATION.

By D. Spence and J. Young.

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This work was primarily undertaken in order to find a rapid and, at the same time, accurate method for the determination of combined sulfur in vulcanized rubber, applicable to samples containing widely different quantities of combined sulfur. A method such as this is well-nigh essential to a study of the kinetics of vulcanization such as we had in view where a large number of simple compounds of rubber and sulfur containing all percentages of sulfur from 0.5 to 32 per cent. had to be investigated. Previous experience in the determination of the sulfur of vulcanization had shown that a method which might be applicable to one compound was not necessarily equally applicable to every other. This was a condition, however, which we had to meet in our work and it is one which is of importance in the every-day analysis of vulcanized rubber.

In view of the ever-increasing importance of methods for the chemical analysis of India rubber and the attention which is being directed towards this subject by committees appointed here and abroad, this present work should be of interest not only as furnishing the solution to our specific problems, but as offering to those engaged in the analysis of India rubber a method for the determination of sulfur at once simple, rapid and accurate, which has not yet received that recognition in this country which it undoubtedly merits.

This is not, and does not pretend to be, a complete study of all the methods which have been published in the literature from time to time for the determination of sulfur in India rubber. We have dealt here only with those methods which, from previous experience or from other reasons, seemed likely to meet the requirements of our work and our attention has, therefore, been confined to a comparative study of the methods of Carius, Henriques (methods involving fusion) and Gasparini (electrolytic oxidation) and to modifications of these by ourselves and others.

The Carius method requires no description here. It has long been recognized as an accurate one for the determination of sulfur in vulcanized rubber and we believe it is still in very general use where the highest accuracy is required. The disadvantages to the method are as well known, however, as the method itself. We need only refer, for example, to the cumbersome and altogether precarious nature of the work involved in the process which even the modifications investigated by us have not succeeded in eliminating. Similarly, the old method of Henriques[1] for the determination of sulfur in rubber and the methods of Frank and Marckwald,[2] Wagner,[3] and others, which are only slight modifications of the former, although perhaps simpler in some respects than the Carius method, require time and attention if reliable results are to be obtained, which, for our work at least, was out of the question. The fusion, namely, of the products of oxidation of the rubber by nitric acid, we have found to be so delicate and precarious an operation, even when carried out by the modified method described in the experimental part of this paper, that if constant care and attention is not given results of very uncertain value may be obtained. Our experience with methods of fusion indeed has been that in the long run more time is involved and less assurance of accuracy in the final result obtained than by a modified Carius method. There is little, if any, advantage, therefore, in fusion methods over Carius methods.

Far more interesting, however, than either of these methods is that of electrolytic oxidation. Of all methods for the estimation of sulfur in India rubber investigated by us, this method proved not only the simplest but also the most reliable. Not only is it unequaled in these respects, but we have found it applicable, and without modification, to the determination of the sulfur in rubber of any degree of vulcanization.

The method was originally evolved by Gasparini[4]

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[1] *Z. angew. Chem.*, **34**, 802 (1899).

[2] *Gummi-Zeitung*, **17**, 71 (1903).

[3] *Ibid.*, **21**, 552 (1907).

[4] *Gaz. chim. ital.*, **37**, II, 426–461 (1907).

for the estimation of sulfur in organic compounds, including vulcanized rubber, and recently has been made use of by Hinrichsen[1] in his work on vulcanization.

The method is an exceedingly accurate one. Indeed, in view of its simplicity and at the same time its accuracy, doing away as it does with all the objectionable features of other methods, it is surprising to us that it has not received more general application. We can only recommend it to the attention of those engaged in the analysis of vulcanized rubber.

To meet the case of complex rubber mixings the method is subject to the same modifications as are common to all existing methods.

In conjunction with a form of volumetric process for the determination of sulfur such as the barium chromate method[2] investigated by us, or the benzidine method of Raschig,[3] we believe the process is capable of still further simplification to meet the requirements of a still more rapid and accurate method for the determination of sulfur in soft-cured rubber. Complex mixings would, of course, require special attention where the volumetric process using barium chromate is introduced. It is only, however, by practical work directed towards the solution of just such problems as these that real progress towards standard methods of analysis of rubber can be hoped to be made.

EXPERIMENTAL PART.

At the outset of this work it was necessary to adopt a standard method of analysis to which all our work could be referred. The Carius method was selected for this purpose in spite of the fact that the values obtained by it are stated to be slightly too high[4] on account of the inclusion in the precipitated sulfate of a very small quantity of silica dissolved from the glass. The error by this method we have found to be very small, however, and constant, if reasonable care is taken. In all our work, therefore, unless otherwise stated, our figures for sulfur are compared with those by the Carius method.

In carrying out the Carius method it has long been customary here to modify the original procedure to the extent of effecting the preliminary solution of the rubber in the acid in a closed bomb at as low a temperature as possible, afterwards opening the tube and heating it on the steam bath until further vigorous action ceases, then resealing the bomb and completing the oxidation by heating the tube to 170° C. for 3 hours. In this way the intense gaseous pressure which is generated in a closed bomb by the first action of nitric acid on India rubber is relieved and the complete oxidation of the rubber takes place under conditions which, while preventing loss of sulfur, are less likely to bring disaster to the estimation by the bursting of the bomb in its final heating. In this modified form the Carius method has been found to be safer and less troublesome than the ordinary Carius process when applied, in particular, to samples of vulcanized rubber having a high content of rubber. The method has been tested by us against the standard Carius method, in which the rubber is first brought in contact with the acid in a closed bomb and is heated before the pressure is relieved, and has been found to give satisfactory results. A comparison of results obtained by this method against those obtained by the electrolytic process will also be found in the section on electrolytic oxidation, which follows.

In the modified method just described the Carius process still, however, remains tedious and somewhat precarious. To further simplify it an experiment was made in which the rubber was added directly but slowly, small pieces at a time, to the acid in the bomb which was warmed or cooled as required in order to complete the solution of the rubber without a too vigorous action ensuing. In this modification, therefore, the preliminary solution and heating took place in *open* bomb. A sample of hard rubber analyzed in this way gave 31.60 per cent. of sulfur as against 31.50 per cent. by the ordinary Carius method. This method of treatment is somewhat simpler and apparently gives accurate results. Even with this modification, however, the Carius method is cumbersome where many sulfur estimations have to be made.

More promising, at first sight, as a rapid method for the determination of sulfur in vulcanized rubber, appears the process of fusion with alkaline oxidizing agents. This process, in its simplest form, consists in the fusion of an intimate mixture of the finely ground material with an excess of powdered sodium carbonate or a mixture of sodium carbonate with potassium nitrate. Such a method has recently been applied with success[1] by one of us to the determination of bromine in the tetrabromide of India rubber and was found to give reliable and satisfactory results in this connection. The process is exceedingly simple. In our efforts to apply it to the determination of sulfur in vulcanized rubber we were confronted, however, with the difficulty of obtaining intimate mixture of the sample with the alkali fusion mixture. Sulfur values were always lower than those by the Carius method. Even in the case of a sample of finely powdered, hard rubber dust, where intimate mixture of the dust with the alkali was possible, 17.53 per cent. of sulfur was found by this method as against 30.80 per cent. by the Carius method. One can only conclude from this that the chemical combination of rubber and sulfur to hard rubber is much more stable towards alkaline oxidizing agents than the corresponding bromine derivative of India rubber. Some incineration experiments carried out, using Eschka's mixture directly, proved equally unsuccessful for similar reasons.

The root difficulty in direct fusion methods as applied to vulcanized rubber undoubtedly lies in obtaining intimate mixture of the rubber material with

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[1] *Koll. Zeitsch.*, **8**, 248 (1911). The statement by Waters and Tuttle, THIS JOURNAL, **3**, 734 (1911), that this method is due to Hinrichsen is, therefore, incorrect. Gasparini has shown how the method may be applied to the oxidation of vulcanized rubber.

[2] *Amer. Chem. Jour.*, **2**, 567 (1880).

[3] *Z. angew. Chem.*, **1903**, 617 and 818. See Sutton's "Volumetric Analysis," 10th edit., p. 353.

[4] Anelli, *Gaz. chim. ital.*, **41**, I, 334.

[1] *Le Caoutchouc et la Gutta Percha*, **8**, 88, 5313 (1911).

the fusion mixture. It was to overcome this difficulty that Henriques[1] evolved the method of first dissolving the rubber in nitric acid, taking the solution thus obtained to syrupy consistency before mixing with the fusion mixture. This is a great advance over simple fusion, and with care and attention the old method of Henriques has been found reliable in the hands of experienced analysts. For the sake of a comparison we made a number of estimations by the Henriques and our modified Carius method on samples of vulcanized rubber having widely different sulfur content. The Henriques method was carried out by us in the modified form as described by Frank and Marckwald.[1] The results obtained by the two methods are given in tabular form in Table I.

TABLE I.

Method.	Total sulfur. Per cent.	Combined sulfur. Per cent.	Total sulfur. Per cent.	Combined sulfur. Per cent.	Total sulfur. Per cent.	Total. sulfur. Per cent.
Carius method.....	13.14	3.95	22.73	5.21	8.04	4.59
Henriques method..	12.97	3.67	21.65 22.17 22.50	5.08 5.05	7.97	4.44

The results are not as satisfactory as we had hoped they would be. Our practical experience with the method, besides revealing to us that it is excessively cumbersome and altogether unsuitable for the work we had in view, showed that it still contains one cardinal weakness which the treatment with nitric acid in the first instance does not overcome. The treatment, namely, of the rubber by nitric acid results in the formation of nitro derivatives of the rubber ("nitrosites") which on fusion with alkali will sometimes cause spurting and small explosions with loss of sulfur even when the utmost care and constant attention is given to the fusion process. The results by the method are usually low in consequence. The trouble lies largely in the fact that it is well-nigh impossible to obtain a uniform mixture of the syrupy products of decomposition of the rubber by nitric acid with the solid alkaline mixture.

We lay no claim to be the first to draw attention to this inherent weakness in the Henriques fusion process. To overcome it, Wagner[2] has suggested the diluting of the syrup obtained by treatment of the rubber by nitric acid with water, rendering the aqueous solution thus obtained faintly alkaline by means of solid KOH and afterwards concentrating to half bulk before mixing with excess of sodium carbonate and fusing. The underlying idea we believe to be a happy one. We have gone further, however, and have modified Henriques' method to the extent of mixing the products of oxidation of the rubber by nitric acid with the alkaline fusion mixture in solution, afterward taking the whole to dryness prior to fusing. In this way complete and thorough mixing of the products of oxidation of the rubber with the fusion mixture is effected and the subsequent fusion can be readily carried out without much difficulty or danger of loss due to ignition of the mixture. The method as carried out by us was as follows:

The rubber is dissolved in a mixture of 10 cc. fuming HNO_3, 5 cc. H_2O and 3 g. KNO_3 with cautious warming, if necessary, to start the reaction. The solution obtained is evaporated almost to dryness, the residue dissolved in a solution of 6 g. Na_2CO_3 in 15 cc. H_2O, thoroughly mixed with same, and again taken to dryness. The drying of the mixture and subsequent fusion are carried out with the usual precautions:

Results.	Modified Henriques. Sulfur found. Per cent.	Carius. Sulfur found. Per cent.
I.	31.26	30.80
II.	23.07	23.34

That no great loss occurs in the process of fusion as carried out by us was shown by an experiment in which the rubber was dissolved in fuming nitric acid and water as above and the solution afterwards made up to a known volume (50 cc.) with fuming nitric acid. One-half of this standard solution was treated by our modified Henriques method while the sulfur in the other portion was determined by Carius:

	a. By fusion. Per cent. S.	b. By Carius. Per cent. S.
Results......................	31.09	31.22

Some experiments on the modified Henriques method, using nitric acid saturated with bromine, as recommended by Waters and Tuttle,[1] were also made.

The results are given in the following table and in comparison with the values by Carius are, on the whole, satisfactory:

Method.	Sample I. Combined S. Per cent.	Sample II. Combined S. Per cent.	Sample III. Combined S. Per cent.
Modified Henriques (Waters and Tuttle)..............	3.01	10.93	31.47
Carius.....................	3.05	11.28	31.44

The experience derived from our study of the methods of fusion outlined above showed, however, that although accuracy can be obtained by these methods, great care and constant attention is required if they are to be reliable in every instance. Even the best of them are cumbersome and are not adapted to rapid and at the same time accurate work. This is an important point where the accurate estimation of sulfur in India rubber is a routine laboratory operation.

Very different, on the other hand, were our experiences with the electrolytic process of decomposition. This process, originally designed by Gasparini[2] for the estimation of sulfur in organic compounds in general, depends on the decomposition of the organic substance by nitric acid in presence of an electric current. Gasparini designed a somewhat complicated apparatus to carry out the oxidation of the organic substance without loss of sulfur. We have found, however, that as far as the sulfur of India rubber is concerned, any complication of this kind is unnecessary and that accuracy can be obtained by very simple means. In the early stages of our work on this method we were confronted, as was to be expected, with difficulties, difficulties not confined,

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[1] *Loc. cit.*

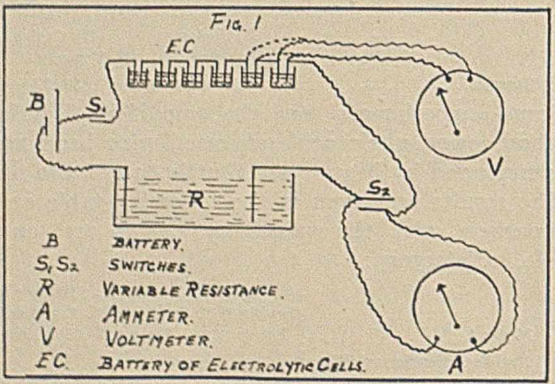
[2] *Gummi-Zeitung*, **21**, 552 (1907).

[1] THIS JOURNAL, **3**, 10, 734 (1911).

[2] *Loc. cit.*

however, to this method only, but these disappeared one by one as we became better acquainted with the method so that in the form in which we now present it, the method can be readily carried out even by the inexperienced.

The sample of rubber weighing about 0.5 gram[1] is put into a tall 200 cc. Jena glass beaker and covered with concentrated HNO_3 (sp. gr. 1.4). The beaker is covered by a clock glass and is then very gently warmed on the steam bath. As soon as the reaction starts the beaker is removed from the steam bath and the solution allowed to continue without further heating. If too much heat is applied at the beginning, it may be necessary to put the beaker in cold water in order to moderate the reaction. In about 2–3 minutes the solution of the rubber is complete and all frothing of the liquid ceases. To this solution is now added 30 cc. of fuming nitric acid (sp. gr. 1.5) with which the clock glass is washed. A current of electricity is now passed through the solution between electrodes of platinum foil. The most suitable current is 3 amperes with a potential of 6–8 volts between the electrodes. The electrical connections are made as shown in the diagram (Fig. 1).



The current may be taken from any d. c. source and if necessary is reduced by means of a variable resistance, R. The ammeter A is shunted at the terminals of the switch S_2 so that by opening the switch it is thrown into the circuit. The voltmeter V is introduced between the terminals of the electrodes. Any number of estimations may be connected up in series, the voltage in each cell being tested separately. The time required for the complete oxidation of the rubber varies with the sample. For soft-cured rubber containing a high percentage of rubber we have found that 2 to 3 hours are required. With hard rubbers containing a lower percentage of rubber the oxidation is complete in $^3/_4$ to 1 hour. At the end of the action the electrodes are removed and washed with water. About one gram of pure Na_2CO_3 is then added and the solution evaporated to dryness on the steam bath. The residue is moistened with conc. HCl and taken to dryness again. The residue which should be free from nitric acid and nitrates is dissolved in hot water, filtered if necessary from insoluble matter and the sulfur precipitated as barium sulfate in the usual way.

The solution of the rubber, when carried out as described, proceeds smoothly and without difficulty. The electrolysis, when the current and voltage have once been determined, proceeds quietly and requires no attention whatsoever on the part of the operator. The final stage of the process is common to all methods for the determination of sulfur where nitric acid is used and requires no criticism here.

In order to still further simplify the method the apparatus shown in Fig. 2 was designed by us. This apparatus enables six estimations to be carried out at one time and does away with all binding screws and cumbersome connections—a very desirable feature, particularly where nitric acid is in constant use.

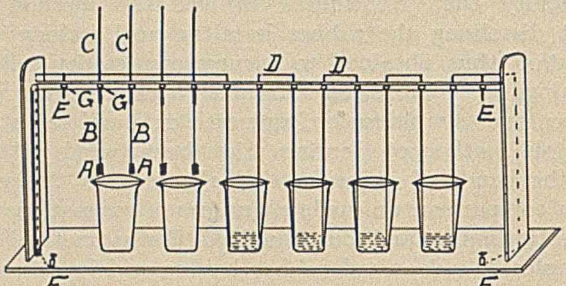


Fig. 2.

The decomposition of the sample is carried out in beakers as before. These are the regular "high form type" of beaker of Jena glass and have the following dimensions approximately: Height 100 mm., diameter 55 mm., capacity 200 cc. The beakers are covered by clock glasses split in two in order to admit of the wires carrying the electrodes. The electrodes A are of platinum foil (one sq. inch in area) riveted to a piece of platinum wire, B. The free end of the wire is fused into a glass tube filled with mercury. The glass tubes slide in grooves cut in the cross support, and the electrodes can in consequence be fixed at any height by means of the wooden binding screws G,G. Connections are made by means of small bridges of copper wire, D, dipping into the mercury in the glass tubes. The binding screws F,F are connected by means of a wire with the mercury cups E,E. With the connections arranged in this way it is a simple matter to remove or introduce an estimation at any stage, connection being made across the gap with a double-length bridge.

If the dimensions and quantities specified above are adhered to, a determination of the potential difference between the electrodes of each cell becomes unnecessary in each estimation, for, with the electrodes placed at the extreme circumference of the beaker, opposite one another and completely immersed in the acid, we have found that the required voltage is at once attained with sufficient accuracy for the purpose of the estimation.

The reaction in the cell, which is fairly vigorous at first giving rise to a considerable evolution of heat, soon moderates and when decomposition is complete almost ceases, the potential difference meantime falling gradually.

Some results of analyses of products of different degrees of vulcanization are given in the following table. These show the applicability of the method to the analysis of rubber of all degrees of vulcanization:

Method.	1. Sulfur found. Per cent.	2. Sulfur found. Per cent.	3. Sulfur found. Per cent.	4. Sulfur found. Per cent.	5. Sulfur found. Per cent.
Electrolytic oxidation.......	1.27	3.02 3.11	4.19	11.35 11.39	31.39 31.39
Carius.....................	1.32	3.05	4.27	11.28	31.44

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[1] More may be conveniently used where the sulfur content of the sample is very low.

The method of electrolytic oxidation is now in regular use here. A great deal of work has recently been carried out by means of it where both total and combined sulfur in vulcanized samples of rubber mixings had to be determined. These results have not only served to establish beyond all doubt the accuracy of the method but they have shown that it leaves little to be desired in the way of a simple process for the determination of sulfur in India rubber.

By introducing a volumetric process for the determination of the sulfur we have found it possible to still further simplify this method. We have found, namely, that the Pennock and Morton[1] rapid process for the determination of sulfur in coal and coke can be advantageously employed where the variation in the amount of sulfur present in different samples is not great.

This process depends on the decomposition of barium chromate by sulfuric acid, the liberation of iodine from potassium iodide in acid solution by the chromic acid set free and the titration of the iodine liberated by sodium thiosulfate. 1 cc. $N/10$ thiosulfate is equivalent to 0.001067 gram sulfur.

A rigorous investigation of this process was first made on standard solutions of potassium sulfate of different concentration. We will refrain, however, from quoting our results in this connection. The method was found to be satisfactory where the sulfur present did not vary within wide limits. Several analyses of India rubber were then carried out by this method and checked against the ordinary gravimetric process. Results:

Volumetric. Per cent. S.	Gravimetric. Per cent. S.
1.602	1.43
3.38	3.29
22.31	23.34

Only the results of the lower values are in agreement with the gravimetric figures. In carrying out this process one of the first essentials appears to be that the sulfuric acid and excess of barium chromate used in each experiment shall be as nearly as possible constant quantities. This is a comparatively easy matter to arrange where, as in the case of normal cured soft rubber, the sulfur does not usually exceed 5-6 per cent. and is a fairly constant quantity. But when, as in the examples cited, the variation is great and the correction to be applied is unknown and a constantly varying quantity, errors arise in the volumetric process. That it is impossible to overcome this difficulty by selecting a suitable weight of sample for analysis is fairly evident. This is not always an easy matter, however, where the sulfur content of the sample may vary between 0.5 per cent. and 32 per cent. In our work, therefore, in the meantime, we have adopted the gravimetric process until the foundations of the volumetric method shall have been more fully investigated.

A METHOD FOR DETERMINING THE VALUE OF COMMERCIAL STARCHES FOR USE IN COTTON MILLS.

By G. M. MacNider.

Received Jan. 16, 1912.

In the manufacture of all grades of cotton cloth the yarn is prepared for the loom by a process known as sizing, in which it is treated with a solution of starch to give it certain properties essential to good weaving. With many grades of cloth, the cloth goes through a process known as finishing, where it is again treated with starch to produce a "finish" before it is put on the market. It is thus seen that the cotton mills use annually large quantities of starch and the purchase of the best starch for the purpose in hand becomes a very important matter.

The value of starch for cotton mill purposes depends on its property of swelling and forming a viscous solution when treated with hot water. It is the purpose of this paper to give a method for determining the viscosity of starch solutions which will show the comparative value of the different starches for use in cotton mills. The sizing and finishing of cotton goods are very technical operations and will not be taken up in detail. Sufficient reference will be made to them to show the function of the starch solution.

The object of sizing is to make the yarn stiffer, increase the strength and put it into proper condition for weaving. To accomplish this, the size must penetrate the yarn to some extent and also form a coating on the surface of the thread, which prevents wear of the thread in the loom. The size is prepared by boiling the starch (and other ingredients) with water and is applied to the yarn while hot. The machinery is so constructed that the threads are dried immediately after passing through the size.

The object of finishing is to give a stiffness to the cloth and produce a certain finish and "feel" which are very important factors in marketing cotton goods. As in sizing, the cloth is passed through a hot solution of the finish and then dried and rolled with hot rollers to bring out the finish. The use of the starch solution alone in these operations would make the goods too stiff and produce a harshness which is not desirable. To modify this, various softening agents are used, *viz.:* tallow, various oils, soaps, magnesium chloride, magnesium sulfate, glycerine, etc., and in many mills various sizing and finishing preparations.

The principal starches used by the cotton mills are corn, potato, cassava, and to a small extent wheat, sago and rice. In England, wheat flour and rice flour are used to a considerable extent, but in America they are used very little. As will be seen later, each one of these starches has a different viscosity and therefore must be used in a different manner. Some authors attribute the differences in the characteristics of the starch solutions to the size and shape of the starch grains. There is no definite relation existing to prove this. The appearance of the different starch grains under the microscope are shown in the following cuts.[2]

A number of methods have been proposed for determining the viscosity of starch pastes, but in none of them has an attempt been made to determine the viscosity of the starch under conditions similar to those under which it is used in the cotton mills; conse-

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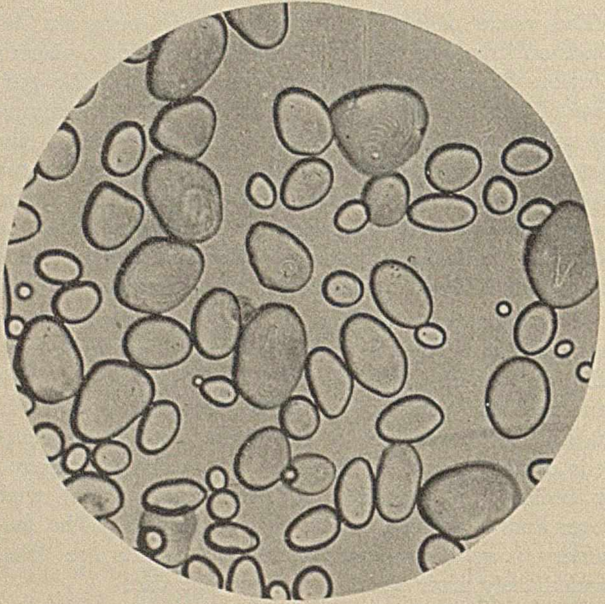
[1] *Jour. Am. Chem. Soc.*, **25**, 1265.

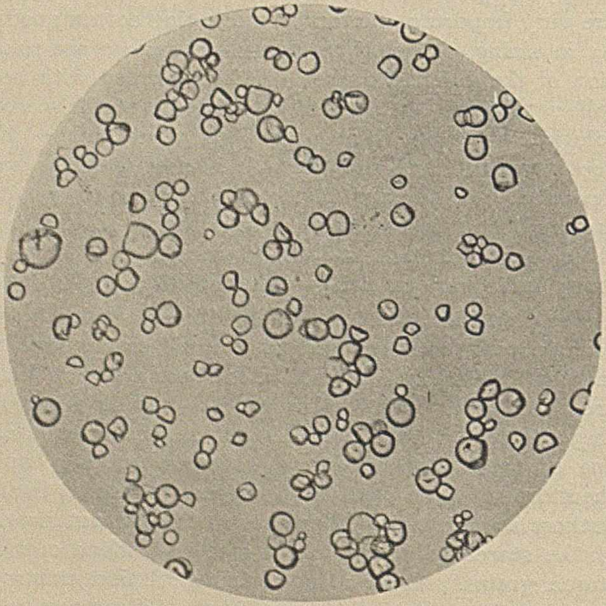
[2] These cuts were very kindly furnished the author by Mr. B. J. Howard, of the Bureau of Chemistry, Washington, D. C.

quently they do not show the value of the starches for these purposes. Following is a brief description of the methods which have been proposed:

Whewell[1] uses a method for determining the viscosity of starch pastes which depends upon measuring the ability of thick pastes, made of definite amounts of starch, to support a known weight for a definite length of time. This method is a measure of the strength of the film formed on the surface of the paste and is not a measure of the viscosity; it frequently gives results which are the reverse of actual viscosity measurements.



POTATO STARCH × 200.



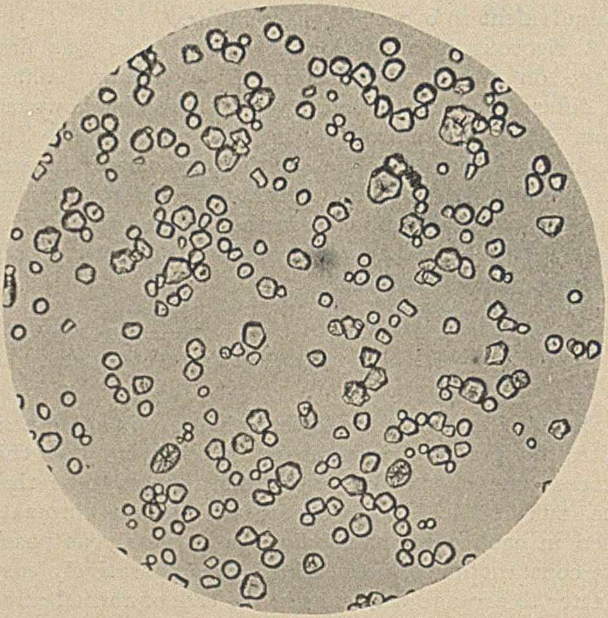
CASSAVA STARCH × 200.

Saare[2] and Martens propose a method, the essentials of which are making in a beaker a paste of definite weight and immersing in it a brass disc attached to a wire; the disc is supported at a definite point in the paste and the whole allowed to stand for 20 hours at 17.5° C.; by means of a balance attached to the disc, the weight required to draw the first weight out of the paste is then measured and the last weight is taken as an indication of the viscosity of the starch.

Benz[1] and Marx propose a method for determining the stiffness of starch paste which is very similar to the one given by Saare and Martens.

Coppenberg[2] describes a viscosimeter for starch pastes in which a spherical weight is drawn upwards through a column of the paste of fixed height and temperature. The time in seconds occupied in doing this, under the pull of a known load in grams, constitutes an observation. The apparatus is adaptable only to thick liquids.

Ermen[3] proposes a method for determining the viscosity of starch in which the starch paste is made by treating the starch with a solution of sodium hydroxide. The paste is allowed to stand for a certain length of time and the viscosity determined in a Redwood viscosimeter.



CORN STARCH × 200.

The use of alkali in making the paste prevents this method from being a measure of the viscosity of the starch, as the paste formed by treatment with alkali has entirely different properties from the straight starch paste.

Bean[4] gives the following method for testing the consistency of wheat flour and starches. The samples are placed in beakers with the proper amount of water; the beakers are immersed in boiling water, allowed to remain 15 minutes, removed and allowed to cool for 12 hours. A sample of the standard starch or flour to be used for comparison is treated in the same manner. "Any variation in the consistency may be judged by pressing the fingers into each sample."

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[1] *Chem. News*, **39**, 97.

[2] *Zeits. Spiritusind.*, **26**, 1903; Abs. in *J. Soc. Chem. Ind.*, **22**, 1903.

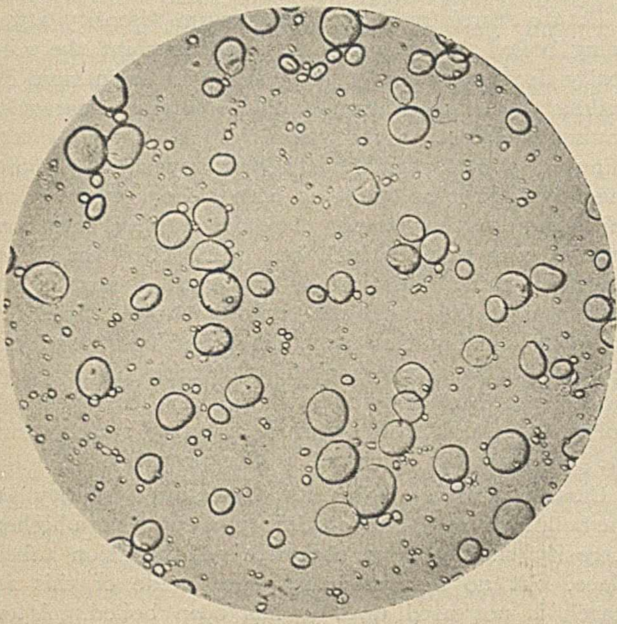
[1] *Chem. Ind.*, **32**, 1909; Abs. in *J. Soc. Chem. Ind.*, **28**, 1909.

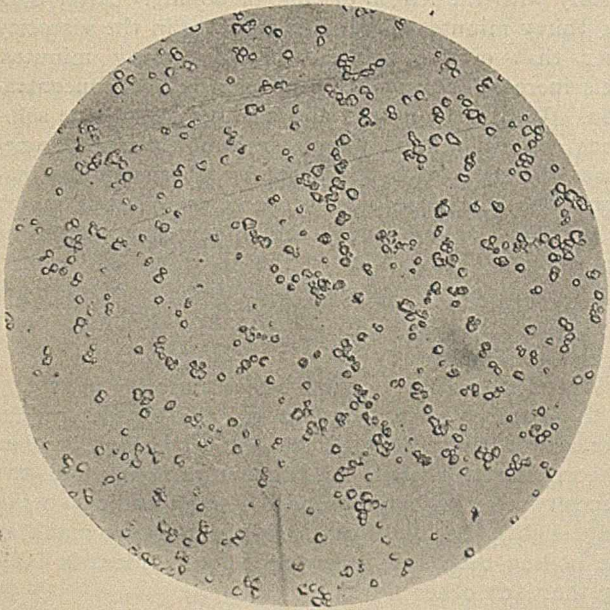
[2] *Chem. Zeit.*, **34**, 1910; Abs. in *J. Soc. Chem. Ind.*, **29**, 1910.

[3] *J. Soc. Chem. Ind.*, **26**, 1907.

[4] "The Chemistry and Practice of Sizing."

In both sizing and finishing the starch is boiled with water for a certain length of time and the solution applied to the yarn or cloth at a temperature a few degrees below boiling. The temperature is not allowed to fall below 70° C. and is usually maintained at about 90° C.


Wheat Starch × 200.


Rice Starch × 200.

These methods do not test the viscosity under conditions similar to those under which the starch is used in the mills, and consequently no deductions can be made from the results as to the value of the starches for mill purposes.

In the following method the starch solution is prepared by boiling the starch with water for a definite length of time and the viscosity of the hot solution is measured by means of a Scott viscosimeter. In this way the viscosity of the starch solution is obtained under conditions practically identical with those under which it is used in the mill.

Before starting the determination, the viscosimeter bath should be filled with water which is kept boiling throughout the operation. The method is as follows:

Twelve grams of the starch are weighed into a 600 cc. beaker, 300 cc. distilled water added (thus making a 4 per cent. solution) and heated over a Bunsen burner with constant stirring to the boiling point and boiled for ten minutes; 200 cc. of this solution are then poured into a viscosimeter cup, the temperature allowed to become constant, and 50 cc. run out into a graduate, the time being accurately measured with a stop watch. The number of seconds required to deliver 50 cc. of the solution divided by the number of seconds required to deliver 50 cc. of boiling water gives the viscosity.

Before the starch is weighed out it should be thoroughly pulverized to remove the lumps. During the heating and boiling it is very necessary that the solution be constantly stirred to prevent the formation of lumps and caking on the bottom and sides of the beaker. Glass beakers break so easily in boiling the heavy solutions that aluminum beakers were substituted and used for all determinations.

A number of determinations were made at first to determine the best amount of starch to use and the necessary length of time to boil the solution. It was found that a four per cent. solution of starch was the most satisfactory strength to use. With thin boiling starches this strength solution is heavy enough to measure the viscosity satisfactorily while the starches forming thick solutions are not too heavy to interfere with the accuracy of the determination. With potato and cassava starch it would be practically impossible to obtain accurate results with a stronger solution. Ten minutes was decided upon as the best length of time for boiling, as this is long enough to develop the characteristics of the starch and at the same time the solution has not been effected by loss from evaporation. The temperature at which the determinations were made was the temperature which the boiling solutions assumed on being poured into the viscosimeter cup, the viscosimeter cup being surrounded by boiling water. With most of the starches this was 94° C. With rice starch the temperature fell to 92.5° C. It was found that at such high temperatures a variation of one or two degrees does not appreciably effect the viscosity, though at lower temperatures a variation of less than a degree produces a marked effect. In all determinations checks were obtained which did not show a variation greater than two-fifths of a second and most of them checked within one-fifth of a second. With the viscosimeter used, the time required to deliver 50 cc. was 9 seconds. This figure was used in calculating all determinations.

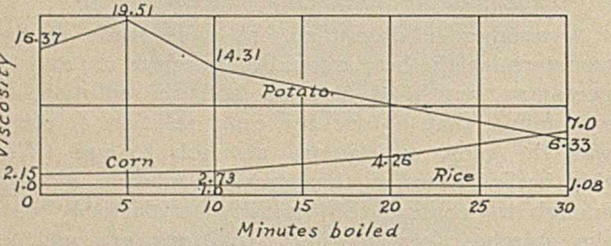
The following table shows the viscosity of the starches examined and the variation in the viscosity of different lots of the same kind of starch:

VISCOSITY OF COMMERCIAL STARCHES.

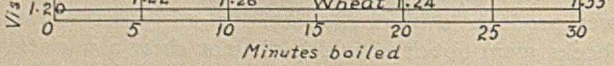
12 grams starch in 300 cc. water; boiled 10 minutes.

No.	Starch.	Seconds to deliver 50 cc.	Viscosity.
510	Corn	22.4	2.49
508	Corn	25.8	2.86
521	Corn	24.6	2.73
502	Potato	128.8	14.31
524	Cassava	35.0	3.88
526	Cassava	35.8	3.97
527	Wheat	11.4	1.26
525	Wheat	11.2	1.24
528	Rice	9.0	1.00

From the above table it is seen that there is a wide variation in the viscosity of the commercial starches and consequently an equally wide variation in their value for mill purposes. It will be noticed that there is a considerable variation in the viscosity of different samples of the same starch. This may be due to several factors: the maturity of the plant from which the starch is made, the method used in manufacture and the manner in which the starch is dried; the latter will effect the amount of moisture in the starch. Starches of the same kind with different moisture content will show a variation in viscosity. This variation will be small unless the variation in moisture content is very large. While no attention is paid to the viscosity at present, it would be very advantageous to the mills for each lot of starch (of the same kind) to have a uniform viscosity. This would enable them to obtain the same results in sizing and finishing without changing the formula for each lot of starch. By the above method a very small variation in the viscosity of a starch may be detected.



In practice the starch solution is boiled for a certain length of time before being used. To determine what effect this has on the viscosity of the solution, viscosity determinations were made at different periods of boiling with each starch. The results obtained are shown by the accompanying curves.



In boiling the starch solutions no attempt was made to keep the volume constant, as the addition of water to a starch solution materially reduces the viscosity. The loss from evaporation was practically the same with all solutions, and as they were carried out under the same conditions the results are comparable. In boiling rice starch 30 minutes the loss from evaporation was greater than with the other starches, but as this starch shows no change in viscosity on continued boiling this need not be considered.

From the curves it will be seen that the viscosity of corn starch increases uniformly with the length of time of boiling. This increase is about what would be expected with the concentration of the solution when there is no change in the starch. This is a very valuable property of corn starch as compared with other starches.

Potato starch reaches its maximum viscosity after being boiled five minutes. From this point the viscosity decreases rapidly with the increase in time of boiling, the concentration of the solution apparently having no effect on the viscosity. After boiling ten minutes, potato starch has a viscosity slightly more than five times as great as corn starch, while after thirty minutes the viscosity of potato starch is less than that of corn starch which has been boiled the same length of time. The author has found a number of references to the fact that potato starch "loses its strength" or liquefies on boiling, but has found no reference to the degree to which this takes place. The data given here show very strikingly the effect of boiling on this starch. Corn and potato starch form the two extremes in regard to this property.

Cassava starch attains its maximum viscosity at the boiling point. The solution apparently has a higher viscosity shortly after complete gelatinization takes place, but no measurements were made of this as starch is not used until it has been boiled. After reaching the boiling point the viscosity decreases uniformly with the length of time of boiling. After boiling thirty minutes there is an increase in the viscosity over that of the solution boiled twenty minutes. This increase is probably due to increased concentration. With both potato and cassava starch the solutions contain a good many air bubbles which sometimes interfere with the accuracy of the determination. As will be seen from the curve, cassava starch behaves in a manner very similar to potato starch as regards the liquefaction of the solution, but not to the same extent. Cassava starch therefore has a much broader application in sizing and finishing than potato starch.

Wheat starch has a much lower viscosity than any of the starches so far considered. It shows a gradual increase in viscosity with the time of boiling, similar to corn starch, though the total increase is small, the viscosity of the thirty-minute determination being only slightly higher than the determination made at the boiling point. Wheat starch foams more in boiling than any other starch.

Rice starch has the same viscosity as water. At the end of thirty minutes' boiling it shows only a very slight increse in viscosity.

It is a fact that starch goes into solution on continued boiling, that is, it is converted into soluble starch. The degree to which this takes place varies with the different starches. This is the only way of accounting for the marked differences in the viscosities of the various starches. Why the rate of solution should be so high in potato and so low in corn is not known. It is a remarkable fact that the starches from roots and tubers, developed under ground, potato and cassava, show a high rate of solution while the starches from the grains, developed above ground, corn, wheat and rice, show a very low rate of solution.

SPECIAL OR TREATED STARCHES.

A number of starches are now used which are sold under a trade name, the advantages claimed for them usually being that they are "thin boiling starches." These are usually corn starch, which has been treated in some way to reduce the viscosity. The viscosities of six such starches are shown in the following table:

Viscosity of Special or Treated Starches.

12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch.	Seconds to deliver 50 cc.	Viscosity.
506	Eagle finishing...........	10.4	1.15
519	N starch, alkaline........	19.2	2.13
511	Blue River, Pearl........	19.2	2.13
529	Famous N..............	10.6	1.17
530	Thin boiling Crystal......	11.2	1.24
531	Thin boiling Pearl.......	11.0	1.22

The Eagle finishing starch is corn starch treated with borax. The viscosity is less than half as great as that of straight corn starch. It will be seen from data given later that this starch has been treated in some manner other than the addition of a small amount of borax.

The N starch is corn starch made slightly alkaline. The alkalinity of this starch is equivalent to 0.001 gram of sodium hydroxide to each gram of starch. The viscosity of this starch is a few points lower than corn starch.

The other samples are treated corn starch, which are neutral and do not show any evidence of the way in which they have been treated.

Some determinations were made to ascertain the effect of several reagents known to be used in treating starches, on the viscosity of corn starch.

The effect of boiling corn starch with borax is shown in the following table:

Effect of Borax on Viscosity of Starch.

12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch.	Borax added. Gram.	Seconds to deliver 50 cc.	Viscosity.
510	Corn................		22.4	2.49
510	Corn................	0.077[1]	19.0	2.11
521	Corn................		24.6	2.73
521	Corn................	1.0	26.0	2.86

From the data given, it is seen that a small amount of borax reduces the viscosity, but a slightly larger amount increases the viscosity. Bean[2] found that borax added to a thick starch paste while hot causes the sticky paste to lose its power of adhering to other substances and develop strong cohesive powers. The paste thus formed has the appearance of a jelly and may be rolled in the hands without any of it adhering to the hands. The properties of the starch are completely changed. The author has found a finishing preparation which is composed of starch treated with borax in this manner. Boric acid does not produce this effect.

The effect of boiling corn starch with alkali is shown in the following table:

Effect of Alkali on Viscosity of Starch.

12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch.	NaOH added. Gram.	Seconds to deliver 50 cc.	Viscosity.
521	Corn................	....	24.6	2.73
521	Corn................	0.06	20.8	2.31

The amount of sodium hydroxide used was calculated from the alkalinity of the sample of N starch. From this it is seen that a very small amount of alkali produces a decided decrease in the viscosity. Some determinations were made using one-half of one per cent. of sodium hydroxide, but as soon as gelatinization took place the solution foamed so much that it was not possible to boil it. This excessive foaming would prevent the use of any considerable amount of alkali in sizing. The data obtained shows that a very small amount of alkali reduces the viscosity of starch, but a larger amount increases the viscosity.

In analyzing some sizing preparations it was found that boric acid was frequently used in them. Some determinations were made to determine the effect of boric acid on the viscosity of starch. The results are given in the following table:

Effect of Boric Acid on Viscosity of Starch.

12 grams starch in 300 cc. water; boiled 10 minutes; temperature 94° C.

No.	Starch.	Boric acid added. Grams.	Seconds to deliver 50 cc.	Viscosity.
508	Corn................	..	25.8	2.86
508	Corn................	1	23.2	2.57
508	Corn................	3	21.8	2.42
508	Corn................	6	23.0	2.55

From this it is seen that a very small amount of boric acid reduces the viscosity, but when the amount is increased to as much as one gram of boric acid to two grams of starch the reduction in viscosity is not as great as when a smaller amount is used. If boric acid is used in sizing it should be used only in small amount.

It is often stated that some starches give a smooth finish to goods while others give a harsh finish. This property adapts the starches which produce a smooth finish for use on the finer grades of cloth which must have a smooth, soft finish, while the starches which do not produce such a finish are better adapted to the heavier grades of cloth. With most grades of cloth, no matter which one of the starches is used, some softening ingredient must be used with the starch to produce the desired result, and it is therefore more economical, in the majority of cases, to use a cheap starch and control the finish by use of softeners than to control the finish by varying the kind of starch used.

From the data which has been presented it is seen that the viscosity of the starch solution is the most important point to be considered in sizing and finishing cotton goods. As has been previously stated, to give satisfactory results the solution must penetrate the yarn or cloth and also form a coating on the outside. The viscosity does not show the stiffness which

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[1] Amount of borax calculated from ash determination of No. 506.

[2] "The Chemistry and Practice of Sizing."

will be given to yarn or cloth. This would be very difficult to determine, but it shows the comparative penetrating ability and the effect of boiling on the starches, and from this can be judged the effect which any given starch will produce on yarn or cloth. As there is so much difference in the viscosities of the several commercial starches it is very important for the manufacturer to use the starch which will give the most satisfactory results. When the costs of the different starches are considered this becomes a still more important matter. If, in sizing and finishing, the manufacturers will use only the kind of starch and softeners which are actually necessary to produce most economically the desired results, it will result in a great saving to all the mills engaged in this class of work.

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THE CHEMISTRY OF ANAESTHETICS, IV: CHLOROFORM.

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(*Continued from May No.*)

VIII. The Examination of Anaesthetic Chloroform.

I. THE TESTS FOR ODOR.

Pure anaesthetic chloroform possesses a characteristic odor,[1] and such chloroform volatilizes entirely without disagreeable or foreign odor. This property may be altered more or less by the presence of impurities, however, and this applies in particular to poorly rectified anaesthetic chloroform and commercial chloroform. The substances giving rise to a foreign or evil odor are the result of impurities present in the alcohol, acetone, etc., employed in the manufacture of the chloroform, or they are produced by various decompositions which occur; yet, as in the case of ethyl ether, there have been instances of sophistication, although these are now rare. There are more frequent cases of contamination resulting either from a lack of control in manufacture or from careless storage. We shall concern ourselves here with the impurities which are less volatile than chloroform, and which may consequently be recognized by evaporation tests.

About 1850, chloroform was found to be frequently contaminated with "oils" and in 1865, and thereabout, it was considered that "empyreumatic oils" were among the principal impurities of chloroform. It was known at this time that chloroform prepared from wood spirit was much less pure than that obtained from ethyl alcohol;[1] and that the first-mentioned was generally specifically lighter than chloroform made from alcohol, possessed a repulsive empyreumatic odor when crude, and, unless carefully purified, produced unpleasant sensations when inhaled.[2] It was learned that such chloroform was contaminated with approximately 6 per cent. of an "empyreumatic oil" containing chlorine;[3] and a similar oil was obtained by Soubeiran and Mialhe,[4] although in smaller quantity, in the preparation of chloroform from alcohol.[5]

About 1875 the presence of fusel oil in commercial chloroform was noted,[6] and it is likely that the anaesthetic chloroform in use from 1860 to about this time was generally contaminated with higher alcohols. A sample of anaesthetic chloroform made in 1863 was found by the authors to contain propyl alcohol.[7] Several even regarded the sickness following the use of chloroform to be due to the presence of amyl alcohol.[8] It was incorrectly pointed out that chloroform containing amyl or butyl compounds had a higher density than 1.500; and Gay[9] proposed a test for the presence of amyl alcohol based on odor.[10] The source of such contamination was both the impure alcohol used in the manufacture as well as that added as a preservative; and it was pointed out by Regnault and Hardy[11] that chlorinated compounds were formed by the action of bleaching powder on isopropyl, isobutyl, and isoamyl alcohols, and that, therefore, the alcohol used in the preparation of chloroform should not contain fusel oil.

In view of the possible contamination of anaesthetic chloroform with such substances, the value of a care-

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[1] Passy (*Compt. rend.*, **116,** 769) made comparative experiments on the odorous power of chloroform, bromoform and iodoform, whjch afforded the following sharp results in millionths of a gram:

Chloroform	30.00
Bromoform	2–5
Iodoform	0.06–0.7

We may mention here that the odor of chloroform vapor may be masked by means of oil of cloves (Nussbaum, *Rundschau*, **1888,** 759), but more satisfactorily, from a medical standpoint, by the use of terpineol, for example. The authors, in conjunction with Dr. J. T. Gwathmey, have devised an effective means of masking the odor of both chloroform vapor and ether vapor; this method is now being used in practice.

[1] Ulex (*Year-Book Pharm.*, **1875,** 109) reported that certain chloroform conforming to all the requirements of the German Pharmacopoeia of that time was still unfit for medicinal use, and that upon the evaporation of a sample the residue developed an empyreumatic odor, resembling that of wood-spirit.

[2] Gregory (*Pharm. J.*, **9,** 580) considered that the unpleasant effect observed by Simpson and Carmichael in using one kind of chloroform was due to oily impurities. He stated that chloroform purified by means of sulphuric acid and then distillation over lime or barium carbonate, contained traces of "oils."

[3] This was found to burn with a smoky flame, to be lighter than water, and to boil between 85° and 133° C.; this oil, it was learned, could not be completely separated by simple rectification, but it was found to be nearly destroyed by distillation with sulphuric acid.

[4] *Ann. chim. pharm.*, **71,** 225.

[5] 20 kg. of chloroform from alcohol (presumably crude) were found to yield, when rectified over a water bath, 40 grams of oil residue; this was heavier than water, had an odor differing from that of the oil from wood-spirit, and possessed a boiling point varying from 68° to 117° C. Pemberton (*Pharm. J.*, **12,** 599) considered that Soubeiran and Mialhe had erred in describing the oily substance as a chlorinated oil; he believed it to be a mixture of paramylene and metamylene, with possibly traces of amylene, and that the slight volatility would prevent injurious effect during inhalation.

[6] Rump, *Archiv. Pharm.*, October, 1874.

[7] In Section IX, of this paper, the results of the examination of this sample will be given.

[8] For example, Martindale (*Pharm. J.*, [**3**], **12,** 734) and Werner (*Archiv. Pharm.*, [3], **12,** 481). Werner rectified about 5 kg. of chloroform and found in the residue a small quantity of a substance resembling fusel oil in odor. Valeric acid was obtained on distilling the residue with sulphuric acid and potassium dichromate, thus showing the presence of amyl alcohol, which undoubtedly owed its origin to the fact that crude 80 per cent. alcohol was often used at that time in the preparation; and during rectification it is possible for vapors of chloroform to carry over traces of fusel oil.

[9] *J. Pharm. Chim.*, **4,** 259.

[10] This test was as follows: A piece of filter paper saturated with the chloroform should dry completely, and the odor remain pleasant to the end; the contrary was said to indicate the presence of amyl alcohol.

[11] *J. Pharm. Chim.*, [4] **30,** 405.

fully conducted test for odor has been generally recognized, notwithstanding the fact that it sometimes happens that only a very impure chloroform will leave any unpleasant odor after evaporation and that occasionally the residue is of a pleasant odor.[1] The first condition is dependent upon the nature of the test, especially its lack of delicacy; but even if the residue possesses a pleasant odor, if this is foreign, the chloroform must be contaminated.

Tilden[2] recommended the hand evaporation test for odor, while Regnault[3] recommended the method which has come into general use—evaporation on paper. It is generally stated that "pyrogenous oils," etc., may be detected in anaesthetic chloroform by allowing a definite volume to evaporate from a large piece of filter paper placed on a warm plate, when no foreign odor should be perceptible. The *British Pharmacopoeia* employs 20 cc. for this test; the *Pharmacopoeia of the United States*, 10 cc.; while the German Pharmacopoeia specifies no particular amount. The *British Pharmacopoeia* requires that no odor should be perceptible at any stage of the evaporation;[4] the *Pharmacopoeia of the United States* that an odor should not be perceptible at the later stages of the evaporation and that the paper should remain odorless;[5] and the German Pharmacopoeia that the paper retain no foreign odor after the evaporation of the chloroform. We have found that the anaesthetic chloroform now on the market rarely imparts an odor to filter paper, on evaporation, even when 50 cc. of the sample are tested, notwithstanding the fact that it frequently contains small amounts of contaminants productive of a foreign odor but unrecognizable by the tests in general use, owing to their lack of delicacy. Since a carefully conducted test for odor is essential, principally owing to the fact that such impurities affect the keeping qualities of chloroform *per se*, although they may not occur in such amounts as to interfere with its physiological action, it has been noted by several investigators that it is necessary to employ a test which will render the presence of these evident.

Schwarz and Will[6] proposed a very rigorous test for the presence of amyl compounds in chloroform. 300 g. are distilled on a water bath until about 2 cc. remain in the flask; on the addition of concentrated sulphuric acid to this residue, no darkening should occur nor should an odor of amyl compounds be developed.[7] Brown[8] proposed that the sample of chloroform under examination be carefully fractionated until a residue of 15 per cent. remains, then that this be slowly evaporated at from 80° to 90°; bad or foreign odors are looked for during and at the conclusion of the evaporation, and the dry non-volatile residue is weighed. Later[1] Brown specified this test as follows: When distilled, the first 10 per cent. fraction and the 15 per cent. residue should be free from color and foreign odor, and the weight of the 15 per cent. residue after evaporation at 32° C. until constant, should not exceed 1 in 900,000 parts by weight. Langgaard[2] recommended a test for odor which is similar to that of Schwarz and Will. According to this method, the chloroform is vaporized in a long-necked flask on a water bath, down to a residue of 2 to 3 cc., care being taken that the chloroform does not boil; this residue is then placed on a watch-glass and allowed to evaporate slowly. The residue should be odorless and should show no reaction with formalin-sulphuric acid.[3] Such a test shows the presence of impurities not made evident by the usual official tests. A modification of these fractional evaporation methods is to be found in the *Pharmacopoeia Nederlandica*,[4] however. In this pharmacopoeia it is stated that "chloroformum ad narcosin" shall conform to the following test: 50 cc. of the chloroform are distilled until about 2 cc. are left; the residue is then allowed to evaporate on filter paper. There should then result no odor of alcohol, fusel oil or pungent matters.

The authors find that when anaesthetic chloroform is fractionated in the usual way, any chlorinated decomposition products, fusel oil, or higher alcohols present are concentrated in the residue remaining above 64°; and that when no indications of the presence of such compounds were had by the test prescribed by the United States Pharmacopoeia, the residue resulting from the distillation of 100 cc. gave a marked response. Anaesthetic chloroform should conform to the following requirement:—

100 cc. of anaesthetic chloroform are slowly evaporated over a water bath until about 10 cc. remain in the flask. This residuum should be colorless and possess no foreign odor; and when it is allowed to evaporate on filter paper, there should result no odor of fusel oil, empyreumatic matter, or other substances than chloroform and ethyl alcohol, as the last portions disappear. If a decided odor is imparted to the filter paper, after the evaporation of the residue or if any foreign odor is observed during the course of evaporation, the chloroform should be rejected for anaesthetic purposes, but for further information may be tested for such impurities as fusel oil, chlorinated derivatives of alcohol, acetone, or the higher alcohols, extractive matter, etc. The nature of the impurity in this case is often indicated by the odor itself. This test is indeed comparatively stringent and its adoption would necessitate rigid chemical

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[1] *Pharm. J.*, [2] **6**, 576.

[2] *Ibid.*, [3] **1**, 623.

[3] *J. Pharm. Chim.*, [4] **29**, 402.

[4] The Ph. Brit. Committee of Reference in Pharmacy recommend that the test for odor be made with 10 cc. (*Chem. and Drug.*, **69**, 863). White (*Pharm. J.*, [4] **25**, 540) has suggested that the test for odor be made as follows: 10 mils. are poured on a 10 cm. filter paper; no foreign odor should become perceptible as the last portion disappears, and the filter paper should be left odorless.

[5] "If 10 cc. of chloroform be poured upon a piece of clean, odorless filter paper laid flat upon a warmed plate, and the plate be rocked from side to side until the liquid is all evaporated, no foreign odor should become perceptible as the last portions disappear from the paper, and the paper should be left odorless" (The *Pharmacopoeia of the United States*, **1905**, 99).

[6] *Pharm. Ztg.*, **1888**, 551.

[7] See the *Test with Sulphuric Acid*.

[8] *Pharm J.*, [3] **23**, 229.

[1] *Pharm. J.*, [3] **25**, 865.

[2] *Therap. Monatsh.*, May, 1902; see also *Apoth. Ztg.*, **17**, 341; *Pharm. Centralh.*, **43**, 543; *J. Pharm. Chim.*, [6] **16**, 305.

[3] See *Tests for Residue* and the *Test with Sulphuric Acid*.

[4] **1905**, p. 90.

control on the part of the manufacturers; but *pure* anaesthetic chloroform may be, and is being, made on a commercial scale.

2. RESIDUE.

Until quite recently anaesthetic chloroform usually contained fixed matter, as shown by the residue remaining after evaporation at 100° C. Such contamination was generally due to carelessness in manufacture[1] and storage.[2]

At the present time, although sufficient care is generally exercised in manufacture and purification to prevent extraction, yet anaesthetic chloroform sometimes contains extractive matter, especially when it has been stored in unprotected cork-stoppered containers. For example, we found that anaesthetic chloroform sold as chemically pure might contain as much as 0.0011 per cent., by weight, of extractive matter non-volatile at 100° C., while in the case of commercial chloroform the residue often amounted to 0.0047 per cent. by weight. It is almost needless to point out that although such matter would not interfere with the applications of chloroform of either grade, for its special purposes, except when employed in certain analytical work, its presence affects the keeping properties of chloroform, and moreover is unnecessary when proper care is exercised in manufacture and storage.

In the opinion of the authors, when 100 cc. of anaesthetic chloroform are allowed to evaporate in a platinum dish at 100° C., there should be left no weighable residue. In every case this should be determined gravimetrically and not by vision.[3]

3 (*a*) THE TEST WITH SULPHURIC ACID.

Pure chloroform is not appreciably soluble in concentrated sulphuric acid; but when anaesthetic chloroform is agitated with that reagent, the alcohol present is removed[4] and decompositiom occurs on exposure to air. It is therefore important that any treatment with sulphuric acid be not unduly prolonged; for even if the conditions are such that the sulphuric acid does not act directly upon the chloroform,[1] it must be borne in mind that its presence accelerates the oxidation of pure chloroform.[2] As has been indicated,[3] it was early ascertained that treatment with concentrated sulphuric acid was an efficient means for the purification of crude chloroform; it therefore followed that the reagent would serve as an indication of purity—that no coloration should be imparted to the acid when it was shaken with chloroform. In fact, the test has been pharmaceutically recognized since 1847,[4] and has been generally regarded as both fair and useful, although it has been variously stated and modified to suit local conditions of production and trade requirements.

Gregory[5] considered that chloroform that was to be employed in surgical operations should not afford any yellow or brown coloration when it was shaken with sulphuric acid; and Vulpius,[6] in the course of a study of anaesthetic chloroform, examined six different grades of chloroform, finding that that which answered most satisfactorily in surgical operations was ordinary chloroform which, however, withstood the test with sulphuric acid. In dissidence with these findings is the view of Abraham,[7] who expressed doubt as to whether the substance which darkened sulphuric acid was always that which produced the unpleasant effects sometimes attributed to chloroform, as claimed by Gregory;[8] Abraham inferred that the substance which blackened or otherwise colored sulphuric acid was not always the same,[9] in agreement with which we have the divergent views which have been expressed as to the source of the coloration.

Morson[10] considered it probable that "heavy muriatic ether" caused the darkening of sulphuric acid; Hager[11] gave the test for the presence of acetone, aldehyde, and ethyl ether; Regnault[12] stated that a coloration indicated the presence of "alcoholic chlorides;"[13] a response has been considered indicative of preparation from methyl alcohol;[14] Schwanert[15] gave the test with an equal volume of sulphuric acid for hydrocarbons; Traub[16] found that chloroform prepared

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[1] From the use of impure chemicals. Scholvien (*Apoth. Ztg.*, **1887**, 14; *Z. anal. Chem.*, **26,** Part 3) found that with many samples of chloroform then on the market, silver nitrate produced, after a short time, a dark brown turbidity, which could be removed by nitric acid and which did not form at all if the solution did contain a little nitric acid from the first; this he traced to the presence of arsenic in the chloroform examined. As a test for this impurity, he suggested that the chloroform be stirred with a dilute potassium hydroxide solution, evaporated, and the residue tested by Marsh's or Bettendorf's method. When such chloroform was distilled, Scholvien found that the arsenic remained in the residue, none passing into the distillate. The presence of arsenic in chloroform could have originated from the use of an arsenical bleaching powder, which, with the alcohol, would form, it is likely, arsenical organic compounds which would first distil over with the chloroform, yet not be capable of distillation from the chloroform itself; but more likely to the use of impure sulphuric acid in purification. Although other experimenters also reported having found traces of arsenic in samples of commercial chloroform, its presence is now improbable, even in commercial chloroform. Mentin (*Pharm. J.*, [3] **19,** 991) reported that 49 cc. of Saxon "Chloroformum Purissimum" gave a residue weighing 0.0006 g., possessing an odor of rancid butter; and that another chloroform manufactured from chloral yielded a residue weighing 0.0011 g., possessing a sweet, aromatic odor.

[2] When chloroform is supplied in tin containers, it sometimes happens that a small amount of zinc chloride, used as a flux in soldering "tins" by manufacturers, is introduced accidentally into the chloroform. Fixed matter is more generally introduced through the use of cork stoppers, however.

[3] White (*Pharm. J.*, [4] **25,** 540) proposed that when 10 mils of chloroform are allowed to evaporate in a clean glass beaker or dish, which is afterwards heated on a water bath, there should be left no *visible* residue.

[4] According to Kessler (*J. Pharm. Chim.*, [3] **13,** 162), chloroform containing alcohol diminishes in volume on agitation with sulphuric acid.

[1] On the action of sulphuric anhydride on chloroform, see Armstrong *Proc. Roy. Soc.*, **18,** 502; *J. prakt. Chem.*, [2] **1,** 244.

[2] See *Decomposition.* Brown (*Pharm. J.*, [2] **6,** 576) pointed out that a sample of chloroform tested with sulphuric acid should not be returned to the stock, since chloroform twice treated with sulphuric acid is likely to decompose. See *Alcohol.*

[3] Under *Purification.*

[4] Cf. *Codex Medicamentarius Hamburgensis,* 1847, wherein it is specified that chloroform should not color concentrated sulphuric acid.

[5] *Proc. Roy. Soc. Ednb.*, **1850,** 391.

[6] *Archiv. Pharm.*, [3] **13,** 37; **25,** 998.

[7] *Pharm. J.*, **10,** 25.

[8] *Chamber's J.*, May 4, 1850.

[9] Abraham stated that pure chloroform left no odor when allowed to evaporate from the hand or cloth, and that impure chloroform afforded an odor which was generally proportional to its effect in coloring the acid. He also reported that the specimen which colored sulphuric acid considerably left, if any, the least odor.

[10] *Pharm. J.*, **8,** 280.

[11] *Kommentar,* **1865,** p. 443.

[12] *J. Pharm. Chim.*, [4] **29,** 402.

[13] Brown (*Pharm. J.*, [3] **23,** 229) suggested that the extent to which sulphuric acid decomposed such impurities be determined.

[14] Cf. *Archiv. Pharm.*, December, 1874.

[15] *Hülfsbuch zur Ausführung Chemischer Arbeiten,* **1891,** p. 169.

[16] *Z. angew. Chem.*, **1892,** 192. Traub reported that sometimes an odor of peppermint was developed when the sulphuric acid test was applied to crude chloroform (*Pharm. Centralh.*, **33,** 245).

from alcohol by means of chloride of lime contained ethylidene chloride and "other impurities" which gave colored products with sulphuric acid;[1] Gay[2] stated that when the sulphuric acid became brown, the presence of chloro-derivatives of ethyl acohol or of the higher homologues was indicated; Schacht and Biltz[3] reported that when chloroform which was pure and free from alcohol, and which did not color sulphuric acid, was left to undergo decomposition, and the sulphuric acid after that became brown, this coloration was due to ethyl chloride;[4] others have employed the test to prove the absence of ethyl chloride and other ethane chlorides,[5] amyl and isobutyl alcohols,[6] amyl compounds,[7] or empyreumatic oily matter;[8] the test has been employed to show the presence of excessive amounts of alcohol or water;[9] and finally it has been stated that "pure chloroform" floats on concentrated sulphuric acid with a contact-surface convex downwards, but if "impure" gives a plane contact-surface.[10]

It has been universally conceded, however, that anaesthetic chloroform should not afford a coloration with sulphuric acid, notwithstanding the fact that the cause of the coloration appears to be variable and consequently has not been determined. As to just how the test should be performed, especially the proportion of reagent to use and the proper time limit, has been the subject of much discussion and even now totally diverse opinions are held—a condition attributable, in the main, to the demand of the trade for pure anaesthetic chloroform at a minimum cost, and the position taken by the manufacturers and their chemists that, on the other hand, if the requirements are rigorous, the price must be proportionally increased, to which the trade is not ready to accede, except, apparently, in Germany, France, Russia, Holland, and Belgium.

Brown[11] suggested that the quantity of sulphuric acid used be fixed at 10 per cent. and that it be shaken with the chloroform continuously for 20 minutes, after which the acid should remain colorless or nearly so;[12] it has been stated that "good and genuine" chloroform should remain colorless when mixed with an equal volume of concentrated sulphuric acid, without specifying a time-limit;[13] Gay[14] directed that 10 cc. be shaken violently with an equal volume of sulphuric acid and that the mixture should remain colorless even for an hour; Vulpius[1] considered that no perceptible yellow color should result within one day; Schwarz and Will[2] proposed that 40 g. of the chloroform be shaken with 30 g. of concentrated sulphuric acid in a glass-stoppered bottle, previously rinsed with sulphuric acid, and that the acid should not darken within 48 hours; and Traub[3] stated that a mixture of equal volumes of chloroform and sulphuric acid, when repeatedly shaken in the dark, should possess no discoloration after six to eight days.[4] From these variable recommendations it can readily be understood why important differences exist in the test as prescribed by various pharmacopoeias.

According to the *British Pharmacopoeia*, chloroform, when shaken with one-tenth its volume of sulphuric acid for 20 minutes, and then set aside for 15 minutes, should acquire practically no color in either the chloroformic or sulphuric acid layer and both should be quite transparent.[5] The Pharmacopoeias of Switzerland and Belgium specify a more rigorous test, namely: 15 cc. of acid are shaken with 20 cc. of chloroform in a stoppered glass cylinder of 3 cm. diameter previously rinsed out with sulphuric acid; the acid should not become colored within one hour. A similar test is given in the Pharmacopoeia of Japan. In Germany, it is now required that "narkose chloroform" give no color to sulphuric acid even after 48 hours, when 20 cc. of the sample are agitated with 15 cc. of acid. Formerly the time-limit was one hour,[6] but at present the test for this period of contact is restricted to chloroform other than that intended for anaesthesia.[7] According to the Pharmacopoeias of France, Sweden, Austria, Hungary and Spain, an equal volume of sulphuric acid is used; that of France states that no coloration should result even at the end of several hours, while the Pharmacopoeias of Austria and Hungary place a time-limit of one hour. The Pharmacopoeia of Denmark specifies that 20 g. of chloroform and 25 g. of acid be employed, and places the time-limit at one hour; the Norwegian requirement is similar; the Pharmacopoeias of Italy and Holland require that the test extend for 24 hours; while the Pharmacopoeia of Russia merely states "some time."

The test as given in the *Pharmacopoeia of the United States*[8] for "impurities decomposable by sulphuric

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[1] Moreover, Traub found that by treating chloroform with sulphuric acid and other reagents, a chloroform might be obtained which in all respects was equal to Chloroform Pictet.

[2] *J. Pharm. Chim.*, **4**, 259.

[3] *Pharm. Centralh.*, **33**, 269.

[4] Dott (*Pharm. J.*, [3] **22**, 1080) maintained that ethyl chloride and ethyl alcohol gave no appreciable coloration with sulphuric acid. He stated that it is easy to arrive at false conclusions from the sulphuric acid test, since chloroform containing a mere trace of linseed oil derived from the luting will give a decided reaction.

[5] E. Schmidt, *Z. angew. Chem.*, **23**, 1547.

[6] Cf. Schacht, *Archiv. Pharm.*, [3] **27**, 865.

[7] E. Schmidt, *Loc. cit.*

[8] *United States Dispensatory*, 18th Ed., p. 380.

[9] *Ibid.*

[10] Allen's *Commercial Organic Analysis*, **1**, 236. According to Soubeiran (*Ann. chim. phys.*, [2] **48**, 131), pure chloroform sinks in a mixture of equal parts of sulphuric acid and water.

[11] *Pharm. J.*, [3] **23**, 229; **25**, 865.

[12] Brown stated that on diluting with 3 volumes of water, the mixture should remain colorless and clear, and should give off only a slight foreign odor.

[13] *Polyt. Notizblatt*, **1875**, 16.

[14] *J. Pharm. Chim.*, **4**, 259.

[1] *Archiv. Pharm.*, [3] **25**, 998.

[2] *Pharm. Ztg.*, **1888**, 551.

[3] *Z. angew. Chem.*, **1892**, 192.

[4] Traub recommended that the chloroform and acid be then separated, and that the acid be next diluted with 5 parts of water, to which 1 cc. of *N*/10 silver nitrate is added; no alteration should result, although, according to Traub, only a "very pure" product will stand this test.

[5] 2 cc. of the sulphuric acid obtained on shaking with chloroform, as described, is then diluted with 2½ times its volume of water, after which it should remain clear, almost colorless, and should possess a pleasant odor. It is required that the liquid should still retain its transparency and freedom from color, even when further diluted with 10 cc. of water and stirred with a glass rod, and that the transparency should not be more than slightly diminished on the addition of 4 drops of silver nitrate solution.

[6] Such a test is given by Krauch (*Testing of Chemical Reagents*, **1902**, p. 78).

[7] See *Deutsches Arzneibuch*, **1910**, 118.

[8] **1905**, 99. For reference to the other Pharmacopoeias mentioned above, see *Specific Gravity* tables.

acid" hardly bears comparison with the above in point of delicacy. It is required that "if 40 cc. of chloroform be shaken with 4 cc. of colorless, concentrated sulphuric acid in a 50 cc. glass-stoppered cylinder during 20 minutes, and the liquids be then allowed to separate completely, so that both are transparent, the chloroform should remain colorless, and the acid should appear colorless, or very nearly colorless, when seen in a stratum of not less than 15 mm. in thickness." This test has been required since 1893,[1] and the test as specified until the seventh revision of the Pharmacopoeia was considerably more stringent, if less specific.[2]

3 (*b*) THE TEST WITH FORMALIN-SULPHURIC ACID.

Langgaard[3] recommended a test, by means of which the slightest traces of amyl compounds are said to be detectable. Concentrated sulphuric acid and chloroform are mixed in the proportion in which the German Pharmacopoeia indicates when testing for amyl compounds, etc., in a glass-stoppered vial which has been previously rinsed with sulphuric acid, and, after the addition of 3 or 4 drops of formalin (35–40 per cent. solution of formaldehyde), the mixture is well shaken; no coloration should result. The *Deutsches Arzneibuch*[4] requires that 20 cc. of "narkose chloroform" shall afford no coloration with 15 cc. of sulphuric acid and 4 drops of formaldehyde solution, but gives the test for the presence of organic decomposition products.

3 (*c*) DISCUSSION OF 3 (*a*) AND 3 (*b*).

A. Sulphuric acid is well-known as a reagent for the presence of furfural in amyl and methyl alcohols; of fusel oil, "empyreumatic oils," or "non-volatile carbonizable organic impurities" in ethyl alcohol and ethyl ether; and of "readily carbonizable organic impurities" in acetic ether, glycerin, and salicylic, lactic and benzoic acids. The authors have pointed out[5] that in the case of ethyl ether, the color reaction may be caused in general by the following:

1. Furfural with isobutyl alcohol, tertiary butyl alcohol, tertiary amyl alcohol, acetaldehyde, acetal, aceto-acetic ether, acetone, methyl alcohol, or isopropyl alcohol, or mixtures of these.[6]
2. Fusel oil.
3. Extractive matter from cork, etc.

We can now report, after examining a number of samples of 24 different varieties of anaesthetic chloroform, that when a properly stored sample of chloroform gives a response when the test with sulphuric acid is applied, this is usually due to the presence of one or more of the above contaminants.

We have found that anaesthetic chloroform which afforded only a faint coloration with sulphuric acid originally, being apparently free from fusel oil, extractive matter, etc., gives a marked reaction on treatment with oxygen, on continued agitation in the presence of air, after lengthy exposure to air and light, and on long standing in anactinic glass with the customary amount of air present. The last condition is of particular interest, since anaesthetic chloroform is frequently one year old, or more, when it reaches the consumers, and for this reason the matter was investigated in the laboratories of one of the large producers of chloroform. This concern reports as follows concerning the experiments made and conclusions arrived at:—

Three varieties of chloroform were used, these being obtained from independent manufacturers of known reputation. They were exposed in two ways: 1st, in amber bottles exposed to only indirect light on the dark side of a room; and 2nd, in white glass bottles exposed to bright, diffused light near a window. The experiments covered one year, from January, 1908, to January, 1909. All samples were tested by the sulphuric acid test of the U. S. P. on fresh samples before starting. In every case the acid showed some color in a 15 mm. layer. This color was matched in every case by a one-thousandth normal iodine solution, the latter being diluted until it exhibited the same color as the acid. In the beginning, the acid in all three samples showed the same degree of color, namely, that corresponding to 0.3 cc. of $N/1000$th iodine solution diluted to 3 cc. After one year's keeping in brown bottles, the color had become more than three times as deep as at the beginning, since now 1 cc. of $N/1000$th iodine solution diluted to 3 cc. was required to match this color. The samples kept in the white bottles showed in some cases the same amount of change in color; others showed a *greater* change, the maximum being five times as deep as the color at starting. All bottles were closed with ground glass stoppers.

In another series of experiments, the samples of chloroform were sealed in white glass test tubes and submitted, as before, to the sulphuric acid test before and after exposure for one year to bright light under a skylight. In this case the color deepened to a tint from *four to thirteen times darker* than at starting.

"It appears, therefore, that the best chloroform to be obtained imparts a very decided color to sulphuric acid when shaken with it after keeping in brown glass

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[1] See *Pharmacopoeia of the United States*, 7th revision, p. 88.

[2] The Pharmacopoeia of 1851 (p. 76) required that with an equal volume of sulphuric acid, chloroform should not assume a reddish brown color nor should the acid become discolored; the Pharmacopoeia of 1869 (p. 87) specified that the acid and chloroform should remain in contact 24 hours, at the end of which time no color should be imparted to either liquid or but a faint yellowish tinge to the acid; in the fifth revision (1873, p. 78) the last-mentioned test was retained; and in the sixth revision (1882) it was required that on shaking 10 cc. of chloroform with 5 cc. of sulphuric acid, no color should be imparted to either liquid after 24 hours.

[3] *Therap. Monatsh.*, May, 1902; on the employment of the reagent of Marquis for testing anaesthetic chloroform, see also Stadlmayr, *Z. angew. Chem.*, **23**, 1548; Linke, *Apoth. Ztg.*, **25**, 189, 285, 426.

[4] **1910**, p. 118; see in this connection, Braun, *Apoth. Ztg.*, **26**, 166, who favors a time limit of 48 hours for the sulphuric acid test, and considers that the formalin-sulphuric acid test is of value only when used upon chloroform before the addition of the alcohol necessary to prevent decomposition. It will be shown later that *pure* anaesthetic chloroform gives no reaction with formalin-sulphuric acid.

[5] THIS JOURNAL, **3**, 306.

[6] It may be mentioned here that the authors have had occasion to examine various samples of so-called higher alcohols and their derivatives, sold as chemically pure. Samples of normal butyl alcohol and iso-amyl ether invariably contained furfural; samples of active amyl, iso-amyl, isopropyl alcohols and propyl aldehyde gave marked reactions with sulphuric acid, but only very faint reactions for furfural; while samples of propyl, iso-butyl, tertiary butyl and methyl alcohols gave a yellow color with sulphuric acid, but no reaction for furfural. All of the samples were properly stored, except that air was invariably present, and we can only attribute the results to oxidation products.

bottles shaded from bright light for one year, and at the end of that time decidedly fails to meet the pharmacopoeial requirement in this regard."

At the end of the series all the samples were submitted to the U. S. P. tests for chlorides and free chlorine. One sample in brown glass showed a faint opalescence under the chloride test and one sample of the same producer in white glass showed a very marked opalescence under the same test. All other samples gave no reaction for chlorides. None of them gave any color when submitted to the test with potassium iodide.

"It therefore appears that the samples of chloroform, after keeping under favorable conditions for one year, show no deterioration as measured by the formation of chlorides or free chlorine, while they nevertheless fail to meet the U. S. P. sulphuric acid test."

It may be mentioned that these samples were examined not merely at the end of the year, but at the end of each quarter, which, of course, necessitated the opening of the containers. The change was *progressive*, although in only one case was there any alteration between the third and fourth quarter.

"We cannot help thinking that these results at least suggest the desirability of considering a modification of the sulphuric acid test for chloroform, possibly in the direction of defining more closely what is meant by 'very nearly colorless.' The use of a standard iodine solution affords a convenient method for defining this color."

The results obtained by the authors on samples of anaesthetic chloroform agree with those given above in these respects:

1. Fresh samples of American anaesthetic chloroform very frequently afford a slight coloration with sulphuric acid.[1]

2. Samples exposed to air in colorless glass bottles are usually oxidized to a greater degree than those stored in bottles of anactinic glass.

3. After prolonged exposure to air and light, a reaction for chlorides is rarely obtained. In a few of the cases where the presence of chlorides was indicated, we found that the oxidation of the alcohol present had reached a maximum and decomposition of the chloroform itself had consequently resulted; but this represents the extreme condition, and only occurred when the anaesthetic chloroform originally contained an amount of alcohol less than 0.25 per cent. and had been very carelessly stored. In most of the cases, the reaction with silver nitrate solution was not due to the presence of chlorides, but to acetaldehyde, etc.

4. The oxidation, as we prefer to term the alteration which undoubtedly occurs, is progressive when constant conditions are maintained, and the presence of air is necessary. It will therefore be seen that repeated opening of chloroform containers favors decomposition; and as more air is introduced after each sampling, the conditions for oxidation are progressively rendered more favorable.

We have previously emphasized the importance of having anaesthetic chloroform free from the so-called "organic impurities," which, as a rule, afford a coloration with sulphuric acid, since these accelerate the oxidation of anaesthetic chloroform. Here we may mention that samples of anaesthetic chloroform which showed absolutely no response to sulphuric acid originally, became only very slightly oxidized after seven months' storage in bottles of anactinic glass, and exposed to diffused daylight, and afforded no reaction with sulphuric acid after this time. We are therefore of the opinion that if *pure* anaesthetic chloroform is properly stored, it may be kept in an unaltered condition for at least seven months, and that it is unnecessary to modify the test with sulphuric acid.

Six samples of anaesthetic chloroform, which had been stored in brown glass bottles for twenty-one months in the factory of a well known chemical manufacturer, were given to the authors for examination, and every sample was found to comply in full with the tests prescribed by the *Pharmacopoeia of the United States*. None contained "impurities decomposable by sulphuric acid," although the presence of higher alcohols, evidently, was detected by the formalin-sulphuric acid test.

In order to ascertain the secondary causes of the reaction with sulphuric acid—that is, to determine what compound or compounds are formed in the oxidation of anaesthetic chloroform which may produce the coloration—the deportment of the following possible oxidation products and chlorinated derivatives was determined in chloroformic solution: acetaldehyde, acetic acid, chloracetic acid, ethyl acetate, ethyl chloride, "ethyl chloride polychlorated" (a mixture of tri-, tetra-, and pentachlorethane), ethylidene chloride, ethylene chloride, carbon dichloride, carbon trichloride, and chloral hydrate. Of these, only "ethyl chloride polychlorated" afforded a decided reaction, although we were inclined to attribute it to the presence of an impurity. Since acetal, which results in the imperfect oxidation of ethyl alcohol, is decomposed by sulphuric acid, the conduct of this compound in chloroform solution towards sulphuric acid was also investigated. It was found that the presence of 1 part of acetal in 2000 of chloroform gave a marked reaction with sulphuric acid,[1] but that 1 part in 3000 afforded only a very faint coloration. We concluded that acetal alone could not cause the reaction, since the coloration afforded by the presence of small amounts is not sufficiently intense and traces gave no reaction; but acetal is one of the possible products of the oxidation of anaesthetic chloroform, and the reaction may be attributed in some cases to its formation.

Another probable contaminant of anaesthetic chloroform is furfural, with which acetal and acetaldehyde give a coloration to sulphuric acid, although "metafurfural" alone gives the reaction. The presence of furfural in anaesthetic chloroform is likely to result

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[1] One large firm of manufacturing chemists state, in fact, that they "have never examined a sample of chloroform that would not become colored to some extent when shaken with sulphuric acid under the conditions of the U. S. P. test."

[1] The acetal used was furfural-free.

either from the use of impure alcohol, in which case a coloration would be had with sulphuric acid just as soon as the alcohol became oxidized; or from the oxidation of anaesthetic chloroform,[1] although, in our opinion, this is less likely, since we have been unable to detect its presence in samples of anaesthetic chloroform exposed to air and light for seven months, even when saturated with water and hydrogen dioxide solution, or in samples one year old customarily stored. In every case where we found furfural in samples of anaesthetic chloroform, higher alcohols were also present, and in these cases its presence was to be attributed to the occurrence of fusel oil in alcohol used in the production; such chloroform, of course, gave a marked reaction with sulphuric acid.

B. In order to determine the value of the test with formalin-sulphuric acid, 20 cc. of various anaesthetic chloroforms were thoroughly shaken with 15 cc. of concentrated sulphuric acid and 4 drops of formalin,[2] and then any coloration was observed. Only those American products were used which gave a negative or very faint reaction with sulphuric acid alone; these were then compared with anaesthetic chloroforms of German manufacture.

The results may be thus tabulated:

AMERICAN PRODUCTS.

Sample.	Results.
1. "Chloroform U. S. P." This sample contained 0.7 cc. absolute alcohol in 100 cc., and conformed to all the U. S. P. tests.	Yellowish brown color at once; brown color after standing 5 minutes.
2. "Purified chloroform." This sample contained 0.97 cc. absolute alcohol in 100 cc., and was of full U. S. P. grade.	Very faint color after 1 minute; faint yellow color after 5 minutes.
3. "Chloroform Purified." This sample contained 0.5 cc. absolute alcohol in 100 cc., and conformed with all the requirements of the U. S. P., except that it gave a faint coloration with sulphuric acid (unprotected cork stopper). This chloroform was made from acetone.	Faint yellow color after 1 minute; faint brown color after 5 minutes.
4. "Purified Chloroform." This sample contained 0.74 cc. absolute alcohol in 100 cc., and answered all the U. S. P. tests. This chloroform was made from carbon tetrachloride.	Very faint after 1 minute; faint yellow color after 5 minutes.
5. A sample of anaesthetic chloroform 21 months old, but of full U. S. P. quality.	Reddish yellow color after 1 minute; marked brown color after 5 minutes.
6. "Chloroform Pure." A sample which contained 0.56 cc. absolute alcohol in 100 cc., and which was of full U. S. P. standard.	No coloration after 5 minutes.
7. "Purified Chloroform." A sample of chloroform made from acetone, containing 0.84 cc. of absolute alcohol in 100 cc. and which passed all the U. S. P. tests, except that it gave a faint color with sulphuric acid.	A very faint yellow color after 5 minutes.

GERMAN PRODUCTS.[1]

Sample.	Results.
1. "Chloroform Pictet," density 1.49 at 15/15°.	No coloration after 5 minutes.
2. "Salicylid-Chloroform," density 1.497 at 15/15°.	No coloration after 5 minutes.
3. "Chloroform chem. rein.," density 1.488 at 15/15°.	No color after 5 minutes.
4. "Chloroform chem. rein.," density 1.4887 at 15/15°.	Exceedingly faint color after 5 minutes.
5. "Chloroformium Purissimum," density 1.4888 at 15/15°.	Very faint after 1 minute; yellow color after 5 minutes.
6. "Chloroform chem. rein.," density 1.487 at 15/15°.	No coloration after 5 minutes.
7. "Chloroform Ph. G. IV.," density 1.489 at 15/15°.	No color after 5 minutes.

These results show that the test with formalin-sulphuric acid is indeed sensitive and that it will serve to detect impurities not made evident by sulphuric acid alone. We found that pure chloroform as well as *pure* anaesthetic chloroform gave no response, when 100 cc. were allowed to evaporate until but 10 cc. remained, and this residue was then tested with formalin-sulphuric acid.

Among the substances detectable by means of formalin-sulphuric acid, are: morphine (Marquis); morphine derivatives, such as codeine, heroine, peronine, and dionine (Kobert); and Linke showed that many alkaloids, phenol, salicylic acid, resorcin, phloroglucin, benzol, toluol, xylol, and other organic compounds, give color reactions. Casein, milk-whey, etc., give a blue color with the reagent. We have observed that samples of ethylene chloride, carbon dichloride, chloracetic acid, ethyl acetate and chloral hydrate, supposedly pure and which afforded no coloration with sulphuric acid alone, gave a yellow color with formalin-sulphuric acid. In fact, it may be said that the reagent gives no distinctive reactions—it cannot be employed for purposes of identification; but we have found that *pure* anaesthetic chloroform gives no coloration with the reagent, and since anaesthetic chloroform should be pure, it is of no direct importance just what the contamination is. We have found that it is generally one or more of the higher alcohols, however, and that the greater sensitiveness of the reagent over sulphuric acid alone is due to the fact that a reaction is had in the absence of furfural—that is, when amyl, propyl or butyl alcohol is present in chloroform, the presence of furfural is unnecessary to obtain a reaction.

Samples of purified isopropyl, propyl, isoamyl, active amyl, tertiary amyl and isobutyl alcohols, free from detectable amounts of furfural, and which gave but a pale yellow coloration with sulphuric acid, afforded a red-brown color with formalin-sulphuric acid; in fact, the deportment was strikingly similar to the conduct of such compounds towards sulphuric acid when furfural is present, and showed the presence of furfural is not essential for a positive response.[2]

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[1] From ethyl alcohol through chlor-acetal (Lieben, *Ann.*, **104**, 114; **146**, 193.

[2] The formalin used dissolved in sulphuric acid to form a perfectly transparent, colorless solution.

[1] All of the above anaesthetic chloroforms of German manufacture were of full Ph. G. IV. quality. It should be remembered, however, that the test with formalin-sulphuric acid was not specified until the 5th revision of the *Arzneibuch*. The comparison with the American chloroforms is thus on a more relative basis.

[2] It may be pointed out in this connection that the test with aniline-acetic acid is not characteristic of furfural, as is generally supposed, since formaldehyde also gives the reaction.

In order to determine the delicacy of the reagent as a test for the presence of higher alcohols in anaesthetic chloroform, the following comparative experiments were made, the observations being recorded immediately after mixing:

Chloroform, 20 cc.	Sulphuric acid, 15 cc.	Result on adding 4 drops of formalin.
Isobutyl alcohol, 1 : 6000	Faint coloration	Yellowish brown color.
Propyl alcohol, 1 : 6000	Faint color	Yellowish brown color; marked after 5 minutes.
Isobutyl alcohol, 1 : 12,000	Very faint color	Dark yellow.
Propyl alcohol, 1 : 12,000	Exceedingly faint color	Yellow color; brownish yellow after 5 minutes.
Isobutyl alcohol, 1 : 18,000	Negative	Yellow color which became more marked on standing.
Propyl alcohol, 1 : 18,000	Negative	Yellow color.
Isobutyl alcohol, 1 : 54,000		Yellow color.
Propyl alcohol, 1 : 54,000		Yellow color, easily discernible after 5 minutes.

We have found that even the presence of 1 part of isobutyl alcohol in 600,000 of anaesthetic chloroform may be detected by means of the formalin-sulphuric acid test, and therefore conclude that this test is indicative of the mere presence of higher alcohols in chloroform. A sample of anaesthetic chloroform complying with the test as prescribed by the *Deutsches Arzneibuch* is assuredly free from such contamination, and the indication is that it has been thoroughly purified, that pure alcohol is present, and that there is no contamination with impurities decomposable by sulphuric acid whatsoever—that is, the chloroform has been properly prepared and stored. Generally, when higher alcohols are present in anaesthetic chloroform, furfural is also present, and therefore the test with sulphuric acid alone is sufficient to show the presence of likely impurities in any probable amounts; but the formalin-sulphuric acid test is much more intense in such cases, and is consequently more rapid and delicate. This is shown in the above experiments, and it is only necessary to mention, in conclusion, that when sulphuric acid alone is used, often the time necessary for the reaction, if any at all is obtained, is four or five, and sometimes even twelve hours, with a sample of anaesthetic chloroform which affords a decided coloration with formalin-sulphuric acid in five minutes as a maximum.

C. It has been stated[1] that "salicylous acid" and concentrated sulphuric acid afford colorations with amyl and other higher alcohols; but owing to the difficulty in obtaining salicylous acid (C_6H_4.OH.COH) which affords no intense red coloration with sulphuric acid alone, this test is not to be recommended for the detection of such compounds in chloroform. It was the authors' original intention to employ pure furfural and sulphuric acid as a test for the presence of higher alcohols in chloroform; but this was rejected, owing to the difficulty of obtaining furfural which affords no coloration with sulphuric acid itself, and also because of the satisfactory delicacy of the formalin-sulphuric acid test.

D. Anaesthetic chloroform should comply with the following test:—

When 20 cc. of anaesthetic chloroform are mixed with 15 cc. of concentrated sulphuric acid in a glass-stoppered tube of 50 cc. capacity, which has been previously rinsed with concentrated sulphuric acid, no visible coloration should be imparted to the mixture after the addition of 0.4 cc. of a pure 40 per cent. formaldehyde solution, and then shaking throughout a period of 5 minutes.

Anaesthetic chloroform which conforms with this requirement, may, when properly stored, be kept for long periods of time without undergoing oxidation; and we have found that for the production of such chloroform it is not necessary to resort to the several special patented processes of purification in use by certain European firms.

(*To be continued in the July No.*)

SOME DATA ON THE MANUFACTURE OF SMOKING OPIUM AND ITS CHEMICAL COMPOSITION.[1]

By A. B. Adams and James M. Doran.

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Under the Federal laws in regard to the manufacture, sale and consumption of opium for smoking purposes, the Internal Revenue laboratory has had occasion during the last two years to do some work on smoking opium. Finding practically no literature on the subject, at least on the manufacture of opium for smoking purposes in the United States, it is thought that some of the information gathered on the subject as a result of the work might be of interest.

Briefly, smoking opium is an aqueous extract of gum opium evaporated to such a consistency that it may be smoked in an opium pipe; that is, the consistency of thick molasses. It has the characteristic odor of opium.

The Federal law of 1890 imposed a heavy Internal Revenue tax on the manufacture of opium for smoking purposes, and up to February, 1909, prepared smoking opium could be imported under heavy duties. In February, 1909, Congress passed a law prohibiting the importation of any opium for other than medicinal purposes, after April 1, 1909.

In the year 1908 there were imported into the United States 147,624 pounds of smoking opium. To supply this almost constant demand for smoking opium in the United States, there are two avenues open; first, to smuggle in smoking opium already prepared in China or other places outside of the United States, or, second, to illicitly manufacture the opium in the United States, thus evading the prohibitory customs laws and the Internal Revenue laws relating to its manufacture in this country. It is in connection with the prosecution of the illicit manufacturing of smoking opium in the United States that practically all of these data were obtained.

Opium is the exuded juice obtained by scarifying the partially ripe seed-capsule of the variety of the poppy, *papaver somniferum*. It is gathered in a partially

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[1] *Chem. Ztg.*, **34**, 470.

[1] Published by authority of the Commissioner of Internal Revenue. Read before the Division of Pharmaceutical Chemistry, American Chemical Society Washington, Meeting, Dec., 1911.

dried gummy mass and packed together in one- to four-pound cakes, which are the crude gum opium cakes of commerce.

The black poppy is cultivated chiefly in Asia Minor. The gum obtained from it is high in content of morphine, making it especially valuable for pharmaceutical purposes.

The white poppy is cultivated in China, India, Persia and Egypt. The opium obtained from it is uniformly low in morphine.

The Chinese gum, likewise the Indian gum, is entirely consumed locally, chiefly in the manufacture of smoking opium.

Thorpe[1] states that the Chinese recognize four varieties of opium, namely:

1. Raw or crude opium (that is, the crude gum opium).
2. Prepared opium (or the finished product for smoking).
3. Dross or pipe cleanings (the ash remaining after smoking. This is known among Chinamen, at least in the United States, as Yen-Shi).
4. Opium dirt, or the exhausted marc after extraction of the gum opium.

The statement is also made by Thorpe under the authority of McCallum that the Chinese of Hong-Kong prepare smoking opium by extracting the gum opium with water and evaporating the clear extract to the consistency of treacle.

In this country, so far as known, practically the same process is followed; the gum opium, broken in small pieces, is extracted with boiling water in a suitable vessel. This extract is drawn off through a suitable strainer, usually cheese cloth, to separate the refuse matter, poppy leaves, crude fiber, etc. In some instances U. S. P. powdered opium has been used by placing it in cloth bags and boiling it in water. In either case the clear extract is evaporated down, or rather boiled down, to the consistency of thick molasses. It is then ready for use.

In this country there is added to the evaporating mass, in some cases, the water extract of the Yen-Shi, or pipe residue, and in other cases the Yen-Shi in toto. This practise is claimed by some to add flavor to the finished product, but as the use of Yen-Shi or Yen-Shi extract has not been detected in smoking opium of known Chinese manufacture, it is fair to assume that its use in this country is purely a matter of economy in the recovery of some of the unconsumed opium in the Yen-Shi, or possibly the familiar process of adulteration.

No record is shown of any importation of Chinese gum into the United States. All gum opium imported and used commercially in the United States is the product of Asia Minor, or Smyrna gum.

It is evident that we may assume that if any gum has been manufactured into smoking opium in the United States it was Smyrna gum; consequently the resulting prepared smoking opium should be of uniformly high morphine content.

On the other hand, smoking opium prepared in China should be of a uniformly low morphine content, owing to its source.

Our analytical results showed this to be the case.

Chinese smoking opium is put up for the market in small bronze boxes about $3^1/_2 \times 4^1/_2 \times 1^1/_2$ inches. The box is usually about $^2/_3$ full, the net weight of the opium being 5 tael or $6^2/_3$ ounces. When these cans were regularly imported they were covered by a gummed customs strip stamp.

A can of customs tax-paid smoking opium with stamp intact is valued at about $95.00, due largely to the fact that the can may be refilled with but little chance of detection as long as the stamp holds together, the opium in the can being in a legal container. A can of smuggled opium is worth about $40.00.

A small quantity of smoking opium was prepared in the laboratory from Smyrna gum. The weight of the gum used was $5^1/_2$ ounces; the weight of the smoking gum obtained was $3^7/_8$ ounces. The best information seems to be that in the illicit manufacture of smoking opium in the United States the weight of the finished is from $^1/_2$ to $^2/_3$ that of the raw material used. At the price of crude gum opium in this country the manufacturing of smoking opium is very profitable, due to the high price that habitues of "smoking" will pay to obtain their "hop."

The old U. S. P. extract of opium is a product similar in every way to the smoking opium illicitly manufactured in the United States, and it is worth noting that considerable U. S. P. extract of opium, made by several large drug firms, has been found and has been known to have been used for smoking in many opium dens or so-called "hop joints."

Several samples of genuine Chinese smoking opium have been analyzed in this laboratory, some being samples smuggled into this country and others imported before April 1, 1909.

The following is a capitulation of the analyses in percentages:

	Smuggled 5 samples.			Regularly imported 13 samples.		
	Morphine.	Moisture.	Ash.	Morphine.	Moisture.	Ash.
Average........	6.41	18.71	5.53	7.86	15.50	5.98
Maximun......	7.40	21.55	6.17	9.59	19.48	6.96
Minimum......	5.30	16.61	4.66	5.91	11.64	5.38

Of the many samples of smoking opium illicitly manufactured in the United States which were examined in the laboratory the five following are typical analyses:

	Morphine. Per cent.	Moisture. Per cent.	Ash. Per cent.
1........................	17.49	17.06	9.43
2........................	14.37	10.51	10.48
3........................	18.47	21.96	...
4........................	16.98	20.68	4.61
5........................	16.53	17.67	...

These samples were manufactured in Denver, New York City, Pittsburgh, Terre Haute, and Buffalo, respectively.

An aqueous extract of Yen-Shi was made in the laboratory and it was attempted to evaporate it down to the consistency of smoking opium. It became hard and brittle when the moisture content was about the

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[1] "Dictionary of Applied Chemistry," Vol. 3, p. 72. See also Hartwitch, "Die Menschlichen Genussmittel."

same as that of smoking opium. It is evident that satisfactory smoking opium cannot be made from Yen-Shi exclusively, due largely to the lack of the resinous and gummy matters that give to smoking opium its proper consistency.

The extract of Yen-Shi is uniformly high in ash, in the above-mentioned instance being 19.00 per cent. It appears that the ash of opium is largely water soluble, and a high ash content of a prepared smoking opium is a rather useful indication of the use of Yen-Shi extract.

Yen-Shi and Yen-Shi extract has a distinctive and peculiar odor. The recognition of this odor in the finished product is a valuable indication of the use of Yen-Shi.

The process of smoking opium is substantially as follows:

A small mass of the material about the size of a pea is taken up on a "dipper" or a small metal rod, known as a Yen-Hook. This lump is dexterously rotated in the flame of a small lamp, usually a peanut oil lamp, until the excessive moisture is driven off and the mass is partly incinerated, or until the "pill is cooked."

It is then placed in the bowl of the opium pipe and held just over the flame of the lamp, and the smoke from the "pill" inhaled. The preparations for smoking occupy 10 to 15 minutes, the actual operation of smoking about 30 seconds.

No attempt is made in this paper to give an exhaustive analysis of smoking opium, which is the same in all essentials as gum opium and its products, on which there is already a mass of literature.

Further work is being done in this laboratory on the composition of Yen-Shi and Yen-Shi extract, the changes that take place in the smoking process and its quantitative composition, with special reference to its detection in finished smoking opium.

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WASHINGTON, D. C.

THE COMPOSITION OF THE PACIFIC KELPS.[1]

By J. W. TURRENTINE.

Received Feb. 20, 1912.

Originally the word "kelp" meant the ashes of sea weeds, a product which was lixiviated for the extraction of alkali salts and iodine. Its preparation constituted an important industry in Scotland and Ireland during the first half of the nineteenth century. The term then came to be applied to the plants from which these ashes were prepared; and at present it is used by many to designate all large, dark colored sea weeds. The most definite sense in which the word is used includes all plants belonging to one of the families of the brown sea weeds, the Laminariaceae. Members of this family are found on both the Atlantic and Pacific littoral, but certain ones are peculiar to the Pacific. The most important, from an economic standpoint, because of their size and remarkable content of potassium salts, are the giant kelps. While the various varieties may grow from two to twelve feet in height, the giant kelps are found from thirty to two hundred feet in length and have been observed as long as fifteen hundred feet.

Comparatively little is known concerning the composition of kelps, especially the Pacific kelps. The non-volatile residues of the incinerated plant can be analyzed easily, but to determine the relationships and the combinations existing between the so-called inorganic and the organic constituents of the live plant is not a simple matter.

The composition of the Pacific kelps has been studied by Mr. David M. Balch, of Coronado Beach, Cal., the pioneer investigator of these kelps, whose interesting article on that subject appeared in THIS JOURNAL.[1] He has analyzed the giant kelps of the northern and southern Pacific coast of the United States, the *Nereocystis luetkeana*, and the *Macrocystis pyrifera* and *Pelagophycus porra*. Within the last few days he has submitted to this Bureau analyses of various other genuses from the Puget Sound region.

Samples.—Specimens of various kelps, 80 in all, were collected for analysis from certain points of Alaska by Mr. E. C. Johnston, of the "Albatross;" from Puget Sound (San Juan Co.), Wash., by Prof. G. B. Rigg, of the University of Washington; from the region of Monterey Bay, Cal., by Prof. F. M. MacFarland, of the Leland Stanford, Jr., University; and from the vicinity of San Diego, Cal., by Captain W. C. Crandall, of the La Jolla Marine Biological Station. These embraced about thirty different varieties of kelps and included specimens of the same varieties from different localities, of the same variety at different ages, and of different parts of the same plant. Those from Alaska were mostly of the smaller varieties and were made up of the entire plant; those from Puget Sound represented various varieties, large and small, and consisted of the entire plant or of special parts of the plants, cut into small pieces and transmitted in the dry state, in glass jars; the same statements apply also to those from Monterey Bay. Specimens from San Diego consisted of part of the two kelps, Macrocystis and Pelagophycus. They were partially dried and put in canvas sample sacks for transmittal. Further drying took place in transit and in the laboratory, as a result of which the specimens were in the form of hard and compact masses, or balls.

In sampling, particular care was taken to distribute throughout the whole sample the salts which had crystallized on the surface of the plants in drying and had subsequently fallen off. In some instances it was found more expedient to grind the entire specimen, thus obviating an arbitrary distribution of the effloresced salts.

Drying and Grinding.—The samples chosen were dried, at 103° C., for at least seven hours. They were then ground in an iron mortar. If hard and woody, they were ground finally to extreme fineness in a ball mill, while, if thin and papery, they were ground with ease in the mortar to the desired fineness,—to pass a sieve of sixteen apertures per linear inch.

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

[1] Balch, THIS JOURNAL, 1, 777 (1909).

Method of Analysis.—The method of analysis here described, while possibly faulty in some particulars, was adopted because of the speed with which analyses would be made thereby. Samples of 0.5 g. or thereabouts, were weighed directly into tared platinum crucibles. The crucibles were then placed on an asbestos covered gauze and heated to a temperature below dull redness, when destructive distillation took place. The gases evolved at the mouths of the crucibles were ignited. On the disappearance of the flame the material was thoroughly stirred, with further heating, until all tarry matter had been driven off. Charcoal remained, black or gray in color, and in the form of a loose powder, if the temperature had not been carried too high. The char was transferred to a 200 cc. beaker containing 50 cc. water, the beaker was covered and the solution evaporated to less than 25 cc. The resulting solution was filtered free of solid matter (the filtrate being caught in a platinum dish), the char washed by decantation with hot water, then transferred to the filter and further washed. To the filtrate was added a small volume of ammonium carbonate solution to precipitate calcium carbonate, and it was then evaporated to dryness on a steam bath. Ammonium salts were expelled by heating for an instant to dull redness. The residue was taken up with water and the resulting solution filtered into tared platinum dishes; hydrochloric acid was added, the solution evaporated to dryness on a steam bath, the dishes and their contents were heated again for an instant to dull redness and cooled in a desiccator. The weights of the solids were taken as *soluble salts.*

This procedure was adopted in order that the salts obtained might represent as closely as possible the actual content of soluble salts of the charred kelp. To have converted them into sulfates by the addition of sulfuric acid to the lixiviate would have lessened the liability of loss of potassium salts through volatilization, but would have changed materially the weight of the soluble salts. Where no value is attached to knowledge of the total content of soluble salts, or when one is content to calculate the total soluble salts from a determination of the potassium, sodium, chlorine and sulfate, the latter procedure is to be recommended.

The soluble salts were dissolved in water, the solutions transferred to graduated flasks and diluted to 50 cc. Portions of this, 10 cc. in volume, were subsequently analyzed for potassium by the chlorplatinic acid method.

The residue of charcoal left on the filter after the final filtration, together with the precipitate caught by the second filtration, was ignited to whiteness. The weight was recorded as *ash.*

The sum of the weights of the soluble salts and of the ash when subtracted from the weight of the sample gives a value which represents the matter which has been volatilized. The value is recorded as *organic matter.*

For the determination of iodine, two-gram samples were charred and lixiviated in the manner already described. Iodine was determined in this solution by an adaptation of the method of Bray and MacKay.[1] The filtered solution was transferred to a separatory funnel of 250 cc. capacity, containing 10 cc. of a solution of sulfuric acid (1 cc. conc. H_2SO_4: 9 cc. H_2O) and 10–15 cc. carbon tetrachloride. The solution was titrated with a solution of potassium permanganate previously standardized against pure potassium iodide, the manipulation during the standardization being identical with that employed in the actual analyses. From the solution undergoing titration the liberated iodine was removed as fast as formed by shaking with the carbon tetrachloride. Persistence in the solution of the pink color of the permanganate was taken as the end point.

It should be pointed out that the iodide solution titrated by permanganate must be free from other substances liable to oxidation under the conditions observed. In the ignition of kelps the sulfur present is liable to appear as sulfide if the ignition be carried on at too high a temperature and in an atmosphere depleted of oxygen. Such a result has not been observed, however, as coming from the distillation of kelp, and it is believed that when the distillation has been conducted in an open crucible and with thorough stirring, the absence of other reducing agents (than iodides), both organic and inorganic, is assured. This belief was borne out in the analysis by the fact that the first drop of permanganate liberated iodine, distinctly visible in the solution, and with the complete setting free of the iodine, the next drop or two gave the end point. Whether the above manner of preparing the solution for titration insured the complete recovery of all the iodine is not known. The determination of iodine in organic matter by the Carius method was too difficult, considering the large number of kelp samples analyzed. In the distillation, some iodine may have been lost through the oxidation of the iodide. Information on this point will have to be acquired through experimentation rather than conjecture.

In order to determine whether iodides remained in the char in recoverable amounts, the char was ignited to whiteness and the solution of the resulting ash titrated; only negative results were obtained.

Mr. T. C. Trescott, of the Bureau of Chemistry, was so kind as to determine the nitrogen content of the various kelps. The analyses were made of the oven-dried samples by the Kjeldahl method.

DISCUSSION OF TABLE OF RESULTS.

In the second column are given the serial numbers of the kelp samples examined. There are four series consisting of four collections of samples secured during the summer of 1911; they are designated by the initial letter of the name of the collector—as, R: Rigg; M: Macfarland; and J: Johnston, with the exception of the Crandall collection, which is designated by the letter S (Station).

In the fourth column are indicated the locations from which the samples were taken. In many intances the locus is given with precision. Crandall

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[1] *J. Am. Chem. Soc.*, **32**, 1193 (1910).

TABLE I.

B. of S. No.	Serial No.	Name of kelp.	Location.	Description of sample.	Potash (K_2O).	Iodine (I).	Nitrogen (N).	Soluble salts (Na KClSO$_4$).	Sodium salts estimated.	Organic matter.	Ash of lixiviated plant.	KCl.
1	R 1	Nereocystis luetkeana	San Juan Co., Wash.	Stipe	25.7	0.08	1.29	55.9	15.3	41.8	2.3	40.6
2	R 2	Laminaria bullata	"	"	15.9	0.41	1.99	36.8	11.6	57.4	5.8	25.2
3	R 4	Agarum fimbriatum	"		12.2	0.12	1.99	28.7	9.4	60.3	11.0	19.3
4	R 5	Laminaria bullata	"		10.4	0.29	1.90	25.0	8.6	60.4	14.6	16.4
5	R 6	Nereocystis luetkeana	"	Fronds	13.3	0.15	2.52	35.0	14.0	61.5	3.5	21.0
6	R 7	Laminaria saccharina	"		16.9	0.41	1.66	35.6	8.9	47.0	17.4	26.7
7	R 8	Alaria valida	"		9.2	0.08	1.94	26.4	11.9	66.9	6.7	14.5
8	R 9	Nereocystis luetkeana	"	Fronds	23.0	0.17	1.35	51.3	14.9	46.2	2.5	36.4
9	R 10	Desmarestia ligulata, herbacea	"		13.5	0.12	1.73	41.9	20.6	48.3	9.8	21.3
10	R 11	Laminaria bullata	"		11.0	0.35	1.95	26.4	9.0	64.0	9.6	17.4
11	R 12	"	"		16.4	0.41	2.01	37.9	12.0	56.4	5.7	25.9
12	R 13	Laminaria saccharina	"		17.8	0.53	1.76	38.4	10.3	50.3	11.3	28.1
13	R 14	Pleurophycus gardneri	"		6.9	0.12	1.93	26.5	15.6	34.7	8.2	10.9
14	R 15	Fucus evanescens	"		3.1	0.06	1.66	20.1	15.1	75.3	4.1	4.9
15	R 16	Egregia menziesii	"		13.3	0.08	2.35	30.4	9.4	61.2	8.4	21.0
16	R 17	Costaria turneri	"		17.0	trace	....	39.1	12.2	54.6	6.3	26.9
17	R 18	Agarum fimbriatum	"		12.4	0.07	1.95	29.5	9.9	60.2	10.3	19.6
18	R 19	Desmarestia ligulata, herbacea	"		6.2	0.06	2.25	24.3	14.5	69.7	6.0	9.8
19	R 20	Cymathaere triplicata	"		13.4	0.06	1.40	32.0	11.0	58.3	9.7	21.0
20	R 21	Laminaria saccharina	"		16.4	trace	1.76	36.3	10.4	50.4	13.3	25.9
21	R 22	Nereocystis luetkeana	"	Fronds	16.2	0.15	2.32	40.4	14.8	55.3	4.3	25.6
22	R 23	Fucus evanescens	"		3.1	none	1.59	19.0	14.1	77.0	4.0	4.9
23	R 24	Cymathaere triplicata	"		13.8	trace	1.56	34.6	12.8	59.7	5.7	21.8
24	R 25	Pleurophycus gardneri	"		7.3	0.12	1.85	27.0	15.5	65.0	8.0	11.5
25	R 26	Egregia menziesii	"		10.3	0.07	2.49	32.1	15.8	60.3	7.6	16.3
26	R 27	Postelsia palmaeformis	Neah Bay, Wash.	Fronds	13.9	0.15	1.83	29.9	7.9	64.4	5.7	22.0
27	R 28	Macrocystis pyrifera	"		19.6	0.20	1.81	32.5	1.5	51.5	16.0	31.0
28	R 29	"	"		14.0	0.22	2.18	30.4	7.3	49.6	19.2	22.1
29	R 30	Pterygophora californica	"	Stipe	0.37	....	....	14.8	14.2	....	5.2	0.59
30	R 32	Postelsia palmaeformis	"	"	20.0	0.17	1.01	41.1	9.5	54.9	4.0	31.6
31	J 1	Rhodymenia palmata linearis	Yakutat, Yakutat Bay, Ala.	Entire plant	2.8	none	....	7.2	2.8	91.0	1.8	4.4
32	J 2	Fucus evanescens macrocephalus	Sitka, Baranof Island, Alaska	"	2.7	none	....	16.3	12.0	81.1	2.6	4.3
33	J 3	Fucus, evanescens, ag. forma	Sitka, Baranof Island, Alaska	"	2.9	(1)	....	13.9	9.3	82.7	3.4	4.6
34	J 6	Alaria (lanceolata ?)	Biorka Island, Symonds Bay, Alaska	Portion of plant	3.0	0.12	....	13.5	8.8	77.9	8.6	4.7
35	J 7	Macrocystis pyrifera	Biorka Island, Symonds Bay, Alaska	"	3.1	0.23	1.96	25.2	20.3	70.6	4.2	4.9
36	J 8	Cystophyllum geminatum	Biorka Island, Symonds Bay, Alaska	"	7.3	0.26	1.95	27.0	15.5	64.7	8.3	11.5
37	J 9	Alaria lanceolata	Sitka, Baranof Island, Alaska	"	3.4	trace	....	13.5	8.1	79.4	7.1	5.4
38	J 10	Halosaccion glandiformis	Sitka, Baranof Island, Alaska	"	6.5	trace	....	24.1	13.8	70.1	5.8	10.3
39	M 1	Pastelsia palmaeformis	Montara Point, Cal.	Dried stems	22.8	0.09	0.94	44.5	8.5	52.3	3.2	36.0
40	M 2	Macrocystis pyrifera	Monterey Bay, Cal.		18.3	0.26	2.32	35.7	6.8	57.0	7.3	28.9
41	M 3	Egregia menziesii	Point Pinos, Cal.		11.9	0.12	2.25	27.7	8.9	65.6	6:7	18.8
42	M 4	Macrocystis pyrifera	Off Point Aulon, Cal.		23.0	0.32	1.83	48.3	7.0	51.2	5.5	36.3
43	M 5	Fucus furcatus	Point Alones, Cal.		4.9	trace	1.42	22.5	14.8	73.2	4.3	7.7
44	M 6	Postelsia palmaeformis	Montara Point, Cal.	Fronds	9.7	0.15	1.40	29.7	14.4	66.0	4.3	15.3
45	M 7	Gigartina radula	Monterey Bay, Cal.		3.9	trace	2.18	24.5	18.3	72.1	3.4	6.2
46	M 8	Fucus evanescens	Point Alones, Cal.		5.6	0.13	1.53	20.5	11.7	75.1	4.4	8.8
47	M 9	Nereocystis luetkeana	Point Pinos, Cal.	Thallus	19.4	0.12	1.70	42.8	12.1	53.1	4.1	30.7
48	M 10	Dictoneuron californicum	Point Pinos, Cal.		15.3	0.09	2.11	33.1	8.9	60.0	6.9	24.2
59	M 11	Costaria turneri	Point Alones, Cal.		14.4	trace	2.10	30.5	7.7	61.0	8.5	22.8
50	M 12	Nereocystis luetkeana	Off Point Pinos, Cal.	Stipes and float	26.1	0.15	1.12	55.5	14.3	40.6	3.9	41.2
51	M 13	Gigantina spinosa	Monterey Bay, Cal.		9.2	trace	1.84	25.9	14.3	70.5	3.6	14.5
52	M 14	Laminaria andersonii	Near Point Pinos, Cal.	Stipes and fronds	6.3	0.6	1.77	19.4	9.4	45.8	4.8	10.0
53	S 1	Macrocystis pyrifera	Station 1		15.7	0.15	0.90	35 0	10.1	60.9	4.1	24.9
54	S 2	"	Station 2		13.4	0.23	0.74	31.2	10.0	62.9	5.9	21.2
55	S 3	"	Station 3		13.4	0.29	1.17	29.3	8.1	66.7	4.0	21.2
56	S 4	"	Station 4		13.6	0.38	1.04	30.6	8.2	64.4	5.0	21.4
57	S 5	Pelagophycus porra	Station 5		12.1	0.27	1.10	29.6	10.5	65.5	4.9	19.1
58	S 5 A	Macrocystis pyrifera	"		12.5	0.24	0.81	28.8	9.0	67.3	3.9	19.8
59	S 6	"	Station 6		13.7	0.29	0.95	30.2	8.5	63.7	6.1	21.7
60	S 7	"	Station 7		12.3	0.2	0.98	28.9	9.5	66.2	4.9	19.4
61	S 8	"	Station 8		12.1	0.17	1.56	29.0	9.9	61.8	9.2	19.1
62	S 9	"	Station 9		12.9	0.17	0.83	28.5	8.1	64.8	6.7	20.4
63	S 9 A	"	"		9.8	0.32	0.9	31.2	15.7	65.1	4.7	15.5
64	S 10	"	Station 10		16.7	0.17	0.995	36.6	10.2	56.7	6.7	26.4
65	S 11	"	Station 11		14.1	0.29	0.898	32.2	9.	63.5	4.3	22.3
66	S 12	"	Station 12		16.9	0.26	1.35	36.3	9.6	58.3	5.4	26.7
67	S 13	"	Station 13		12.6	0.26	0.95	30.4	10.5	64.4	5.2	19.6
68	S 14	"	Station 14		17.4	0.32	1.57	44.1	16.6	49.4	6.5	27.5
69	S 15	"	Station 15		17.4	0.26	1.09	39.0	11.5	55.7	5.3	27.5
70	S 16	"	Station 16		16.4	0.29	1.54	41.2	15.3	50.6	8.1	25.9
71	S 16 A	"	"		8.4	0.41	1.01	22.1	8.8	71.7	6.2	13.3
72	S 17	Pelagophycus porra	Station 17	Young plant	19.5	0.5	1.01	41.0	10.2	52.4	6.6	30.8
73	S 17 A	"	"	Leaves	15.6	0.27	1.63	37.38	12.8	56.2	6.4	24.6
74	S 17 B	"	"	Bulbs	29.9	0.35	0.53	60.6	13.1	36.4	3.0	47.5
75	S 17 C	Macrocystis pyrifera	"	Stems	18.7	0.38	1.24	40.3	10.7	54.4	5.3	29.6
76	S 17 C X	"	"	Stems and leaves	12.4	0.38	1.04	28.3	8.7	64.8	6.9	19.6
77	S 18	"	Station 18		10.6	0.19	0.53	28.6	11.9	61.3	10.1	16.7
78	S 19	"	Station 19		...	0.41	....	....	...	....	....	....
79	S 19 X	"	"		7.2	0.32	0.53	19.2	7.7	76.3	4.5	11.5
80	S 20	"	Station 20		....	0.38	0.62	27.95	....	67.0	5.1	....
81	S 20 A	Pelagophycus porra	"		22.4	0.41	0.69	46.8	12.4	48.4	4.8	34.4

[1] Faint trace.

has marked as Stations the points from which his samples were collected, and has "placed" each station in degrees, minutes and seconds, as follows:

Station	1.	Off Pt. Loma	32° 39′ 30″ 117° 16′
"	2.	Off Bird Rock	32° 45′ 6″ 117° 17′
"	3.	La Jolla	32° 51′ 30″ 117° 16′ 6″
"	4.	San Juan	33° 27′ 117° 43′ 6″
"	5.	Pt. Fermin	33° 43′ 12″ 118° 21′ 30″
"	6.	Malaga Cove	33° 48′ 36″ 118° 24′ 26″
"	7.	Bet. Pt. Gorda & Las Pitas	34° 14′ 20″ 119° 15′
"	8.	Summerland	34° 24′ 15″ 119° 35′ 45″
"	9.	Santa Barbara, outside edge	34° 24′ 119° 40′ 36″
"	9*a*.	Santa Barbara, inside edge	
"	10.	St. Naples	34° 25′ 12″ 119° 56′ 45″
"	11.	C. Quemada	34° 27′ 24″ 120° 7′
"	12.	Little Caxo	34° 26′ 15″ 120° 24′ 30″
"	13.	Anacopa, Wreck of W. Scott	34° 0′ 55″ 119° 23′ 22″
"	14.	Santa Cruz, Gull Is	33° 56′ 30″ 119° 49′ 15″
"	15.	San Miguel, Cuyler Cove	34° 3′ 10″ 120° 21′
"	16.	Tylers Bight, San Miguel	34° 0′ 33″ 120° 24′ 15″
"	16*a*.	Johnstons Lee, Santa Rosa	33° 53′ 45″ 126° 0′ 0″
"	17.	St. Nicholas	33° 16′ 50″ 119° 1′ 6″
"	17*a*.	St. Nicholas Is	33° 16′ 50″ 119° 37′ 45″
"	18.	Santa Barbara Is	33° 28′ 6″ 119° 1′ 6″
"	19.	Clemente, West side	32° 57′ 9″ 118° 35′ 12″
"	20.	Clemente, Smugglers Cove	32° 48′ 12″ 118° 23′

Where no statement is made concerning the nature of the sample it should be understood that it was composed of the leafy parts of a large variety, or the entire plant, of a young, smaller kelp. Thus the samples of the southern Macrocystis consisted, in practically every instance, of branches, bearing fronds and floats.

The soluble salts, given in the ninth column, represent the weights of the combined sodium and potassium sulfates and chlorides and the soluble magnesium salts. The solution from which these had been precipitated had been treated with ammonium carbonate and were probably free from calcium salts.

In the test analyses it was found that there were but negligible amounts of both calcium and magnesium salts in the solution obtained on lixiviating the charred kelp. Whether it is safe to conclude that the lixiviate from the char of every kelp is so free from calcium and magnesium salts is an open question. It is the writer's opinion that the question is answerable in the affirmative. In very rare cases did the addition of ammonium carbonate to the lixiviate produce any precipitation of calcium carbonate; this shows a constant freedom from calcium salts and may be taken, by analogy, as an indication of a similar absence of magnesium salts.

In the tenth column the estimated sodium salts are recorded. These values are mere estimates and most probably are inaccurate. They are obtained by subtracting the percentage of potassium chloride from the percentage of soluble salts; were both potassium and sodium present as chloride alone in the absence of magnesium, these values would be accurate. It has been shown that sulphates are present in variable amounts. To calculate the potassium to chloride when it is present wholly or in part as sulfate, throws the entire error thereby introduced upon the sodium, making it appear disproportionately large.

When the average potassium chloride content of the twenty-nine samples of the northern kelps (from Puget Sound) is compared with that of the twenty-seven samples of the southern (from the region of San Diego), the respective values being 21.3 per cent. and 23.4 per cent., it appears that the content of the southern plants exceeds that of the northern. It is seen, however, that the northern collection comprises numerous varieties not included in the southern. Choosing the four varieties in the northern collection which occur in the greatest quantities (the genuses, Nereocystis, Macrocystis, Postelsia, and Egregia—nine specimens), the average KCl content is 25.7 per cent. Drawing the comparison still closer and comparing the two genuses of the North considered as a commercial source of potash, Nereocystis and Macrocystis, with the two of the south likewise so considered, Macrocystis and Pelagophycus, the average content of the former (six specimens) is 29.4 per cent. KCl, a value considerably in excess of that obtained for the southern varieties (23.4 per cent.). The average content of the two specimens of Macrocystis from Puget Sound is 26.5 per cent.; that of the twenty-two specimens from the South is 21.6 per cent. It is hardly just to draw conclusions from the last comparison; but considered as a whole, indications are that the northern kelps are richer in KCl than the southern.

The average iodine content of the thirty specimens from Puget Sound is 0.155 per cent. and of the four main varieties (ten specimens) is 0.14 per cent. The average of six specimens of the two giant kelps, the Nereocystis and the Macrocystis, is 0.16 per cent. The average percentage content of the southern kelps is 0.29, a value nearly twice that from the northern kelps. From these figures it appears safe to conclude that the northern kelps are richer in potash but poorer in iodine than the southern kelps.

The average KCl and I content of the three giant kelps as derived from the table are:

	Percentage KCl.	I.
Nereocystis	32.6 (av. of 6)	0.14 (av. of 6)
Macrocystis	22.2 (av. of 27)	0.27 (av. of 29)
Pelagophycus	31.3 (av. of 5)	0.36 (av. of 5)

In addition to the variations in composition between the varieties of kelps it will be noted that there is a marked variation between members of the same genus from different localities and from the same locality. There is also a variation strikingly shown in the case of Pelagophycus (Nos. 72, 73 and 74) between the different parts of a single plant. These differences have been pointed out by Balch.[1]

Phosphorus.—Phosphorus was determined by the official method proposed for the determination of that element in organic substances. The results obtained are given in the following table:

Table II.—Analyses by J. A. Cullen.

No.	Serial No.	Name of Kelp.	Location.	P_2O_5. Per cent.
1	R 1	*Nereocystis luetkeana*	San Juan Co., Wash.	0.70
2	R 16	*Egregia menziesii*	"	1.79
3	R 27	*Postelsia palmaeformis*	Neah Bay, Wash.	1.04
4	R 28	*Macrocystis pyrifera*	"	0.81
5	M 2	*Macrocystis pyrifera*	Monterey Bay, Cal..	1.84
6	M 9	*Nereocystis luetkeana*	Point Pinos, Cal.	0.83
7	S 10	*Macrocystis pyrifera*	St. Naples, Cal.	0.66
8	S 15	*Macrocystis pyrifera*	San Miguel, Cuyler Cove, Cal.	0.71
9	S 17 B	*Pelagophycus porra*	St. Nicholas, Cal.	0.51

Sulfur.—Sulfur was determined as barium sulfate in the lixiviate of the charred kelp and ash combined. The char from two-gram samples was lixiviated in the manner described in a foregoing paragraph and then burned to whiteness. The ash was dissolved in hydrochloric acid and the resulting solution evaporated to dryness to dehydrate silicic acid. The residue was taken up with acid, the solution filtered and the filtrate added to the lixiviate from the char. Sulfuric acid was determined in the combined solution in the usual way. The results are recorded in the following table:

Table III.

No.	Serial No.	Name of Kelp.	Source.	SO_3. Per cent.
1	R 6	*Nereocystis luetkeana*	San Juan Co., Wash.	1.68
2	R 29	*Macrocystis pyrifera*	Neah Bay, Wash.	2.24
3	M 4	*Macrocystis pyrifera*	Off Pt. Aulon, Cal.	2.42
4	M 12	*Nereocystis luetkeana*	Off Pt. Pinos, Cal.	1.08
5	S 14	*Macrocystis pyrifera*	Santa Cruz, Gull Is.	3.45
6	S 20 A	*Pelagophycus porra*	Clemente, Smugglers Cove, Cal.	2.33

Organic Constituents.—Little or nothing is known concerning the organic constituents of the Pacific kelps. From the figures in Table I, it can be seen that the organic matter in them rarely falls below 50 per cent. or exceeds 75 per cent. On the average they contain about 1.5 per cent. of nitrogen which, if calculated to protein by the usual factor, is equivalent to 9.4 per cent. protein. This value is about equal to that of other sea weeds examined for that constituent.

Our knowledge concerning the organic constituents of sea algae in general, from which we may derive some idea of what may occur in the Pacific kelps, may be summed up thus: The simple sugars have been identified in certain algae, but they are of rare and scanty occurrence; starch has been said to occur in some varieties, but its identification has not been substantiated; mannan and levulose are of rare occurrence; galactan is common and abundant, and pentosan is the most abundant of all.

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[1] *Loc. cit.*

A NOTE ON THE DETERMINATION OF IODIDES BY DIRECT TITRATION.[1]

By J. W. Turrentine.

Received February 20, 1912.

Bray and MacKay[2] have described a method for the determination of iodides in the presence of bromides and chlorides wherein the iodine is liberated from the iodides by standardized potassium permanganate, added titrimetrically, and is extracted as formed by shaking with successive portions of carbon tetrachloride. When the last of the iodine has been set free, the carbon tetrachloride extract is run off from the supernatant aqueous layer and is shaken with a solution of potassium iodide for the extraction of the iodine. The potassium iodide extract is titrated in the usual way with standard thiosulfate solution.

In the analysis of kelps for iodine a method was sought which would admit of the determination of small amounts of iodide with the minimum expenditure of time. For this purpose the initial liberation of the iodine was effected by standardized potassium permanganate and the amount of iodide thereby determined. The method then became strictly a direct titration of iodide in the presence of bromide and chloride. The results obtained were satisfactorily consistent, and the rapidity with which determinations could be made by means of it was such that this account of the method is deemed warranted.

The permanganate solution was standardized against solutions of potassium iodide of known concentration (1.0 g. KI to 1000 cc. H_2O), the iodide of which had been purified by recrystallization and thorough drying.

Portions of the standard iodide solution were transferred, in graduated pipets, to a 250 cc. dropping funnel; 15 cc. of sulphuric acid solution (10 cc. conc. H_2SO_4 to 90 cc. H_2O) and 15 cc. of carbon tetrachloride were added. For the removal of reducing agents, the carbon tetrachloride had been treated for several hours with iodine which was subsequently removed by shaking with sodium thiosulfate solution.

The solution of the permanganate was run in from a burette, and as the titration proceeded the liberated iodine was removed from the aqueous layer by shaking. With the decrease in the concentration of the iodide in this layer, the solubility of the iodine therein decreased, until, as the end of the titration was approached, the solution became entirely colorless. The persistence for one minute of the pink color of the permanganate was taken as the end point. The procedure was identical with that observed in the actual analysis.

At first the color of the carbon tetrachloride layer caused some trouble in discerning the end point, but with experience the trouble disappeared.

Bray and MacKay have pointed out that in the direct titration of iodides by a permanganate solution there is an error introduced by the incomplete reduction of the last of the permanganate to a form intermediate between the heptavalent and the divalent condition. This would appear to be due to the de-

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

[2] *J. Am. Chem. Soc.*, **32**, 1193 (1910).

crease in the active mass of the iodide, since it is not observable in the presence of an excess of that substance. For a definite amount of the permanganate, then, the intermediate form of the manganese should not be present in the solution until after the iodide had been reduced to a definite concentration. When the concentration of the former is very low (as is normally the case as the end of the titration is approached), that of the iodide likewise would be very low before the reaction leading to the formation of the intermediate manganese compound appeared. In the titration, accordingly, the incomplete reduction does not occur until a definite and very low concentration of the iodide is reached. This point, it follows—since the reaction is irreversible—must be independent of the original active mass of the iodide. For that reason the error should be a constant rather than a variable one; and if the latter, certainly a correction could be introduced whereby it would be neutralized.

It was observed that values obtained for small amounts of iodide undergoing titration were relatively greater than those obtained for larger amounts. When the blank solutions were titrated in the absence of the iodide, it was found that a small amount of the permanganate (0.2 cc.) was reduced. As this was not observable in the absence of the carbon tetrachloride, the reduction of the permanganate was attributed to the carbon tetrachloride, or to some constituent thereof. When a correction was made for this error the values obtained from the titration of the various volumes of standard iodide were found to be concordant within the probable error of experimentation. These values are given in the following table:

No.	Cc. KI.	Cc. $KMnO_4$ corrected.	KI value per cc. $KMnO_4$ corrected.
1	10	1.6	0.00625
2	10	1.6	0.00625
3	10	1.55	0.00645
4	10	1.5	0.00666
5	10	1.6	0.00625
6	10	1.55	0.00645
7	20	3.2	0.00625
8	20	3.2	0.00625
9	20	3.3	0.00606
10	25	4.05	0.00617
11	40	6.55	0.00611
12	40	6.5	0.00615
13	40	6.5	0.00615
14	100	16.5	0.00602
		Mean,	0.00624

The range in values in iodide of the solutions titrated in the standardization was the same as that which was expected to be found in the substances to be analyzed. For that reason they cover only a small range. Whether the method is applicable to the determination of larger amounts of iodide can not be said, but *a priori* considerations indicate that it may be employed. It should only be necessary to remove the iodide with successive portions of carbon tetrachloride in order that that layer might not become too concentrated in iodine. Whether new corrections would have to be introduced or not could be determined experimentally.

The permanganate solution was standardized with solutions containing no chlorides or bromides, while the solutions analyzed contained large amounts of chlorides and presumably some bromides. Bromides in small amounts are commonly found among the saline constituents of sea algae. Whether they were present in the specimens analyzed has not been determined. In this particular, then, the conditions existing during the standardization were not strictly reproduced in the analysis. However, the authors whose method is here applied have explained the conditions under which chlorides and bromides are liable to introduce an error in the determination of iodide and, it is believed, those conditions were strictly observed in the adaptation of the method to the analysis of kelps.

It is a truism that any titration method is reliable in which the solutions employed are standardized against the compound which is to be determined, provided the standardization and the analyses be made under identical conditions.

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DETERMINATION OF TOTAL POTASSIUM IN MINERALS.

By CHARLES J. SCHOLLENBERGER.

Received December 18, 1911.

In very many instances only the percentage of potassium in a sample is required to be determined, while the amount of sodium present is a matter of indifference. In such cases, the method of J. Lawrence Smith is long and tedious; the modification of Smith's method, described by Pettit and Ystgard in Proceedings of the Association of Official Agricultural Chemists (1906), while shorter, leaves much to be desired. It has the disadvantage that a large amount of an alkaline solution must be evaporated in glass, with the attendant liability of contamination. The calcium carbonate which separates during this evaporation is non-crystalline, adherent, and difficult to wash. Even after filtration, much silica remains in the solution, causing trouble in later operations. In order to overcome these difficulties, and, if possible, to further shorten the time required for a determination, the following method was worked out in this laboratory:

Proceed as in the regular Smith method for total alkalies, until the filtrate from washing out the alkalies from the fusion is obtained. To this add a moderate excess of hydrochloric acid and evaporate to dryness on a steam bath, remote from ammonia fumes. Take up with about 2 cc. of concentrated hydrochloric acid and 25 cc. of hot water, and filter through a special suction filter into a 150 cc. beaker, washing the large beaker and filter well. Add the proper amount of hydrochloroplatinic acid solution, and evaporate on steam bath until of a semi-solid consistency. The large amount of calcium chloride present crystallizes out on cooling, but is readily soluble in acidulated alcohol. The crystalline precipitate of the potassium chloroplatinate is washed with acidulated alcohol,[1] Gladding wash, and 80 per cent. alcohol, on a filter designed especially for this work. After drying to re-

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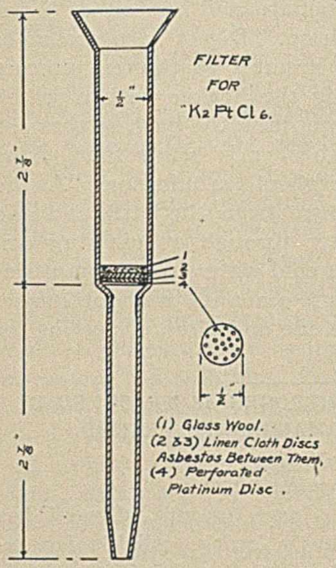
[1] *Jour. Am. Chem. Soc.*, **20**, 341.

move alcohol, the precipitate is dissolved in hot water, the solution being received in a tared platinum dish, and after evaporation, dried and weighed.



The special filter mentioned was designed by Professor J. W. Ames, chief of the chemistry department, and is of the form and dimensions shown in the drawing; the filtering medium, supported by a perforated disc of platinum, consists of a neatly fitting circular piece of linen cloth, a small amount of purified asbestos, and a small plug of glass wool, to prevent the asbestos being disturbed.

The filter is intended to be used with suction; it has many advantages over a funnel and paper, or a Gooch crucible, filtering much more rapidly, and being much more easily washed free from soluble salts, by reason of the decreased area of the filtering medium.

The advantages gained by using this method of filtration are increased accuracy of results, as well as a great saving of labor and time.

The above-described method has been in use for some time and has given very satisfactory results on several hundred soil samples.

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NOTE ON THE NEUTRAL PERMANGANATE METHOD FOR THE AVAILABILITY OF ORGANIC NITROGEN.[1]

By John Phillips Street.

Received January 12, 1912.

When the neutral permanganate method was devised some years ago by the writer, a series of mixtures of known composition was prepared by which it was possible to determine the availability of the organic nitrogen both in the raw material and when mixed with the usual phosphatic and potassic ingredients of commercial fertilizers. In these mixtures arbitrary amounts of acid phosphate and muriate of potash were used, the total weight of the mixtures always equaling 50 grams, the acid phosphate varying from 10 to 34.5 grams, and the muriate being constant at 10 grams. The mixtures, with one exception, each contained an equivalent of 1.50 per cent. of organic nitrogen in varying forms. The agreement in availabilities of the organic form, when used alone and when mixed, was considered quite satisfactory; at any rate the figures obtained were sufficient, in the writer's estimation, to allow of a differentiation between the valuable and the relatively useless forms of organic ammoniates.[2]

A more extended series of tests, however, has shown that the method as originally published might give misleading results, which in certain cases would be most unfair to high-grade materials. In other words, under certain conditions, a high-grade material like dried blood, which showed a high permanganate availability unmixed, when mixed with acid phosphate and muriate of potash showed availabilities which would class it with garbage tankage and only a little above peat. Apparently the cause of this discrepancy in results lay either with the acid phosphate or the potash. Accordingly, another series of mixtures were made in which the quantity of these ingredients was varied, while the amount of organic nitrogen was kept constant at 0.0450 gram. These experiments showed at once that the muriate of potash had no effect on the results. A sample of dried blood which unmixed showed an availability of 97, when mixed with muriate showed 95 and 96. This same blood, however, when mixed with 2 grams of acid phosphate, showed only 90, and with 4 grams only 59. In three samples of blood the presence of 4 grams of acid phosphate reduced the availabilities from 96, 94 and 96 to 53, 70 and 67, respectively. While this discrepancy was most marked in the case of dried blood, a decreased availability was also noted in tankage, fish, hide and skin meal, tartar pomace, solubilized organic nitrogen and peat. With knuckle bone and cottonseed-meal the acid phosphate seemed to have less effect, and with garbage tankage the availability of the nitrogen in the mixture was, as has always been my experience, considerably higher than in the raw material.

It was thought at first that the relatively large amount of acid phosphate (4 grams), compared with the charge of dried blood (0.34 gram), prevented complete action of the permanganate. Experiments carried on by Mr. J. E. Breckenridge, in which the permanganate mixture was agitated much more frequently than directed in the method, however, gave no better results. Thinking that the acidity of the acid phosphate might be the determining factor, another series of tests were carried out in which one gram of sodium carbonate was added just prior to the introduction of the permanganate solution. The results obtained were most satisfactory, as the table shows. A 96 blood with 2 grams of acid phosphate showed 96, with 4 grams, 90. A 91 tankage with the same amounts of acid phosphate showed 94 and 85. A 97 bone showed 93; a 93 fish, 92; a 92 cottonseed-meal, 95; a 54 tartar pomace, 48; a 65 solubilized organic nitrogen, 65; a 46 peat, 42. Garbage tankage again showed a high result, the availability increasing from 47 to 68, but even this high figure is too low to mislead any one as to its value.

The writer makes no attempt to explain just what causes these discrepancies. That they exist, however, is an undoubted fact, and the simple modification, at least in the materials tested, appears to give true and reasonable results.

In using the neutral permanganate method, it must be remembered that it is not an absolute method, and that no pretense is made that by it the exact

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[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] This Journal, **2**, 312 (1910).

agricultural value of an organic nitrogenous material may be determined. A long series of tests, however, shows that it does differentiate between the good and the bad materials of generally recognized value like blood, tankage, ground bone, dried fish, cottonseed-meal and castor pomace rarely showing availabilities less than 90, while leather, mora meal, tobacco stems, peat, sheep manure, garbage tankage, tartar pomace, beet root manure and fillerine show availabilities from 17 to 69. The method possesses the further advantages of simplicity of manipulation, of easy maintenance, of uniform conditions (a very important matter) and of measuring a definite chemical action, namely, the amount or organic nitrogen not decomposed by a definite quantity of permanganate of potash solution of fixed and uniform strength, acting for a definite time at a uniform temperature on a definite amount of organic nitrogen. Every condition can be definitely controlled and the personal equation is almost negligible.

The method as now used by the writer is as follows:

	Nitrogenous material.	Acid phosphate.	KCl.	Na_2CO_3.	KMnO₄ solubility.	
					Raw material.	Mixture.
Blood, No. 22160	−0.34	2.00	0.50	....	96	83
	−0.34	3.00	0.75	....	96	70
	−0.34	4.00	1.00	....	96	53
	−0.34	2.00	....	1.00	96	96
	−0.34	4.00	....	1.00	96	90
Blood, No. 24003	−0.33	....	1.00	....	97	96
	−0.33	2.00	....	....	97	90
	−0.33	2.00	1.00	....	97	89
	−0.33	4.00	1.00	....	97	59
Blood, No. 22406	0.44	4.00	1.00	....	94	70
Blood, No. 22965	0.56	4.00	1.00	....	96	67
Tankage, No. 22346	−0.96	2.00	0.50	....	91	80
	−0.96	3.00	0.75	....	91	82
	−0.96	4.00	1.00	....	91	78
	−0.96	2.00	....	1.00	91	94
	−0.96	4.00	....	1.00	91	85
Knuckle bone, No. 22360	−1.17	2.00	0.50	....	97	88
	−1.17	3.00	0.75	....	97	84
	−1.17	4.00	1.00	....	97	90
	−1.17	4.00	....	1.00	97	93
Fish, No. 22667	−0.70	2.00	0.50	....	93	89
	−0.70	3.00	0.75	....	93	88
	−0.70	4.00	1.00	....	93	85
	−0.70	2.00	....	1.00	93	92
Cottonseed-meal, No. 22393	−0.75	1.95	0.67	....	92	90
	−0.75	2.00	....	1.00	92	95
Hide and skin meal, No. 24009	−0.58	2.00	1.00	....	75	60
	−0.58	4.00	1.00	....	75	45
Garbage tankage, No. 22383	−2.25	0.75	0.75	....	47	70
	−2.42	4.00	1.00	....	47	55
	−2.42	2.00	....	1.00	47	68
Tartar pomace, No. 24013	−1.29	4.00	1.00	....	54	34
	−1.29	4.00	....	1.00	54	48
Solubilized organic nitrogen, No. 23998	−0.93	4.00	1.00	....	65	20
	−0.93	4.00	....	1.00	65	65
Peat, No. 23392	−1.67	4.00	1.00	....	46	22
	−1.67	4.00	....	1.00	46	42
	−1.67	2.00	....	1.00	46	45

MODIFIED NEUTRAL PERMANGANATE METHOD.

Weigh a quantity of the fertilizer, equivalent to 45 mg. of water-insoluble organic nitrogen,[1] on a moistened 11 cm. filter paper, and wash with successive portions of water at room temperature until the filtrates amount to 250 cc. Transfer insoluble residue with 25 cc. of tepid water to a 300 cc. low-form Griffin beaker, add one gm. sodium carbonate and 100 cc. of 2 per cent. permanganate solution. Digest in a steam or hot-water bath for thirty minutes at the temperature of boiling water, covering the beaker with a watch glass and setting well down into the bath so that the level of the liquid in the beaker is below that of the bath. Stir twice at intervals of ten minutes. At the end of the digestion remove from the bath, add 100 cc. of cold water and filter through a heavy 15 cm. folded filter. Wash with cold water, small quantities at a time, until total filtrate amounts to about 400 cc. Determine nitrogen in residue and filter, correcting for the nitrogen of the filter.

ACTIVITY OF ORGANIC NITROGEN AS MEASURED BY THE ALKALINE PERMANGANATE METHOD.[1]

By C. H. Jones.

Received January 12, 1912.

During the past year a large amount of work has been done toward securing a quick, reliable laboratory method for determining the activity of organic nitrogen in crude stock and commercial fertilizers.

A committee of Experiment Station Chemists, appointed in March, 1910, has been given opportunity to observe the methods employed in "wet mixing" and to secure samples of both the raw materials used and the finished product. These have been tested by laboratory methods and vegetation experiments, and, as a result of this work, the following method, perfected by the writer, and known as the Alkaline Permanganate Method, was adopted in March, 1911, by the directors of the Experiment Stations of New York, New Jersey, and the New England States.

ALKALINE PERMANGANATE METHOD FOR ORGANIC NITROGEN ACTIVITY.

(1) *With Mixed Fertilizers.*—Transfer an amount of material equivalent to *50 milligrams of water insoluble organic nitrogen*[2] to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When it is found necessary to use four or more grams of the original material to secure the 50 milligrams of water insoluble nitrogen, *i. e.*, when the percentage of water insoluble nitrogen is 1.25 or less, weigh the required amount into a small beaker, wash by decantation, finally transfer to the filter and finish the extraction as previously directed. When a relatively large amount (7 to 10 grams of a fertilizer) is to be extracted it is desirable to weigh out duplicate portions. One is used for the determination of nitrogen activity by the alkaline permanganate method, and the other is Kjeldahled for its nitrogen content. Compare the latter figure with the result previously obtained from the two gram extraction (see footnote) and in case of any marked discrepancy, *i. e.*, over 0.05 per cent. of nitrogen, calculate the nitrogen activity on the basis of the exact nitrogen equivalent used.

(2) *With Raw Materials.*—Transfer an amount of

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[1] Determined by washing one gram of the material on a 11 cm. filter with water at room temperature, to a volume of about 250 cc. Dry and determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

material equivalent to *50 milligrams of water insoluble organic nitrogen*[1] to a small mortar, add about 2 grams powdered rock phosphate, mix thoroughly, transfer to a filter paper and wash with successive portions of water at room temperature until the filtrate amounts to about 250 cc. When much oil or fat is present, it is well to wash somewhat with ether before extracting with water. Dry the residue at a temperature not exceeding 80° C. and *transfer from the filter* to a 500–600 cc. Kjeldahl distillation flask (round bottom preferred, but, if flat bottom is used, incline at an angle of 30°). Add 20 cc. water, 15 to 20 small glass beads to prevent bumping, and 100 cc. alkaline permanganate solution (25 grams pure potassium permanganate and 150 grams sodium hydroxide, separately *dissolved* in water, the solutions cooled, mixed and made to volume of one liter). Connect with an upright condenser to which a receiver containing standard acid has been attached. Digest slowly, *below distillation point, with very low flame*, using coarse wire gauze and asbestos paper between flask and flame, for *at least 30 minutes. Gradually* raise the temperature and when danger (if any) from frothing *has ceased*, distil *until* 95 cc. of distillate are obtained, and titrate as usual. In cases where a tendency to froth is noticed, lengthen the *digestion* period and no trouble will be experienced when the distillation is begun. During the digestion, gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides. It is recommended that as nearly as possible 90 minutes be taken for the digestion and distillation. The nitrogen thus obtained is the *active water insoluble organic nitrogen.*

The results are expressed in the following form:

1. Nitrogen in nitrates.
2. Nitrogen in ammonium salts.
3. Water soluble organic nitrogen.
4. Active insoluble organic nitrogen.
5. Inactive insoluble organic nitrogen.
6. Total nitrogen.

The first two divisions include the mineral forms of nitrogen derived mainly from nitrate of soda and sulphate of ammonia. Both are water soluble and readily available for plant growth.

The third division includes that portion of the organic nitrogen which is soluble in water. It is considered highly available as plant food.

The fourth division comprises that portion of the water insoluble organic nitrogen which is liberated by the alkaline permanganate method. It is likewise available for plant food, and hence is termed "Active."

The fifth division, listed as "Inactive Insoluble Organic Nitrogen" is that portion unaffected by the alkaline permanganate treatment and is of little value for the immediate use of plants. It is, therefore, rightly termed "Inactive."

In this connection it should be mentioned that results secured by the alkaline permanganate method have been confirmed by vegetation trials on a considerable number of prominent crude stock nitrogenous materials, as well as on the water insoluble portion of many high and low grade commercial fertilizers.

To fully illustrate the adaptability of the method, and form used to express the results, the accompanying table has been prepared, giving results by the alkaline permanganate method on crude stock, commercial fertilizers and mixtures of known composition. The samples reported have been carefully selected from a large list and may be regarded as typical of the ordinary materials now met with in the fertilizer industry.

The interpretation of results, when the suggested form is used, is very simple. It is, however, necessary at the outset to understand that results by the laboratory method under discussion deal wholly with the *quality*, not quantity, of the *organic nitrogen* and that any amount of nitrate or ammonia has no effect on the activity of the organic nitrogen present.

To determine whether the organic nitrogen has been derived from materials of known high availability, *i. e.*, blood, tankage, cottonseed-meal, etc., or from more inert or slowly available sources, *i. e.*, garbage tankage, peat, etc., a comparison of the columns headed "Active" and "Inactive" will at once tell the story. *Organic nitrogen is derived from high grade materials in proportion as the stated percentage in the "Active" column is greater than that in the "Inactive" column and its class and its availability as plant food can be accurately inferred by then noting the relative quantity of water soluble organic nitrogen present.*

The availability of the total nitrogen in a fertilizer should not be confused with the availability of the organic nitrogen present. Total availability can easily be calculated by assuming nitrates and ammonia salts to be entirely available.

To further illustrate the interpretation of results, let us consider some of the individual samples reported in the table.

Crude Stock, Nos. 1–14.

No. 1, Dried Blood. More than twice as much "active" as "inactive" insoluble nitrogen. A high grade material.

No. 2, H. G. Tankage. More than twice as much "active" as "inactive" insoluble nitrogen. Contains a large percentage of water-soluble organic nitrogen which is characteristic of many tankages. High grade.

No. 5, Base Goods (wet mix) made under Station supervision. A small percentage of "active" and "inactive" organic nitrogen, the latter in excess, indicates a small amount of some low grade material. The relatively large water soluble percentage 1.03, which is readily available, is characteristic of the wet mix process and at once places the material in the high grade class.

No. 6, Cottonseed-Meal. "Active" well in excess of "inactive." High grade.

No. 12, Garbage Tankage. "Inactive" more than twice as much as "active." A low grade material.

No. 13, Peat. "Inactive" in excess of "active." A low grade material.

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[1] Determined by extracting 2 grams of the material on a filter paper with water at room temperature, until the filtrate amounts to about 250 cc. Determine nitrogen in the residue, making a correction for the nitrogen in the filter paper if necessary.

Commercial Fertilizers, Nos. 15–22.

No. 15, "Active" nearly twice the "inactive" and a generous allowance of water soluble organic nitrogen is present. High grade.

No. 16, "Inactive" greater than "active." A small amount of water soluble organic nitrogen. Poor grade. The large percentage (2.46) of nitrate and ammonia present would make the total availability of the nitrogen in this fertilizer quite high, but does not alter the fact that the organic nitrogen came from low grade sources.

TABLE I.

Number.	Crude stock. Material.	Nitrogen per cent.						Organic and volatile matter in the water insoluble material. Per cent.	Per cent. of nitrogen in the organic and volatile matter.
		In nitrates. 1.	In ammonia salts. 2.	Water soluble organic. 3.	Active water insoluble organic. 4.	Inactive water insoluble organic. 5.	Total. 6.	7.	8.
1	Dried blood	....	0.06	0.25	9.82	4.01	14.14	84.9	16.3
2	High grade tankage	....	0.12	3.75	4.28	1.93	10.06	60.4	10.3
3	Fish	....	0.08	0.40	7.26	2.35	10.29	83.9	11.7
4	Hoof meal	....	0.14	0.94	9.47	4.25	14.80	81.4	16.9
5	Base goods (wet mix)	....	0.25	1.03	0.21	0.34	1.83	12.1	4.5
6	Cottonseed meal	....	0.09	0.54	4.09	2.30	7.02	67.7	9.4
7	Castor pomace	....	0.06	0.82	2.55	1.85	5.28	58.6	7.5
8	Medium tankage	....	0.27	0.92	2.85	1.61	5.65	48.7	9.2
9	Bone meal	....	....	0.59	1.39	0.68	2.66	24.4	8.5
10	Treated leather	....	0.27	0.63	2.88	2.76	6.54	75.2	7.5
11	Charred leather	....	0.04	0.07	0.12	0.79	1.02	22.5	4.0
12	Garbage tankage	....	0.06	0.31	0.84	1.95	3.16	54.9	5.1
13	Peat	....	0.02	0.04	1.24	1.79	3.09	71.5	4.2
14	Mora meal	....	0.03	0.31	0.75	1.60	2.69	51.0	4.6
	Commercial Fertilizers.								
15	Guaranteed 3 per cent. plus nitrogen	....	0.77	1.26	1.30	0.70	4.03	14.7	13.6
16	Guaranteed 3 per cent. plus nitrogen	1.15	1.31	0.24	0.36	0.48	3.54	12.6	6.7
17	Guaranteed 2 per cent. plus nitrogen	0.21	0.11	0.51	1.06	0.55	2.44	14.8	10.9
18	Guaranteed 2 per cent. plus nitrogen	0.81	0.98	0.09	0.43	0.48	2.79	13.2	6.9
19	Guaranteed 1 per cent. plus nitrogen	0.46	0.14	0.36	0.40	0.27	1.63	7.7	8.7
20	Guaranteed 1 per cent. plus nitrogen	....	0.63	0.18	0.29	0.31	1.41	11.9	5.1
21	Guaranteed 0.8 per cent. plus nitrogen	....	....	0.40	0.34	0.26	1.00	6.4	9.4
22	Guaranteed 0.8 per cent. plus nitrogen	....	0.21	0.27	0.37	0.40	1.25	15.8	4.9
	Mixtures of Known Composition								
23	50 Garbage tankage, 70 Ac. phos., 20 KCl	....	0.05	0.01	0.27	0.78	1.11	20.4	5.1
24	30 Garbage tankage, 10 Am. sul., 70 Ac. phos., 20 KCl	....	1.62	0.10	0.22	0.52	2.46	14.7	5.0
25	10 Blood, 70 Ac phos., 20 KCl	....	0.04	0.10	0.99	0.45	1.58	11.5	12.5
26	25 Blood, 70 Ac. phos., 20 KCl	....	0.04	0.10	2.12	0.86	3.12	22.1	13.4
27	26 Base (5) plus 3 blood (1)	....	0.22	0.87	1.19	0.70	2.98	22.1	8.6
28	26 Base (5) plus 3 H. G. tankage (2)	....	0.23	1.18	0.59	0.53	2.53	18.1	6.3
29	26 Base (5) plus 3 fish (3)	....	0.22	0.90	0.89	0.62	2.63	19.6	7.7
30	26 Base (5) plus 3 C. S. meal (6)	....	0.22	0.94	0.61	0.55	2.32	18.2	6.4
31	26 Base (5) plus 3 med. tank (8)	....	0.25	0.97	0.49	0.46	2.17	16.6	5.7
32	26 Base (5) plus 3 garbage T. (12)	....	0.22	0.94	0.27	0.43	1.86	16.7	4.2
33	26 Base (5) plus 3 peat (13)	....	0.22	0.90	0.33	0.44	1.86	19.2	3.9
34	10 Dried blood, 5 C. S. M., 50 Ac. phos., 7½ KCl	....	0.03	0.04	1.75	0.68	2.50	19.3	12.6
35	20 Treated leather, 15 garbage tankage, 10 peat, 50 Ac. phos., 5 KCl	....	0.08	0.09	0.85	1.07	2.09	32.1	5.9

Similarly, the organic nitrogen in Nos. 17, 19 and 21 is of high availability, while that in Nos. 18, 20 and 22 is derived from inferior sources.

Mixtures of Known Composition, Nos. 23–35.

No. 23, "Inactive" far in excess of "active." A low grade material.

No. 24, "Inactive" far in excess of "active." A low grade material furnished the organic nitrogen. The total nitrogen availability of No. 24, owing to the presence of ammonium sulphate, is not questioned, but, nevertheless, the organic nitrogen in the mixture is low grade.

Nos. 25 and 26, "Active" over twice as much as "inactive." High grade.

Nos. 27 to 33 are mixtures of 26 parts base goods (wet mix) No. 5 with 3 parts of eight different organic ammoniates. Nos. 27 to 31, owing to excess of "active" over "inactive," are rated as high grade.

In Nos. 32 and 33, the introduction of garbage tankage and peat is in evidence, as shown by the excess of "inactive" over "active."

No. 34. The nitrogen is obtained from dried blood and cottonseed-meal and shows nearly three times as much "active" as "inactive" nitrogen. High grade.

No. 35. The nitrogen is obtained from treated leather, garbage tankage and peat. It shows an excess of "inactive" over "active," and the low grade of the nitrogen material is thus indicated.

A laboratory method for nitrogen availability should not only differentiate between crude nitrogenous stock of high and low agricultural values, but must also make similar distinctions when the crude stock is incorporated into the ordinary mixed fertilizer. A comparison of the results under crude stock with those obtained in mixtures of known composition will show a very close agreement between "theoretical" and "actual" results. This indicates that "acid phosphate" and other ingredients are not "disturbing" factors and that the manufacturer having determined in advance the nitrogen activity of his crude stock may be assured of getting full credit for the nitrogen activity of his finished product.

ORGANIC AND VOLATILE MATTER.

A determination of the organic and volatile matter in the water insoluble portion of crude stock or a fertilizer will furnish a reliable clue to the character of the organic nitrogen in the material. The procedure in use at the Vermont Experiment Station laboratory is as follows: Weigh two grams of material onto a filter paper and wash with about 250 cc. of water at room temperature. Dry the residue at about 80° C. and transfer from the filter to a small tared porcelain dish (E. & A. 2963, No. 09). Place in an air bath and dry for 3 hours at 100° C. Cool in desiccator and weigh. Burn off organic and volatile matter over a Bunsen flame, stirring occasionally. Cool in desiccator and weigh. Calculate percentages of organic and volatile matter and ash.

The nitrogen in the washed residue (previously determined for the alkaline permanganate activity) multiplied by 100 and divided by the organic and volatile percentage gives the "per cent. nitrogen in the organic and volatile matter."

Reference to the last column in the table shows that this figure varies in crude stock from 4.0 to 16.9, the relatively high figures corresponding to materials of recognized high grade and the low figures to those classed as inferior for plant food purposes. Thus dried blood shows 16.3 "per cent. of nitrogen in organic and volatile matter," fish 11.7, cottonseed-meal 9.4, medium tankage 9.2, while garbage tankage contains 5.1, peat 4.2, and mora meal 4.6 per cent.

Applying this procedure to commercial fertilizers licensed in Vermont from 1908 to 1911, inclusive, a range from 4 to 13.6 per cent. has been found, the low figures without exception corresponding to low organic nitrogen activity.

The organic and volatile matter in different mixtures of acid phosphate and muriate of potash has been found to vary from 3 to 3½ per cent., but as only a comparative figure is wanted, we have thus far made no correction when using the method on commercial fertilizers.

Fertilizer.	Per cent. nitrogen in the organic and volatile matter.	Activity by alk. Permanganate method.	Fertilizer.	Per cent. nitrogen in the organic and volatile matter.	Activity by alk. Permanganate method.
1	12.0	65[1]	9	5.3	37
2	13.6	65[1]	10	5.2	33
3	11.8	73[1]	11	9.0	69[1]
4	4.0	39	12	9.1	68[1]
5	5.1	49	1499	11.6	83[1]
6	5.1	48	1546	9.6	73[1]
7	5.5	48	1560	8.9	74[1]
8	10.6	71[1]	1573	6.7	52

As yet, we have found no sample of crude stock or fertilizer that does not show the desired relationship between the percentage of "nitrogen in the organic and volatile matter" and activity of the water insoluble nitrogen, as measured by the alkaline permanganate method and vegetation tests. Thus, selecting at random from our results with commercial fertilizers collected during the past four years, the accompanying table indicates the general trend of results.

The point that the writer wishes to establish is that this determination of "nitrogen in the organic and volatile matter" will show whether the source of the water insoluble organic nitrogen is from materials rich in nitrogen or from those poor in this element.

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[1] Nitrogen readily available for plant use.

THE EFFECT OF THE "WET PROCESS" ON THE AVAILABILITY OF LOW GRADE NITROGENOUS MATERIALS.[1]

By BURT L. HARTWELL AND F. R. PEMBER.

Received January 12, 1912.

It has been known for a long time that the nitrogen in such materials as roasted leather, garbage tankage and peat is of very low availability, and for that reason the fertilizer laws of certain states do not permit their use in fertilizers.

The claim has been made, however, by certain manufacturers that the so-called wet process of treating such materials so completely changes their physical and chemical nature that their availability is materially increased; and that, after having been subjected to the wet process, they should not then be considered in the same class as the original materials, nor discriminated against in the same way. Although these claims seemed reasonable, those charged with the inspection of fertilizers could hardly accept them without experimental proof.

Largely through the influence of a certain manufacturer of fertilizers, a fertilizer works was finally thrown open in 1910 to a committee, consisting of C. H. Jones, chairman, J. P. Street and B. L. Hartwell, which had been appointed by the Directors of the agricultural experiment stations of the New England States, New York and New Jersey to investigate the subject of the determination, by laboratory methods, of the availability of organic nitrogen.

This committee witnessed the mixing of about a hundred tons of hair tankage, garbage tankage, roasted leather, phosphate rock and sulfuric acid, by the wet process, took samples of all materials used in the mixture, and securely sealed the "den" containing the manufactured material. Two days later, the chairman of the committee, who was present at the breaking of the seals and opening of the den, took samples of the finished product. The identity of the nitrogenous material had been practically destroyed by the treatment. The maximum thermometer placed near the bottom of the den had registered 208° F.

The following determinations made by C. H. Jones show some of the changes which took place in the nitrogenous material during the process.

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[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

Per Cent. of Total Nitrogen Present in Different Forms.

	Before putting into the den.	After removing from the den.
In ammonium salts	6.5	14.3
In water soluble organic matter	7.8	57.7
In water insoluble organic matter	85.7	28.0

For vegetation experiments, the authors secured from the committee samples of the different nitrogenous materials which formed a part of the mixture, as well as of the final "base goods." Through the coöperation of Mr. Jones they were also supplied with similar low grade nitrogenous materials both in their unacidulated condition, and after they had been subjected individually to laboratory treatment with phosphate rock and sulfuric acid in a manner similar to that employed in the factory; in the case of each nitrogenous material, 500 grams of it were mixed with 750 grams of phosphate rock and 1250 grams of sulfuric acid.

Mr. Jones kindly furnished the following analyses of the material treated in the laboratory.

	Per cent. of nitrogen in the material.			
	Ammoniacal.	Water soluble organic.	Water insoluble organic.	Total.
Garbage tankage	0.02	0.23	2.61	2.86
Garbage tankage, acidulated	0.06	0.20	0.27	0.53
Treated leather	0.03	0.65	4.74	5.42
Treated leather, acidulated	0.04	0.78	0.16	0.98
Hair	0.28	0.60	10.77	11.65
Hair, acidulated	0.13	1.23	0.22	1.58

The nitrogen content of base goods made at the factory and of the identical materials which formed a part of the mixture, as finally used in the experiments, was as follows:

	Nitrogen. Per cent.
Hair tankage	6.28
Treated leather (roasted)	6.49
Garbage tankage	2.87
Base goods, including the above	1.68
Water soluble nitrogen in base goods	1.28
Water insoluble nitrogen in base goods	0.40

The materials which were treated with phosphate rock and sulfuric acid in the laboratory ("acidulated"), and those mixed in the factory, were of about the same grade with the exception of the hair goods. The hair tankage used at the factory was a mixture of hair, wool, etc., which had undergone some decomposition, with the formation of ammonia, whereas that treated in the laboratory was clean, fine hair, on account of this difference, both grades were included in the pot experiment.

The vegetation experiments were conducted in eight-inch Wagner pots. Natural soil from two different localities was used. Optimum amounts of lime, potassium, and phosphorus were provided in hydrated lime, sulfate of potash, Thomas phosphate and acid phosphate, in order that the differences in growth might be attributable only to differences in the availability of the nitrogen. Unless stated otherwise the same amount of nitrogen for each crop (0.1 gram) was added per pot in the different materials.

The results are given in the accompanying table.

Grams of Air-dry Crops Grown Successively with the Same Amount of Nitrogen, unless Otherwise Stated, Added per Pot for Each Crop.

	Grown in "Station" soil.			Grown in "Larkin" soil.		
Source of nitrogen.	Japanese millet.	Oats.	Buckwheat.	Oats.	Japanese millet.	Average relative increase in yield (Blood = 80).
None (check)	48.5	22.0	10.3	42.0	37.5	0
	50.0	23.5	9.3	48.5	35.5	
	49.5	24.0	8.0	44.0	35.5	
Hair tankage	53.0	30.5	14.5			
	49.5	32.0	11.3			59
Hair	48.5	28.0	11.0			
	49.5	30.0	11.5			33
Ditto, acidulated	55.5	31.0	12.5			
	52.0	31.0	11.0			64
Treated leather	51.0	25.5	12.5			
	50.5	24.0	10.5			23
Ditto, acidulated	56.0	33.0	16.5			
	56.0	29.0	10.0			80
Garbage tankage	48.0	22.5	10.5	48.0	40.0	
	48.0	24.5	9.5	46.0	41.5	13
Ditto, acidulated	49.0	22.0	8.5	50.5	34.0	
	48.5	21.5	10.0	54.0	34.5	8
Hair tankage, garbage tankage, and treated leather	48.0	29.5	11.0	54.0	43.0	
	47.0	29.5	10.3	56.0	44.0	49
Ditto, acidulated (base goods)	52.5	30.5	17.0	54.0	52.0	
	50.0	31.5	12.5	57.0	49.0	84
Insoluble part of base goods	43.5	22.0		44.0	36.0	
	48.0	20.6		46.0	43.0	0
Dried blood	50.5	33.0	12.0[1]	50.0	48.0	
	53.0	32.5	12.5	52.0	50.5	80
	52.0	30.0	21.0	54.5	49.0	
Ditto, with extra phosphorus	54.5	38.0[2]	26.5[2]	53.0	44.0	
	50.5	40.5[2]	26.0[2]	53.0	46.5	
Water soluble part of base goods	55.0	41.5[2]		53.0	51.0	
	58.7	40.0[2]		62.0	47.0	
Extra amt. blood	56.5	40.0	28.0	55.0	61.0	
	60.0	42.0	24.3	57.0	61.0	
Nitrate of soda	57.0	50.0[2]		61.0	49.0	
	56.5	46.5[2]		54.0	52.0	

In spite of the fact that an attempt was made to secure soils which were deficient in nitrogen, the first crop in the case of each soil proved to be nearly as large from the check pots, which received no nitrogen, as from the others. This is not an uncommon experience even with soils which have grown crops for some time without nitrogenous manures. It results from the fact that the application of lime, which proved necessary to maintain a soil reaction which was neutral to litmus paper and conducive to the utilization of organic nitrogen, led to the liberation of sufficient nitrogen to support a nearly maximum crop.

Although in the case of both soils, for the reason stated previously, distinct differences did not result from the different applications, it was decided nevertheless to include the results with those secured with the subsequent crops grown in the same soils after renewing the manurial applications including the nitrogenous materials.

The different nitrogenous substances, therefore, not only had an opportunity to exert their effect upon the crop immediately following their application,

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[1] Omitted from the average.

[2] Received the same amount of nitrogen as was in the extra amt. of blood.

but also their after-effect upon one or two succeeding crops.

In the last column of the table is given the relative availability of the nitrogen in the different materials, arbitrarily considering 80 as the availability of the nitrogen of the dried blood (13.62 per cent. nitrogen), and deriving the availability of the nitrogen in the other materials from the increase in growth in each case over the appropriate check crops as compared with the increase caused by the dried blood. It is evident that only such of these values as are based upon results with the same number of crops should be strictly compared.

The comparisons which should be emphasized in this connection are those concerning the availability of the nitrogen in the materials before and after being "acidulated," or subjected to the wet process.

It may be seen that although the availability of the nitrogen is 33 in the unacidulated hair and 23 in the treated leather, the availabilities are increased to 64 and 80, respectively, in the same material after being subjected to the wet process in the laboratory. The nitrogen in the garbage tankage, however, had a very low availability both before and after treatment. When the identical hair tankage, garbage tankage and treated leather, which were used in the fertilizer factory for the manufacture of the base goods, were applied to the pots in the same proportions as used in the works, the availability of the nitrogen was 49, whereas that in the base goods made from the same materials was 84.

About 90 per cent. of the nitrogen in the various unacidulated materials was insoluble in water, and although a half of the total nitrogen in the garbage tankage was still insoluble after acidulation, only about a fifth of the nitrogen in the acidulated roasted leather and hair tankage remained insoluble.

That part of the nitrogen of the base goods which was rendered soluble by the wet process seems to have had an availability higher than that in blood, whereas the insoluble nitrogen was practically useless.

Vegetation experiments to determine the availability of the nitrogen in such material as base goods, containing large amounts of available phosphorus, have to be conducted with every possible precaution to prevent the results being influenced by the phosphorus. The details of the consideration given to this matter in the present instance would be out of place in this brief paper. The principle was followed of supplying phosphorus so liberally that more would be without influence on the crops. It may be seen by reference to the table that when an extra amount of phosphorus was furnished in addition to the application of the dried blood, which served as a standard, no increase of crops resulted. Nevertheless, it is best to be conservative in comparing the nitrogen availability of highly nitrogenous non-phosphatic materials, like hair, leather and blood, with the same materials when existing in a mixture with a nitrogen content of less than 2 per cent. and with a high content of phosphorus. Furthermore, when such comparatively small differences as exist in experiments of this kind between the weights of the crops from the check and from the dried-blood pots are divided into 80 parts, it is evident that the "limit of error" is wide, and that certainly a difference of less than 10 in availability is of very little significance.

In view of these considerations, the claim is not made, therefore, that the nitrogen in acidulated leather and base goods is as valuable as that in dried blood. It is believed, however, that the experiments prove the efficiency of the wet process, when properly carried out, for materially increasing the availability of certain low-grade nitrogenous materials.

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NEUTRAL AMMONIUM CITRATE SOLUTION.[1]

By A. J. PATTEN AND C. S. ROBINSON.

Received January 12, 1912.

Since the proposal of the ammonium citrate method for the determination of available phosphoric acid, much trouble has been experienced in preparing a strictly neutral solution of the reagent. The weakness of both the acid and the base renders the end point quite indistinct with ordinary indicators, and much time and patience are required on the part of the operator to obtain the desired results. Several modifications of the simple titration method have been proposed, but each has objections which prohibit its common acceptation by practical chemists. The importance which the method has assumed in agricultural work demands, however, that some convenient means be devised for preparing the necessary solution. Such a method has recently been proposed by Hall and Bell[2] and was later shown by Hall[3] to be quite suitable for laboratory use. At the time these articles appeared, the authors of this paper were engaged in working out the same method, and the results are here offered, not with the hope of claiming the credit for originating the method, but simply as corroborative evidence in favor of its general adoption.

Of the several methods proposed as substitutes for the present official method, that recently suggested by Hand,[4] using purified litmus solution or azolitmin, seems to be the most promising. In order to test it out and compare it with the official corallin method as well as to obtain some data as to the accuracy of the latter an acid solution of ammonium citrate was made up and neutralized by these two methods by each of four analysts working independently.

An acid citrate solution was chosen of which 50 cc. required 7.50 cc. of the dilute ammonia solution for neutralization as determined by the conductivity method to be described later. The dilute ammonium hydroxide solution (about 3 per cent.) was kept in a burette enclosed in opaque paper to prevent the reading being taken until the supposed neutral point had been reached. In this way each operation was made independently of the others. Great care was taken that no loss of ammonium hydroxide should occur

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[1] Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

[2] *Jour. Am. Chem. Soc.*, **33,** 711 (1911).

[3] THIS JOURNAL, **3,** 559 (1911).

[4] U. S. Dept. of Agric., Bur. of Chem., *Bull.* **132,** p. 11.

during the process. The results are given in Tables I and II:

TABLE I.

With corallin as the indicator.

Cubic centimeters dil. NH_4OH.		Cubic centimeters dil. NH_4OH.	
Number.	Per 50 cc. sol.	Number.	Per 50 cc. sol.
P I	12.30	M I	16.00
P II	12.10	M II	15.00
P III	16.20	M III	16.40
P IV	12.70	M IV	16.60
R I	12.00	I I	12.20
R II	12.00	I II	13.60
R III	14.30	I III	19.60
R IV	13.60	I IV	15.90

TABLE II.

With purified litmus as the indicator.

Cubic centimeters dil. NH_4OH.		Cubic centimeters dil. NH_4OH.	
Number.	Per 50 cc. sol.	Number.	Per 50 cc. sol.
P I	15.00	M I	14.00
P II	13.76	M II	15.00
P III	16.00	M III	12.50
R I	15.00	I I	15.82
R II	17.50	I II	15.82
R III	14.00	I III	15.00

An inspection of these results reveals the fact that the Official Method gives extremely inconsistent results even in the hands of one person. In only one case was an exactly neutral solution secured. The variation in the results obtained by one analyst using this method amounted to seventy-four cc. of the dilute ammonium hydroxide solution per liter of the acid citrate solution. While this is the maximum variation in the four sets of determinations given, it must, nevertheless be accepted as a possibility in actual practice. Such a condition is surely anything but derirable and demands immediate attention. The other method showed to much better advantage. Not only were the results more consistent, but one-third of the trials actually gave neutral solutions.

These examples fairly illustrate the difficulty in making an exactly neutral reagent by the methods most in use, and it is quite possible that in many cases the character of the "neutral" ammonium citrate solution varies more than in the cases cited and that considerable error may be introduced into determinations in this way. It is evident that not only is there a wide variation in the solutions made by different individuals, but that even the same person can rarely duplicate his own results.

It has long been realized that it was impossible to get consistent results in neutralizing ammonium citrate solution by the Official Method, but it has been assumed that the differences in the acidity of the solution were too small to cause any appreciable error in the determinations made with them.

In order to test the correctness of this assumption, several actual determinations were made. The solutions used were R II, C,[1] M IV, and I III. They were carefully diluted to a specific gravity of 1.09 and the determinations were all made at one time so that there could be no variation due to temperature of the bath. Determinations were made on two samples of fertilizer, one containing a small percentage of insoluble P_2O_5 and the other a large percentage. The results are given in Table III:

TABLE III.

	cc. dil. NH_4OH.	Sample I.		Sample II.	
Number.	Per 50 cc. sol.	Insol. P_2O_5. Per cent.	Average.	Insol. P_2O_5. Per cent.	Average.
		2.84		8.86	
R II	6.00	2.81	2.83		8.84
		2.83		8.82	
		3.54		9.82	
C	7.50	3.80	3.69		9.81
		3.74		9.80	
		4.23		10.10	
M IV	8.30	4.07	4.17		10.04
		4.21		9.98	
		4.79		10.56	
I III	9.80	4.77	4.82		10.46
		4.90		10.36	

An inspection of these results shows a marked relationship between the reaction of the ammonium citrate solution and the amount of phosphorus pentoxide extracted.

These variations, amounting to 1.99 per cent. in one case and 1.62 per cent. in the other, are certainly significant. The results prove that perfect neutrality of the citrate solution is of the utmost importance in securing consistent results, as the above differences are of sufficient magnitude to make the method extremely uncertain.

CONDUCTIVITY METHOD.

The above-mentioned method, proposed by Hall and Bell, was found to be much more satisfactory.

It depends upon the fact that when different quantities of alkali are added to an acid solution (or *vice versa*) the electrical conductivity or resistance of the

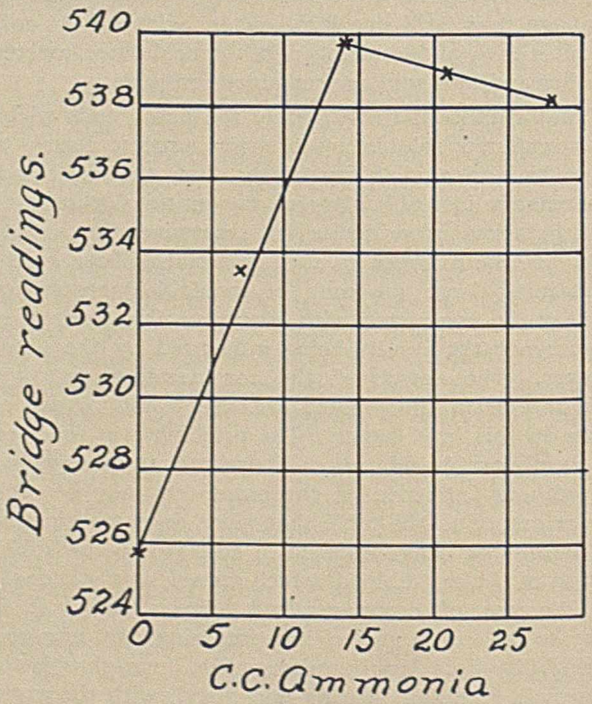

Fig. 1.

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[1] Neutralized by the conductivity method.

solution will vary with each addition, and if these resistances or conductivities are plotted against the amounts of alkali or acid added, there is a sharp change in the direction of the curve at the neutral point. This property has been made use of for the titration of various liquids where color changes were difficult to observe and has given very good results.

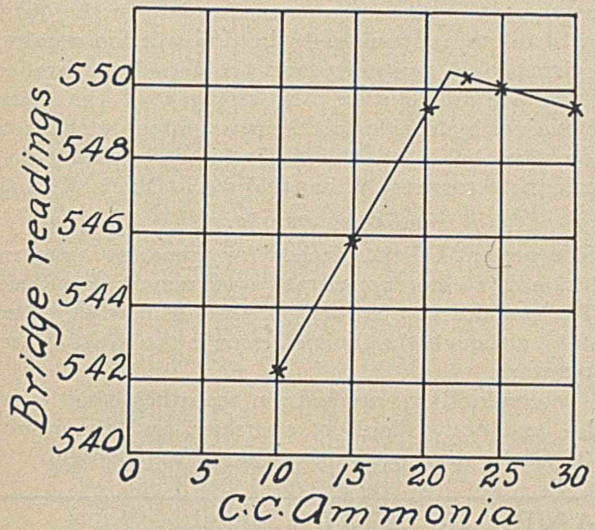

Fig. 2.

The method of procedure as given by Hall is quite satisfactory. A solution of citric acid is almost neutralized, the density being kept above 1.09. Small samples of this solution are then titrated with a dilute solution of ammonium hydroxide, using corallin as an indicator, to determine the approximate amount required to neutralize the remaining acid. Definite quantities of the citrate solutions are removed with a pipette and transferred to clean, dry, volumetric flasks. To these portions of the original solution varying quantities of the dilute ammonium hydroxide are added in such a way that some of the flasks contain more and some less than the approximate amount required for exact neutralization as determined by the titration with corallin. These solutions are then made up to the same volume with distilled water, placed in a thermostat, the temperature of which is held constant, and allowed to come to the temperature of the bath after which their resistances are measured by the Wheatstone bridge method. Plotting the cubic centimeters of ammonium hydroxide against the bridge readings gives a curve from which may be read the exact amount of ammonium hydroxide required to neutralize the acid in a given quantity of the citrate solution.

The following are some of the results obtained and illustrate the sharpness with which the neutral point may be read:

TABLE IV.

No.	Cc. dil. NH_4OH per 50 cc. sol.	Bridge readings.	No.	Cc. dil. NH_4OH per 50 cc. sol.	Bridge readings.
1...........	0.0	525.75	4	21.0	539.00
2...........	7.0	533.50	5...........	28.0	538.25
3...........	14.0	539.75	6...........	35.0	537.25
			Neut........	14.0	539.75

No.	Cc. dil. NH_4OH per 100 cc. sol.	Bridge readings.	No.	Cc. dil. NH_4OH per 100 cc. sol.	Bridge readings.
1...........	10.0	542.25	4...........	22.5	550.25
2...........	15.0	545.75	5...........	25.0	550.00
3...........	20.0	549.50	6...........	30.0	549.50
			Neut........	21.6	550.35

ACCURACY OF METHOD.

In order to test the accuracy with which results may be duplicated by different operators, a stock solution of acid ammonium citrate was made up and neutralized independently by four laboratory assistants, three of whom had never before made any conductivity measurements. One hundred cubic centimeter portions of the acid solution were transferred to 250 cc. volumetric flasks, the designated amounts of ammonium hydroxide added, and the bridge readings taken. Each operator made four sets of determinations on the same solution, the conditions being altered each time so as to give different readings for each set, thus eliminating any error due to the operator attempting, unconsciously or otherwise, to duplicate his previous results. Each one was required to plot his own results and report independently the amounts of ammonium hydroxide required to neutralize the acid in the quantity of citrate solution taken. The results are given in the following table:

TABLE V.

No.	Cc. dil. NH_4OH per 100 cc. sol.	No.	Cc. dil. NH_4OH per 100 cc. sol.
P I..............	13.80	M I..............	13.50
P II..............	13.60	M II..............	14.20
P III..............	13.80	M III..............	13.00
P IV..............	13.80	M IV..............	13.90
R I..............	14.00	I I..............	13.50
R II..............	13.50	I II..............	13.00
R III..............	13.00	I III..............	13.60
R IV..............	13.90	I IV..............	13.20

For the sake of comparison, averages of the several determinations made by each method are given in Table VI:

TABLE VI.

Average of	Corallin method.	Litmus method.	Conductivity method.
P series....................	13.32	14.92	13.75
R series....................	12.98	15.50	13.60
M series....................	16.00	13.84	13.65
I series....................	15.32	15.54	13.32
Av. of all series............	14.41	14.95	13.58
Maximum variation........	3.02	1.70	0.43
Maximum variation........	+1.59	+0.59	+0.17
Above (+) and below (—) average.................	—1.43	—1.11	—0.26

The determinations by the corallin and litmus methods were made on the same solution, but the determinations by the conductivity method were made upon a solution of slightly different strength. The advantages of the conductivity method over the other two is well illustrated in the above table. The results by the corallin and litmus methods are very variable, the greatest variation in the first case being 3.02 while in the second maximum variation is 1.70. The results by the conductivity method are very much closer, the maximum variation in the averages being only 0.43. If we assume the average of all the series, by this method, to be the true result, then the maximum variation below this result is only 0.17 and the maximum variation above is 0.26.

These differences might well be considered within experimental error.

RATIO OF AMMONIA TO CITRIC ACID.

Dr. McCandless, the referee on phosphoric acid for the Association of Official Agricultural Chemists, in 1909, suggested that a reagent be used which should have the same ratio of ammonia to citric acid as the pure triammonium salt. This ratio is 1 : 3.765. He made some coöperative tests with three other chemists, in which solutions were obtained having ratios from 1 : 3.775 to 1 : 4.189. Some time later the Division of Fertilizer Chemists of the American Chemical Society recommended a solution in which the ratio of ammonia to citric acid was 1 : 4.25. A neutral solution was made up by the conductivity method and the ratio of ammonia to citric acid determined. An average of three determinations gave a ratio of 1 : 3.785. This would probably have approached still closer to the theoretical ratio if the neutral solution had been made up immediately after making the conductivity measurements. During the several days that elapsed between the determinations of the quantity of dilute ammonium hydroxide solution required to give perfect neutrality and the actual preparation of the neutral solution, the strength of the dilute ammonium hydroxide solution was probably changed. It seems probable that this method could be used to give more satisfactory results than the present Official Method.

CONCLUSIONS.

The present Official Method for preparing a neutral solution of ammonium citrate is extremely unreliable.

The purified litmus method gives somewhat better results, although the limit of error is too great for reliable work.

The conductivity method, on the other hand, is reliable and not difficult of operation and the results obtained by different workers agree very closely.

LABORATORY AND PLANT

THE MANUFACTURE OF GELATINE.[1]

By Ludwig A. Thiele.

Received Dec. 22, 1911.

INTRODUCTION.

The manufacture of gelatine, originating in the remote past, when jelly was produced by boiling calves' feet in the kitchen, with the most crude and primitive methods, has now arrived at such a state of perfection, through the application of chemical as well as engineering science, that this industry may justly be proud of its progress.

To-day gelatine is manufactured in millions of pounds, and plays a great role in the nutrition of the people.

While the bulk of gelatine is manufactured for edible purposes—for jellies, jams, for the candy industry and for ice cream, which product comes under the Pure Food Law—the gelatine used in the arts, for photographic dry plates and papers, for medical purposes in the form of capsules, for bacteriological purposes and for decoration of fancy goods, does not come under this law; nevertheless, all these varieties are made practically the same, with like care and precaution, from the most select raw materials, and under the most sanitary conditions which may be applied to such an industry.

The manufacture of gelatine comprises the following distinct operations:

I. Treating and cleaning the raw material.
II. Dissolving the gelatine.
III. Concentrating the gelatine solution.
IV. Chilling and spreading.
V. Drying.
VI. Finishing (grinding and packing).

The most important raw material consists of:

a. Bones (osseine), hornpiths and button bones.
b. Hidestock (calf-pates, trimmings and fleshings).

(*a*) Osseine is the organic substance contained in the bones, the manufacture of which originates from France.

Raw bones are not used in the manufacture of gelatine at all, but have to undergo a preliminary treatment in order to produce osseine. The treatment for osseine and hidestock is then practically the same. Let us therefore first consider the preliminary treatment of the bones.

Bones, as obtained either direct from the slaughterhouses in raw and wet state, or in dried form through dealers, have to be washed, crushed and degreased in special extraction plants by means of benzine or carbon tetrachloride. In this stage of manufacture, from 8 to 10 per cent. of bone fat is produced from the bones, while the water contained in the raw bones is nearly eliminated. The crushed, degreased bones now undergo the same treatment as the East India crushed bones, which contain practically no fat, by extracting the mineral substance by means of diluted acids. This process, called maceration, produces about 60 per cent. of acid phosphate, a very valuable by-product. The acids to be used in the manufacture of osseine are either hydrochloric, phosphoric or sulphurous, or, according to the process of Bergmann, hydrochloric combined with sulphurous acid. Until quite recently, the drawbacks attending the use of sulphurous acid prevented its application in the extraction of osseine from bones. In order to prevent the surface of the bones from becoming coated with a layer of tribasic calcium phosphate, it was necessary to keep either the liquid or the bones in constant motion.

In the *Bergmann process* these difficulties are obviated by causing the solution of sulphur dioxide to circulate through a battery of closed tanks in which the bones are treated, the solution being continually

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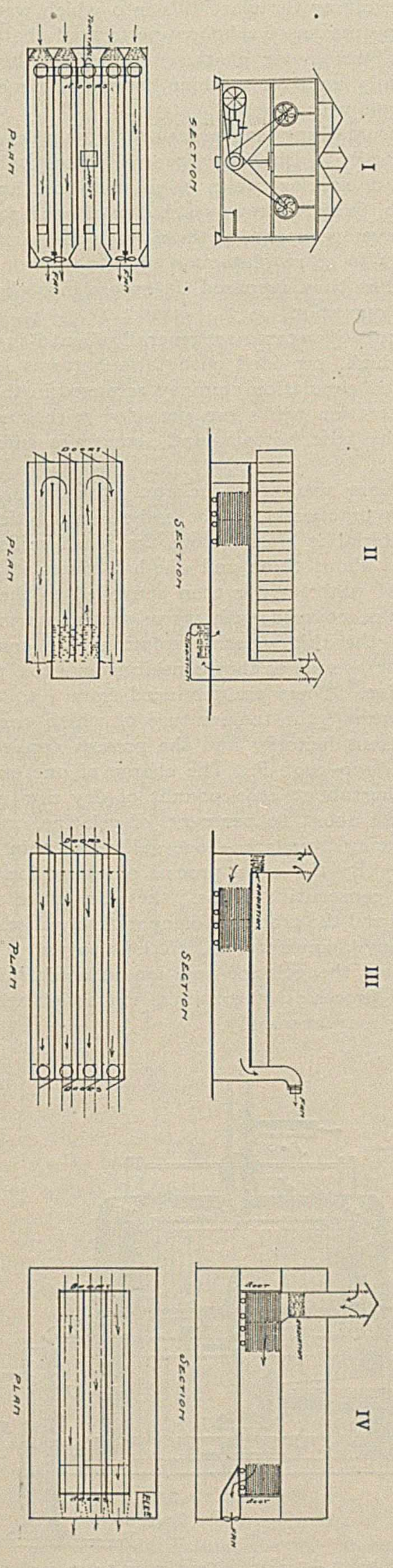
[1] Presented at the Fourth Annual Meeting of the American Institute of Chemical Engineers, Washington, Dec. 22, 1911.



PLANS OF DRYING KILNS. BY LUDWIG A. THIELE.

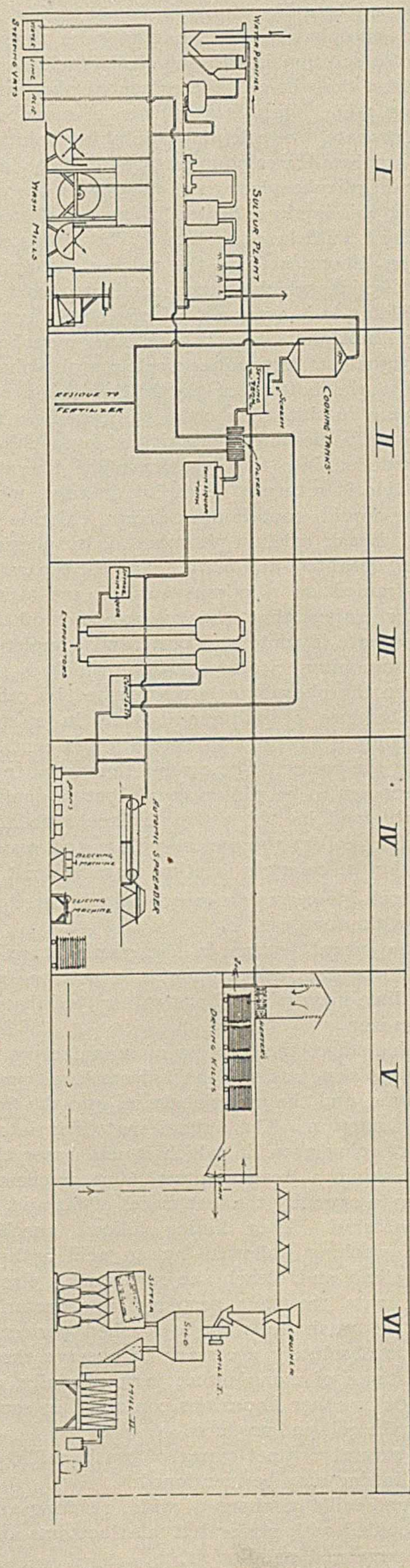


DIAGRAM SHOWING MANUFACTURE OF GELATINE. BY LUDWIG A. THIELE.

enriched by sulphur dioxide as it is neutralized by the calcium phosphate. After having gone through four tanks the solution is still sufficiently acid to retain in solution the whole of the extracted phosphate. The resulting saline liquid is a solution of monobasic calcium phosphate in calcium bisulphite solution. In order to separate the calcium phosphate in the form of dibasic calcium phosphate, and to recover the sulphur dioxide, this liquid is heated by means of steam in a lead-lined autoclave, termed "The Digester." This reaction liberates from the calcium bisulphite its sulphur dioxide, which is then conducted back to the acid tanks. At the same time one equivalent of the calcium bisulphite reacts with the monobasic calcium phosphate to form dibasic calcium phosphate, which falls to the bottom of the boiling liquid and normal calcium sulphite. In order to decompose the latter, an exactly measured quantity of hydrochloric acid is introduced into the Digester. The liberated sulphur dioxide is returned to the acid tanks, while the aqueous liquid containing calcium chloride in solution and dibasic calcium phosphate in suspension, is withdrawn, decanted, and filtered, and the separated phosphate drained on a porous surface and dried. The inventor claims that the so obtained dibasic calcium phosphate is white and pure, and completely soluble in ammonium citrate solution, which is not the case when the phosphates are separated by other methods. The loss of sulphur dioxide in a well managed factory is said not to exceed 5 per cent. of the weight of the bones. The osseine thus freed from phosphate appears to be whiter and of better quality than that obtained by the use of hydrochloric acid entirely, which renders the osseine yellow and makes the preparation of colorless gelatine more difficult.

(*b*) Hidestock is received in green, salted, limed or dried form at the factory.

Another important feature in the manufacture of gelatine is the water, which should be soft, nearly free from lime-magnesia-carbonates or sulphates, and free from iron.

I. From this stage, the process of manufacture of gelatine from osseine, as well as hidestock, is practically the same, and the material passes into the first stage of manufacture. The animal matter is introduced into steeping vats, in which it undergoes the process of washing, a treatment with lime or caustic soda in order to saponify the last traces of fat and to swell the material. After liming follows another operation of washing, followed by an acid bath to destroy the alkali and bleach the raw stock. From the steeping vats the thus prepared raw material passes into the wash mills to be washed perfectly neutral. It is absolutely necessary to observe these preliminary stages of manufacture very carefully, as traces of acids or other impurities contained in same may discolor the gelatine produced.

There are several distinct types of wash mills, of which the following may be mentioned:

1. Half-round mills of about 6′ wide, 12′ long and 42″ deep, provided with perforated false bottoms and eccentrically arranged paddles.

2. Revolving Circular Mills into which water is injected by means of a hollow perforated shaft passing through the center of the mill. Both these types are mainly used for washing osseine and material of finer structure.

3. For washing calf-pates or hidestock, the so-called Roller Wash Mill is generally used, which consists of a circular tank, 16′ in diameter and about 40″ high, in which revolves a cone-shaped roller.

The average speed of these wash mills ranges between 14 to 20 revolutions a minute. After the raw material is thus prepared, it enters into the second stage of operation.

II. Extraction tanks are generally about 6′ in diameter and 5′ high, provided with false bottoms and with perforated circulation chimney arranged in the center. The extraction tanks are provided with steam coils below the false bottom, and sometimes surrounding the tank.

There are also steam-jacketed tanks, which otherwise are practically of the same construction. The raw material is rinsed from the wash mills, having absorbed about three and one-half times its original weight of water. It is then conveyed to the extraction tanks, covered with warm water, steam turned on, and the thin gelatine solutions are continually drawn off, as soon as they contain from 4 to 6 per cent. of gelatine. There are produced from 4 to 8 subsequent "runs," the temperature of which varies with the different factories and the process applied, ranging from 130–200° F. The charge of one extraction tank being about 2000 pounds of dry raw material, containing about 60 per cent. of gelatine, will result in producing from 3000–4000 gallons of thin gelatine solution. By the usual process of extraction making different consecutive "runs," these are all of different densities and the process is comparatively slow. Therefore, many manufacturers, anxious to find a process to produce the gelatine solution in a continual run, patented processes of continual extraction which the following may exemplify.

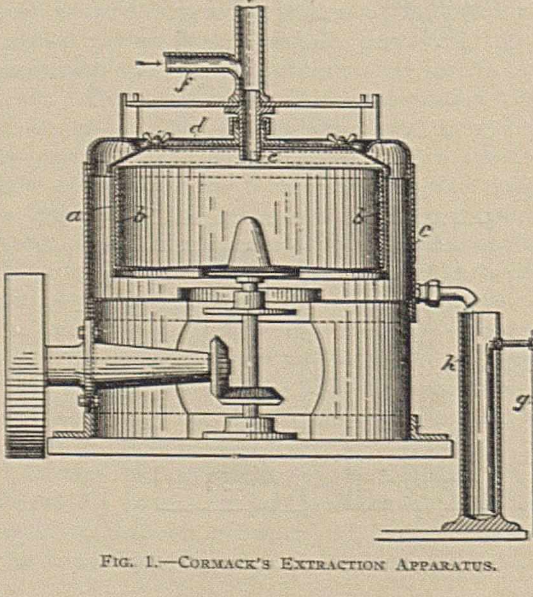


FIG. 1.—CORMACK'S EXTRACTION APPARATUS.

In 1903 *Cormack* obtained U. S. patent No. 728,205 for a process under centrifugal force, consisting in washing the gelatinous material, cutting it up, and subjecting it in this divided state to the simultaneous action of condensing steam and centrifugal force, dissolving the gelatine out of the material, passing the solution from the material by gravity and centrifugal force, and thereby filtering, collecting, and finally drawing off the solution.

In 1910, *Lehmann*, Paris, obtained U. S. P. No. 964,980, describing the combination in a gelatine manufacturing apparatus, of a casing for the reception of liquid, means for heating the liquid, and rotable drum composed of perforated material located in said casing, means for feeding the material to be operated on into said drum, a screw in said drum consisting of a shaft and rotary curved blades mounted on the shaft for the purpose of discharging the insoluble materials from the drum, a conical outlet pipe in said casing, means for clarifying the extracted gelatinous solution comprising a filter, a rotary pump and a grease reservoir, means for desiccating the clarified solution comprising a hopper under said grease chamber, and a rotary heated drying cylinder mounted beneath said hopper, a blade in contact with the cylinder mounted beneath said blade, and means for hastening the cooling of the finished product.

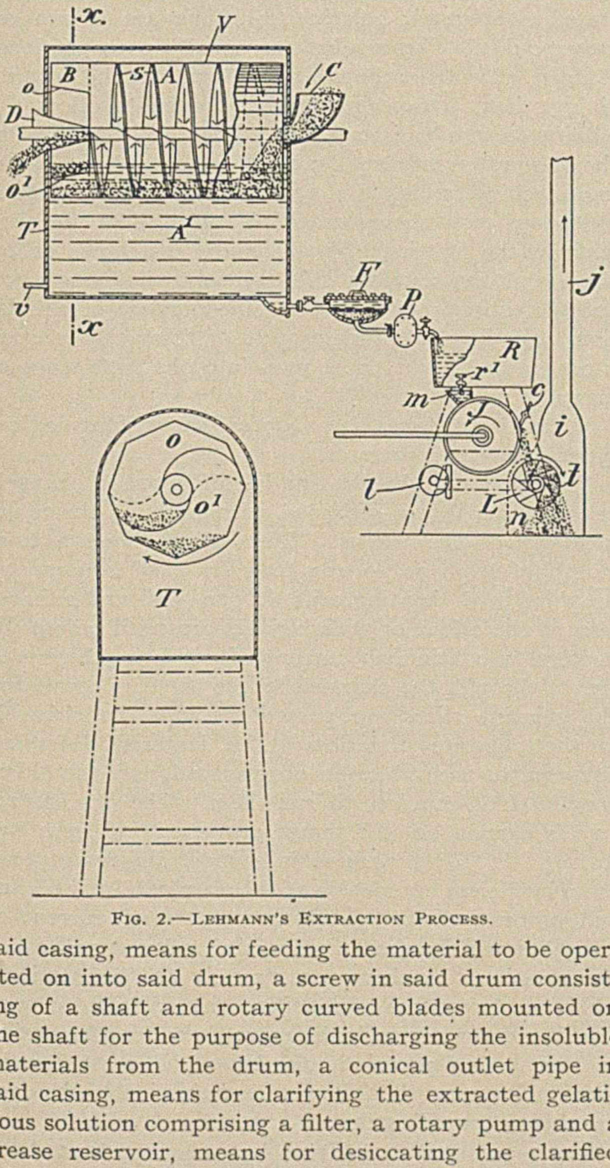


Fig. 2.—Lehmann's Extraction Process.

In 1911, *Thiele* obtained U. S. P. No. 989,826, an appliance for reducing animal matter to gelatine, a steam-tight tank, and inner perforated cage, a steam coil between the tank and cage, a steam heater, a water pipe passing through said heater, and into the tank, a spraying device on said pipe within the tank, a steam pipe leading to the steam coil and to the steam heater, shut-off valves in the steam pipe between the steam heater on one side and the steam coil on the other side, a settling chamber including a filtering device below the cage, a receptacle below the filtering device for receiving the filtered substance from the cage, and a siphon for drawing off the contents of the receptacle.

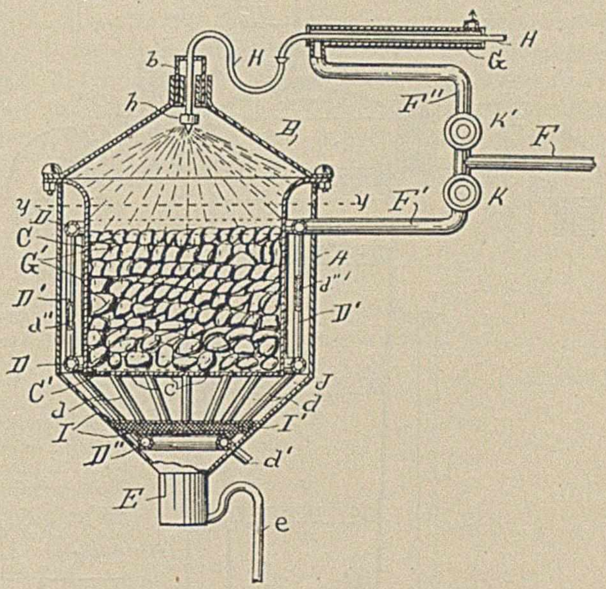


Fig. 3.—Thiele's Extraction Apparatus.

This latter device, arranged in pairs, enables continual operation, producing but one grade of gelatine from the entire batch. In case the production of different qualities is required, the thin gelatine liquors should be divided according to the time of efflux. Neither of the extraction processes produce gelatine liquors which are exactly clear. They should be screened into a settling tank, from which these thin gelatine solutions pass through a filtering device. Some efficient filters for gelatine are the Karl-Kiefer filter, the Union Schalen filter, or the International filter. Filtering paper or paper asbestos pulp is generally used in these constructions.

Utley, in U. S. P. No. 961,180, describes a charcoal filter which, besides giving a brilliant filtrate, claims to eliminate discoloration.

In some cases the last extracted portions or runs of gelatine are very cloudy and the filters before described are not in state to render the filtrate of great brilliancy. In such cases these runs should be clarified, either by the alum-phosphoric-acid, blood albumen-SO_2 or egg albumen processes. The only drawback to these chemical clarifications is that the gelatine solutions are weakened, and in some other processes there remains a soapy odor, with a tendency to foam and quicker putrefaction. The clarified thin gelatine solutions are usually kept in storage tanks for 6–8 hours, giving time to settle. Usually a very slight precipitation occurs in these solutions. These purified gelatine solutions now pass into the third stage of manufacture.

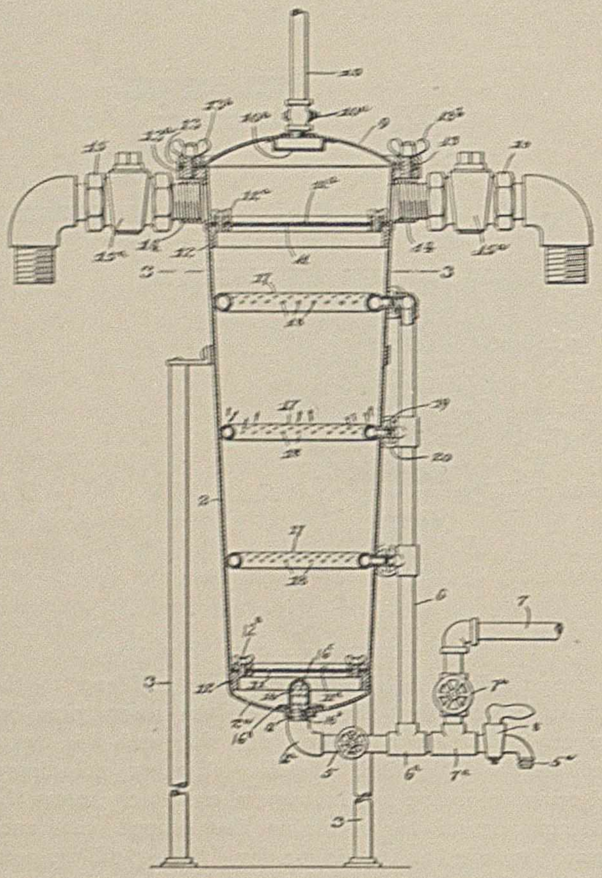


Fig. 4.—Utley's Filtering Apparatus.

III. The concentration of the thin gelatine solutions is usually made by evaporators. Concentration in open pans is probably entirely eliminated by this time. Single, double and triple effects are used as evaporators, depending on the size of the factory and the quality of gelatine to be produced. Very common systems of evaporators are those of Yaryan, Swenson, Zaremba, and Kestner.

The thin gelatine solutions are concentrated in the evaporators from 4–6 per cent. to 10–20 per cent., depending on the quality of gelatine to be produced. If it is the object of the factory to produce gelatine in thin sheets, it is not advisable to concentrate the thin solutions too strong, but rather to draw off the solutions at from 5–6 per cent. and chill them direct. It is a difficult matter to spread these jellies containing but 4–6 per cent. of dry gelatine by hand. This drawback caused many attempts, which date back as early as 1870, to construct apparatus which would eliminate spreading by hand.

Following are some patents obtained on apparatus of this nature:

1870, Andrew Dietz, New York, U. S. P. No. 103,852; 1870, Wm. Adamson, Philadelphia, U. S. P. No. 106,448; 1877, Chas. O. Garrison, New York, U. S. P. No. 185,825; 1878, E. W. Leggett, Elizabethport, U. S. P. No. 205,968; 1886, King Upton, Salem, Mass., U. S. P. No. 338,374; 1886, Wm. P. Upham, Melrose, Mass., U. S. P. No. 343,507; 1888, Chas. Keller, Springdale, Pa., U. S. P. No. 386,590; 1893, F. A. Wolff, Heilbronn, Germany, U. S. P. No. 496,469; 1894, Peter Cooper Hewitt, New York, U. S. P. No. 521,371; 1894, Chas. W. Cooper, New York, U. S. P. No. 521,947; 1899, Schill & Seilacher, Stuttgart, Germany, D. R. P. No. 119,477; 1907, O. Koepff, Goeppingen, Germany, Aust. P. 33,510.

At the present time the constructions of *Wolff, Hewitt, Schill & Seilacher, Koepff, and Clyde* are in use. These mechanical spreading devices are used only where the gelatine is to be manufactured in thin slices or sheets, to be later sold in packages, or for the shredded qualities. In most cases these apparatus consist of rotary drums or endless belts upon which the solution is run, and by cooling devices chilled, scraped off, and directly laid on the nettings. By nettings is understood a frame 6′ × 3′ upon which is stretched a cotton or wire netting. After evaporation the material enters into the fourth stage of manufacture.

IV. If no automatic spreader is used, the thin, concentrated evaporated gelatine solutions are drawn off into moulds. The moulds are usually pans 36″ long, 5″ deep, 9″ wide at the top and 8″ wide at the bottom, giving them a tapering form in order to allow the jelly to be easily turned out. These jelly blocks are then separated into smaller blocks by means of a blocking machine, which are again made into thin slices by means of a slicing machine. The slices are then laid on the nettings by automatic machines or by hand and the nettings subsequently piled one upon another, about 1½″ apart for the purpose of circulation, to a height of twenty-five or thirty racks upon a car or truck, and now pass into the fifth stage of manufacture.

V. In the sketches on p. 447 are shown four distinct types of drying processes.

The drying of the gelatine is conducted in channels or kilns, which are provided with rails for the easier handling of the trucks. These alleys have a total length of from 70 to 100 feet, by 6′ 6″ square, are provided with heating coils at one end and exhaust fans at the other, or with blowers arranged before the heaters, a continuous current of air being blown or drawn through the channels, while the cars conveying the gelatine slices are passed through the channels in the opposite direction. The material difference between the use of blowers or exhaust fans is the difference in H. P. required to run them. The drying process is carried on at a temperature varying from 85° to 105° F. This process is a most important one, as an inefficient circulation of saturated air in the kilns will produce moldy goods, a too strong current of air will warp the sheets, a too slow current will cause the gelatine to adhere too strongly to the nettings, while too great heat will cause the gelatine to turn liquid and run through the nets; therefore, the design of the drying plant should have the most careful consideration, as the following explanation of the drying theory may illustrate.

The process of desiccation by means of heated air rests entirely upon its avidity for humidity, but the capacity of absorption varies enormously with increased temperature. At 0° F. the absorption is very low, at 152° F. considerable, while at 212° F. it is infinite. If the air, for example, contains a certain quantity of vapor, it is said this vapor has a certain elastic force, which is expressed in inches of mercury. When air is charged with all the humidity it can carry, it is said to be saturated. The following table gives the data of the elastic force of vapor in saturated air at temperatures ranging from zero to 212° F.

The weight in pounds of the vapor mixed with 100 pounds of pure air at any given temperature and pressure is given by the formula

$$\frac{62.3 \times E}{29.92 - E} \times \frac{29.92}{p},$$

where E equals elastic force of the vapor at the given temperature in inches of mercury, p equals absolute pressure in inches of Mercury = 29.92 for ordinary atmospheric pressure.

Temperature.		Elastic force of vapor.		Weight of vapor		Weight of vapor mixed with 1 lb. of air.
° F.	° C.	Inches	M/M Mercury.	Pounds per cu. ft.	Gram per cu. m.	
0	—17.8	0.044	0.11	0.000079	1.25	0.00092
12	—11.1	0.074	0.18	0.000130	2.08	0.00155
22	— 5.6	0.118	0.30	0.000202	3.22	0.00245
32	± 0	0.181	0.46	0.000304	4.86	0.00379
42	— 5.6	0.267	0.67	0.000440	7.04	0.00561
52	11.1	0.388	0.98	0.000627	10.01	0.00819
62	16.7	0.556	1.41	0.000881	14.08	0.01179
72	22.2	0.785	1.99	0.001221	19.53	0.01680
82	27.8	1.092	2.77	0.001667	26.68	0.02361
92	33.3	1.501	3.81	0.002250	36.02	0.03289
102	38.9	2.036	5.17	0.002997	47.96	0.04547
112	44.4	2.731	7.63	0.003946	63.16	0.06253
122	50.0	3.621	9.20	0.005142	82.31	0.08584
132	55.6	4.752	12.11	0.006639	106.22	0.11771
142	61.1	6.205	17.90	0.008473	235.65	0.16170
152	66.7	7.930	20.14	0.010716	171.56	0.22465
162	72.2	10.099	27.91	0.013415	214.76	0.31713
172	77.8	12.758	32.58	0.016682	266.91	0.46338
182	83.3	15.960	40.53	0.020536	328.78	0.71300
192	88.9	19.828	50.54	0.025412	402.52	1.22643
202	94.4	24.450	62.10	0.030545	488.79	2.80230
212	100.0	29.921	76.00	0.036820	589.49	Infinite

The above table shows that the capacity of air for water is not in proportion to the temperature, but progressive. The degree of saturation or relative humidity of the air is determined by the use of the dry and wet bulb thermometer (pychrometer) which instrument necessitates the use of hygrometric tables.

A very handy device for the determination of the humidity in air is manufactured by the Taylor Instrument Company under the name of "Hygrodeik." In order to get the most satisfactory results in drying, it is necessary to make the aforesaid observations in the ingoing and outgoing air, as well as to determine the velocity of the air current by means of an anemometer.

In the process of drying there will also be observed that (1) the more concentrated a solution, the longer it will take to dry; (2) the thinner the solution is chilled, the easier the process.

This paradox may be explained in this way: A slice of gelatine of 4 per cent. jelly weighs about 75 grams; a dried sheet will weigh 3 grams. Therefore, from one sheet of gelatine 72 grams of water must be extricated. The first 50 parts of water will be readily taken up by the air current, but after this, the surface of the gelatine sheet has already hardened to such an extent that it is more difficult for the remaining 22 parts to escape. The more concentrated a solution, the harder the surface will become during the first part of drying, and a much slower final process will be the result. On the other hand, the spreading of thin solutions requires very much more labor, a greater number of trucks and nettings, a larger space in the alleys, and, consequently, a larger investment, as will be explained in the following example based upon a production of 2400 pounds of gelatine daily. This production has been chosen, as manufacturing on a lower scale has proved uneconomical.

2400 Pounds (1090 Kg.) Gelatine to be Produced.

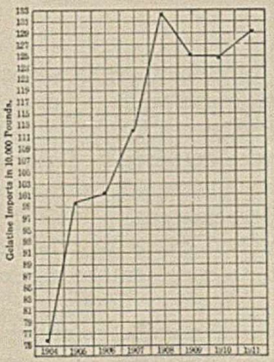
Requires 4000 lbs. (1818 kg.) raw material at 60 per cent.	In thin sheets at 3 gr.	In medium sheets at 9 gr.
There will be drawn off of 4 per cent. solutions.	7200 gal. (27270 liters)	
Of 12 per cent. concentrated solutions..........		2400 gal. (9090 liters)
On molds required.....	1818	606
Gelatine slices made.....	363600	121200
Frames and nettings required...............	7575	2525
Trucks required..........	252	84
Water to be extricated in alleys...............	57576 lbs.	17592 lbs.
Alleys necessary (theoretical).............	10	4
Alleys necessary (practical)...............	14	7

After passing through the drying channels the gelatine enters into the last stage of manufacture.

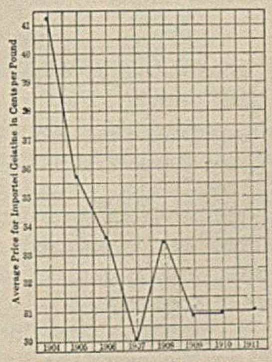
VI. The dried gelatine sheets are taken from the nettings, thrown into a crusher, running at 250 revolutions a minute, and requiring about two-horse power. The crushed gelatine, so-called "Flake," passes into a silo, from thence into a mill of the dismembrator or disaggregator type, is screened to different granulations, and barreled up in the different forms as required. For still finer powdered goods it is necessary that the gelatine pass through another mill which will reduce all the crushed or granulated gelatine to powdered form, from 50 mesh upward, according to requirements:

Proportion of power to production = HP : 12–20 lbs. gelatine (according to conditions)
Capital required for production of 1 pound gelatine = 31c. to 25c.
Consumption = 55 gr. per capita, U. S. A.

Curve I shows the imports of gelatine into the United States during the past eight years, while Curve II shows the fluctuations in price during the same period.



Curve I.



Curve II.

A PUNCH FOR STRAIGHT RUBBER TEST PIECES.

By Harry P. Mills.

Received Jan. 5, 1912.

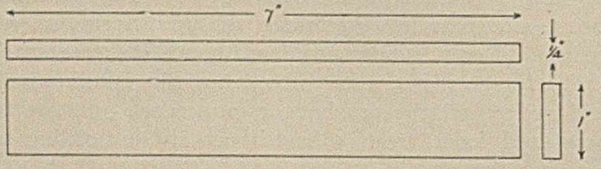
Although the ring form of test piece has recently become popular, many workers still prefer the straight test piece, as the use of the latter does not involve certain serious errors to which the ring piece is subject.

The devices for preparing ring test pieces have been perfected beyond those for handling straight pieces, and the ring pieces are therefore easier to manipulate; but by the use of the punch herein described the strip pieces can be prepared with even less trouble than the rings.

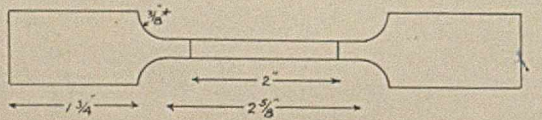
All those who have tried punching test pieces will appreciate the difficulty in preparing uniform pieces of a regular cross section that can be easily measured. The softer the stock the more it yields under the knife or punch, and the more likely will the section depart from the desired shape. Our work deals largely with pure gum stocks, and the method described has been found to work quite satisfactorily.

Several workers have attempted to mould the strips into the desired form, but it is difficult to obtain uniformity throughout the narrow portion. It is essential that the section should be uniform and easily measured; also that the edges should be clean, as a tear will readily follow a slight check. It has been found much more satisfactory to punch away the sides of a flat strip, leaving the test portion between two stout ends, as in Fig. 2.

The strip is moulded to the form shown in Fig. 1, in bolted moulds, each mould producing eight strips.



—Fig 1—



—Fig 2—

The punch (Fig. 3) is equipped with a sharp, thin, curved knife, set firmly in the vertical slide. A stop prevents it from touching the cast iron bed plate. A "nest" into which the strip fits snugly prevents the rubber from spreading while being cut.

The nest is secured to the bed plate by thumb screws, and it can be adjusted to regulate the thickness of the strip.

To operate, a few thicknesses of manilla paper are laid in the nest: the knife cuts into these, but does not reach the bed plate. The strip is then placed in the nest and one side punched out by operating the pedal. The knife is so shaped that a little of the rubber at each end is left uncut; thus, when the strip is lifted out, the punched piece still adheres to it. Without removing this piece the strip is replaced in the nest, this time with the cut edge forward. Care is taken to have the same surface up in both cases, as the parallelism of the width of the test pieces is thereby assured. The second side is punched out, the strip taken out of the nest and the punched pieces torn or cut free. Two marks at a unit distance are then placed on the strip and after measuring is ready for testing.

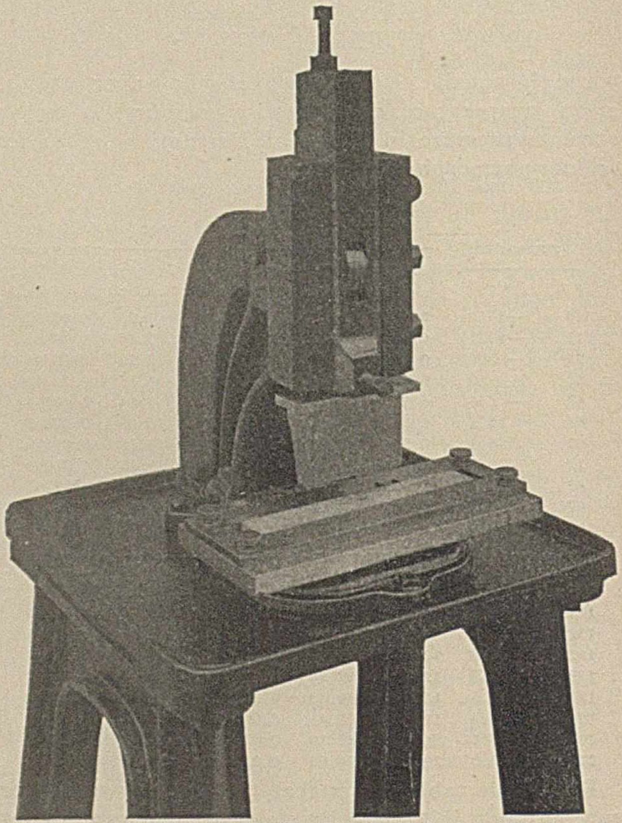


Fig. 3.
"Punch for Straight Rubber Test Pieces."

The strips are uniform to within a few thousandths of an inch, and the cross section is almost a rectangle, which permits of accurate measurement by platen calipers.

The knives are removable, and test pieces of various lengths and widths may be cut from strips of any thickness.

Research Laboratory,
Continental-Mexican Rubber Company,
Torreon, Coah., Mexico.

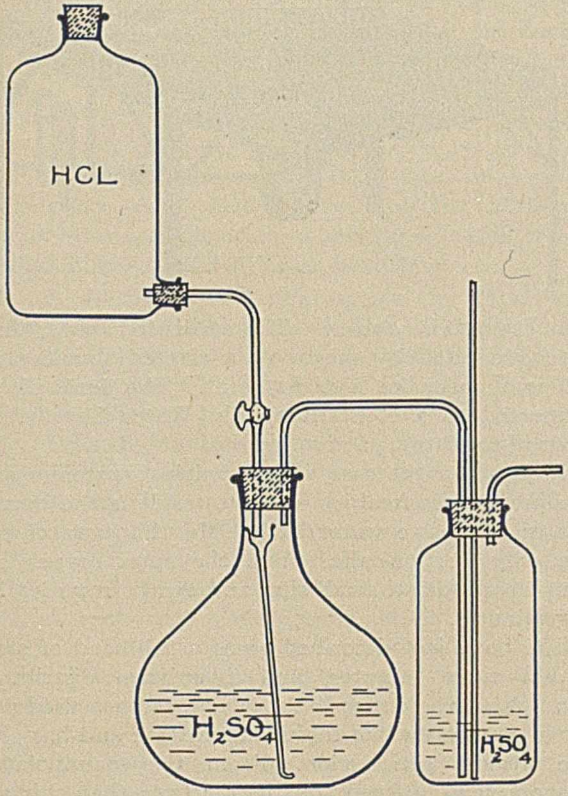
A LABORATORY GENERATOR FOR HYDROCHLORIC ACID GAS.

By Edwin Dowzard.

Received January 4, 1912.

In laboratories where dry hydrochloric acid gas is frequently or occasionally required, the apparatus illustrated in the sketch will prove of value.

On referring to sketch, the apparatus will be seen to consist of a storage bottle for commercial hydrochloric acid, a flask to be half filled with concentrated sulphuric acid, and a bottle containing concentrated sulphuric acid for drying purposes. The storage bottle for hydrochloric acid should be not less than thirty-six inches higher than the flask.



By means of the thistle headed funnel, the lower part of which is drawn out to not more than $^1/_{16}$ inch diameter, commercial hydrochloric acid is delivered to the bottom of the flask containing concentrated sulphuric acid.

The advantages of this apparatus are that hydrochloric acid gas is evolved immediately after turning on the acid. On turning off the acid, the evolution of gas ceases within a few seconds. A steady flow of gas can be maintained for long periods of time with practically no attention.

Unless the lower portion of the thistle-headed funnel is drawn out as described above, the apparatus will not work in a satisfactory manner.

The drawn out portion should commence above the sulphuric acid in the flask.

The above apparatus has been in use for some time and has given great satisfaction.

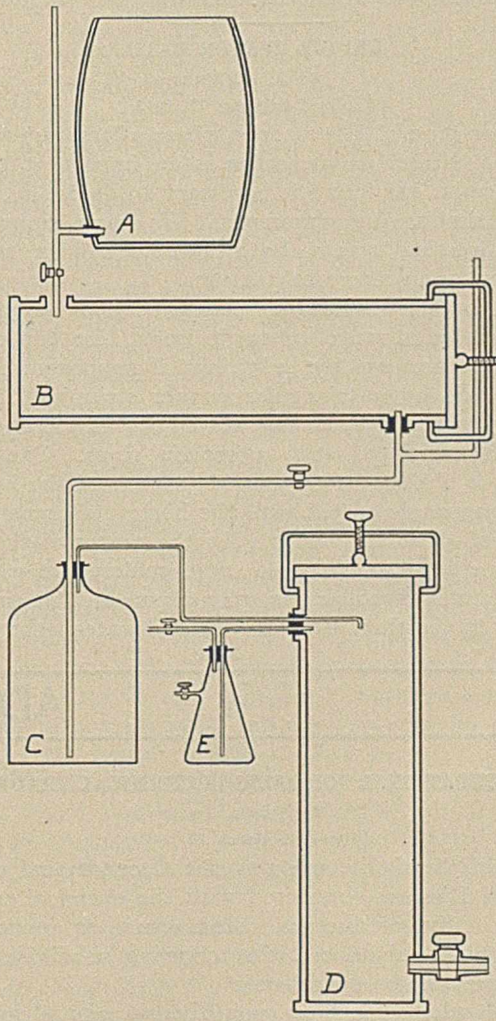
Analytical Department,
Parke, Davis & Co.,
Detroit, Mich.

TWO PIECES OF LABORATORY APPARATUS.

By Harold Canning Chapin.

Received January 29, 1912.

The hydrogen sulfide generator here illustrated has been in use in this laboratory for more than two years, supplying classes of over 175 men. For an apparatus of its capacity it is simple, inexpensive, and requires but little personal attention. With the exception of the iron clamps securing the cylinder heads, and glass gauges and connections which can be put together by an amateur glass-blower, the parts are all stock articles. *A* is an ordinary ice-water tank, *B* and *D* 30-liter earthenware filter cylinders, *C* a 15-liter glass bottle, and *E* a filter flask. It is regulated by a device of Ostwald,[1] already found efficient on a smaller scale. Sulphuric acid, previously diluted in *A* with 6 parts of water, flows from *B* through glass and rubber connections by way of *C* into *D*, which contains ferrous sulphide. The gas thus generated passes through the upper outlet of *E* to the piping of the laboratory. When the supply exceeds the demand the excess gas stores itself under pressure in *C* by displacement of acid into *B*, at the same time stopping generation until it is itself exhausted. The flask *E* catches and renders visible the overflow in case *D* fills with spent liquor. Its lower cock serves to admit air and relieve suction when liquor is drawn off through the cock on *D*. To prevent small pieces of sulfide from clogging this last outlet a layer of brick is placed in the bottom of the cylinder, and to aid distribution of the acid an inverted dish is laid on top of the sulfide. The acid reservoir *B* is placed horizontally to lessen fluctuations in the gas pressure, which is dependent upon the difference in level of the contents of *B* and *C*. The connections between



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[1] Z. anal. Chem., **31**, 183 (1892).

the cylinders and their covers, which are ground to fit one another, are made tight with soft paraffine.

Another apparatus, exceedingly simple but so efficient as to merit brief description, is a glass siphon for emptying carboys. It has at its delivery end a cock of the diameter of the tube, and at the bend a smaller cock through which it can be exhausted. While one arm is being sucked full of acid from the carboy the other is by the same operation exhausted, so that if the tube be of large diameter the liquid having reached the summit trickles over and fills the siphon completely.

WALKER LABORATORY.
RENSSELAER POLYTECHNIC INSTITUTE.

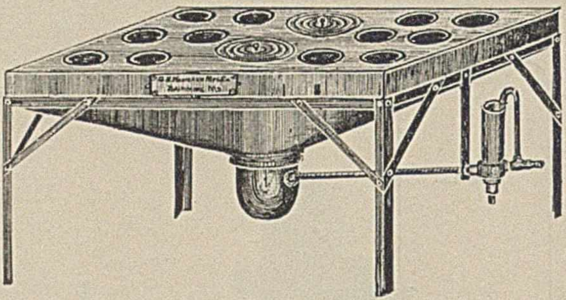
UNIQUE WATER BATH.

BY S. W. WILEY.

Received February 15, 1912.

In commercial laboratories where a large amount of work is carried on and time is an important factor, the chemist has found it necessary to devise and construct time-saving apparatus. We have designed a rapid heating steam bath that combines several practical and economical features.

The bath is made of heavy copper supported on a braced stand of 1″ angle iron. The top of the bath measures 25″ by $14\frac{1}{2}''$, and is supported on the under side by a triangular copper stripping to prevent sagging; it contains twelve $3\frac{1}{2}''$ holes, and two $5^{3}/_{4}''$ holes, fitted with porcelain rings. The bath proper is 2″ deep at the outside edge, and the bottom makes an angle of 30° with the horizontal, reaching a depth of 4″ at the center. To the center of the bottom is riveted a threaded ring, soldered to make a tight joint. A collar fits over a cup and when connected to the threaded ring makes a water-tight joint; the cup, made of heavy spun copper with a $^{1}/_{8}''$ flange at the top, measures $3^{3}/_{8}''$ inside diameter, and is $3\frac{1}{2}''$ deep. To the point of supply, $2^{1}/_{4}''$ above the bottom, it contains 250 cc. The cup is fed by $^{1}/_{4}''$ brass pipe connected by means of a riveted shoulder and soldered to make a tight joint. The feed pipe is connected to a constant supply Water Level Regulator of the latest pattern.



As is often the case with municipal water supplies the pressure is freakish and the result is the burning out of expensive water baths. In this type of bath the only portion affected is the spun copper cup, which costs but a small sum and can be replaced in a few minutes.

The bath just described gives a full head of steam within three minutes, and a uniform distribution throughout the entire bath. One has been used daily for a year and a half in our laboratory, and has given the utmost satisfaction. From the standpoint of economy and upkeep, the writer feels that this type of bath may be found to be of value in other laboratories besides our own.

LABORATORY OF
WILEY & COMPANY,
BALTIMORE.

ADDRESSES

OCCUPATIONAL POISONING IN CHEMICAL TRADES.[1]

BY W. GILMAN THOMPSON.

Received March 19, 1912.

In this brief discussion of the Occupational or Industrial Diseases connected with the chemical trades, either in the production, manufacture or application of chemical substances, the following subdivisions of the topic will be considered:

I. To what extent do such diseases prevail in New York City?

II. To what extent are such diseases fatal or incapacitating?

III. What measures should be undertaken to mitigate or prevent the manifold evils of the occupational disease hazards?

I. Prevalence.—Only within a very short time has any effort been made to secure accurate data bearing upon this phase of the question. In September, 1911, a law became operative requiring physicians to report to the New York State Labor Bureau all cases observed of six diseases, namely, poisoning by lead, mercury, arsenic and phosphorus, together with anthrax (or wool-sorters' disease) and the caisson disease. In January, 1912, a sub-committee for the investigation of occupational diseases was appointed by the New York State Branch of the American Association for Labor Legislation. This committee, mainly through a salaried investigator, has already gathered many interesting facts. In the past few years isolated reports have appeared in medical publications on the diseases under discussion, a number of which have been made by members of my Medical Clinic Staff in the Dispensary of the Cornell University Medical College and Bellevue Hospital, where we meet annually with many thousands of workers in all manner of trades. The latter institution, especially, affords perhaps as large an experience of this type as may be met with anywhere in this country. In the absence of extensive published data, some reference to my personal experience may be permitted, derived mainly in the two institutions mentioned and in the wards of the Presbyterian Hospital. In

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[1] Read before the New York Section of the American Chemical Society, March 8, 1912, by Dr. Thompson, Professor of Medicine in the Cornell University Medical College in New York City.

the records of these three institutions, covering the past eight years, I find 283 cases of serious chronic lead poisoning, in most of which there was total incapacity for work lasting for months or years. Some of these patients had complete paralysis of the hands, many had lead colic, and most had hardening of the arteries. Some acquired chronic Bright's disease and practically all suffered from anemia, digestive disorders and muscular weakness. One youth of 23 years had been employed for eight years in a paint manufactory as a helper. He had the hardened arteries of an octogenarian, a greatly enlarged heart, diseased kidneys, and difficult breathing.

Dr. E. E. Pratt, investigating for the Committee of the Labor Legislation Association, recently found 18 cases of lead poisoning among men employed in the Brooklyn Navy Yard to scrape red paint from the hulls of the battleships.

Dr. John B. Andrews, in *Bull.* 95, of the State Bureau of Labor, reported 60 fatal cases of lead poisoning occurring in New York State in 1909–'10. Three more fatal cases recently occurred in a single smelting establishment in New York City.

Dr. Alice Hamilton, in a report on the white and red lead industry for the United States Department of Labor, found examples of lead poisoning in 33 of 56 establishments where lead was used in process of manufacture, with a yearly average of 665 cases. It is a very striking fact that in England, in the white lead works near Newcastle, compulsory medical inspection has so far reduced the cases of lead poisoning that in 1910 the ratio was 1 case among every 264 employees, whereas in Illinois, without legalized inspection and control, the ratio is one case among every 7 employees. There are fully 150 different trades in which lead constitutes a serious hazard.

With arsenic there are 27 trades in which this constituent constitutes a similar hazard. I have seen complete paralysis from arsenical neuritis, and a man employed in mixing Paris green paint came recently to my clinic with a diffuse brownish black pigmentation of the skin, derived from his occupation. The lessened use of arsenical pigments in wall papers and artificial flowers has, however, considerably reduced the number of cases of arsenic poisoning which formerly were much more common. Arsenic also irritates the hands and eyes, and produces grave digestive disorders.

Some time ago a man came to my clinic showing a perforating ulcer between the two nasal cavities, large enough to admit the forefinger, which was the result of chromic acid chronic poisoning. He had also suffered from double vision, nausea, vomiting, and difficulty in fixing the attention. On his hands were round depressed scars of old ulcers or "chrome holes" as the workmen term them. The patient, who was a chemist, had found chromic acid in the abundant nasal mucus and in his urine. There were 40 workmen employed in the chrome works with this patient, all but four of whom had chronic inflammation in the nose, and half of them had perforation of the nasal septum. A boy employed in the works had recently died in a sanitarium having violent vomiting and a yellow skin, the results of chrome poisoning. Some years ago Dr. Heise examined 176 men who had worked in a chrome manufactory in Germany; 126 of them had perforation of the nasal septum and 20 others presented ulcers which had not yet perforated. Thirty-nine men had unhealed chrome sores of the hands. Perforation has been known to occur in the nose in less than two months after entering upon the employment. "Chrome holes" may appear not only on the hands and arms, but on the feet, legs and eyelids, and sometimes on the gums and back of the mouth. Such ulcers are very slow in healing and may incapacitate the workman for many months.

Brass poisoning, giving rise to "brass founders' ague," is a well known condition among workers in moulding or founding, dipping and the filling or polishing of brass tubing and other articles of manufacture. As the cheaper grades of brass contain a small percentage of lead and tin, some of the symptoms may arise from poisoning by these metals, but the typical ague is believed to be due to the zinc rather than the copper component of brass. Doctors H. J. Schwartz and M. H. Sicard have reported in detail two cases seen in my clinic. One of the men, a brass moulder, had suffered from repeated attacks of severe chills, nausea, vomiting, sweats, headache and muscular pains—symptoms not unlike those of malaria, but unaccompanied by fever. The attacks are worse in wet or foggy weather when the fumes of the metal linger in the foundry. The other patient, a founder, had similar symptoms, and both declared that practically all their fellow-workmen suffered from time to time in the same manner. Other common symptoms among brass workers are catarrh of the stomach and bowels, nervousness and hypochondriasis. The tartar on the teeth is colored green by the copper. Brass filings, if inhaled in a dusty workroom, irritate the respiratory passages, and may give rise to "hardening of the lungs" or fibroid phthisis.

The Secretary of the Moulders' Union declares that he has found over 300 cases of founders' chills among brass workers in New York State, but as his report is not yet published, I am unable to refer to it in detail.

Mercury poisoning was formerly common among makers of mirrors, but the extensive substitution of silver in the process has lessened the number of cases of mercurialism. The latter, however, are very common among the makers of felt hats, in which manufacture mercury is volatilized in a process of hot pressing. Mrs. Linden W. Bates, in a report made for the Woman's Welfare Department of the National Civic Federation of New York, studied 102 cases of chronic mercurial poisoning. The fumes of the metal give rise to loosening of the teeth, ulcers of the mouth, diseases of the jaw bones, anemia, weakness and serious digestive disturbances.

Phosphorus poisoning acquired in the manufacture of matches has been the subject of an admirable study by Dr. John B. Andrews, of the American Association for Labor Legislation. The results of this poison, although the cases are numerically few, as compared with those of poisoning in many trades, are more disfiguring than those of any other substance, for the phosphorus fumes entering the mouth cause decay of the teeth, and rapidly progressive ulceration and destruction of the jaw bones, which must be removed, in whole or in part, to save the victim's life. Mr. Andrews found records of 40 cases of necrosis of the jaws in a single factory "of which 15 resulted in the loss of one or both jaws and several cases resulted in death." In another small factory were records of 21 cases, 6 of which developed in a single year.

Wood alcohol, often used as a solvent in varnish, if inhaled in concentrated form, gives rise to acute poisoning, causing permanent blindness and grave disturbances of the circulation which may occasion death by paralysis of the heart. A number of fatal cases have occurred in New York City, and recently three men who went down into a large beer vat in a brewery in Buffalo, to varnish it, became overcome by the vapor of wood alcohol, with the result that two died and the third became permanently blind.

The making of pottery offers many hazards to the workmen. Those employed in mixing the damp clay suffer from bronchitis and joint pains. Those employed in applying the glaze may acquire lead poisoning, and the grinders and polishers inhale dust which may contain silica, alumina, charcoal and flint which are highly irritant to the respiratory mucous membranes, giving rise to chronic bronchitis and pneumokoniosis or fibroid phthisis. Such victims often subsequently acquire pulmonary tuberculosis, which is graphically called "potter's rot" among them.

Time does not permit a more exhaustive reference to the many other forms of hazardous chemical trades. Enough examples have been cited, however, to afford some idea of the great prevalence of the occupational disease hazards, which in many instances in this country are still regarded as necessary evils, but which, in reality, are practically all preventable by the exercise of common sense precautions, if not by enforced restrictions.

In concluding this subdivision of the topic, I will merely mention the very large group of skin diseases due to occupation, such as handling tar, creosote, paraffine, acids, alkalies, lime and many forms of dyestuffs. The resulting injuries, which are very common and may incapacitate the workman for months, include such serious conditions as ulcers, boils, a form of cancer or epithelioma, fissures and chronic eczema.

II. What is the Nature of the Disease Processes Caused by Chemical Irritants?—Apart from symptoms of acute poisoning, which are not under present discussion, the metals produce a large group of symptoms in common, besides a few special symptoms. Being inhaled in the mouth as dust or fumes, or taken into the mouth by means of food or tobacco handled by unclean hands, or in some few cases, being absorbed by the skin, they lower the tone of the blood, causing serious anemia, disorder digestion, injure the stomach and bowels and irritate the nerves, giving rise to paralysis, neuritis, and painful cramps. Moreover, constantly circulating in the blood, they produce progressive hardening of the arteries. The arteries become rigid and impose great strain upon the heart, which becomes enlarged. The kidney arteries may be affected, or the kidneys themselves irritated by the constant effort to eliminate the poison, so that in time chronic Bright's disease develops. It is these latter changes especially which constitute the most serious factor in chronic chemical poisoning, for a man with hardened arteries, an enlarged heart and Bright's disease has acquired structural changes in his system which are incurable and progressive. He may die of such lesions years after he has quitted the trade which produced them, or he may die at any time from the effects of some intercurrent disease which, under more normal conditions, he might easily resist.

With many chemicals, the insidious effects of chronic poisoning may definitely be detected at a comparatively early stage, at least before permanent disability threatens. This is notably the case with lead poisoning in which, in addition to ordinary anemia, there are specific changes in a particular variety of white blood corpuscle, a blue line of lead deposit appears in the gums, and the metal may often be detected in the urine. All these symptoms may be recognized by skilful medical inspection, even before the workman is conscious of any ailment whatever.

In another large group of cases, the hard particles of the metal dust of filings, etc., are inhaled and prove severely irritating to the respiratory passages, causing chronic catarrhs, bronchitis and cirrhosis or hardening of the lungs. These forms of irritation are not only serious in themselves but predispose to the acquisition of pneumonia and tuberculosis.

In other cases, fumes, especially of phosphorus and mercury, besides completely disordering digestion, give rise to a horribly destructive disease of the bones, as above mentioned. The various toxic gases and vapors affect chiefly the respiration and circulation, and in some instances, notably in carbon monoxide poisoning, form a destructive compound with the red blood corpuscles. Such poisons may at once paralyze the heart as in the case of wood alcohol, or cause vertigo and possibly coma as in the case of naphtha, gasolene and similar products. The various acid and ammoniacal fumes produce intense irritation and swelling of the bronchial mucous membrane, with often fatal suffocation.

III. The means of mitigation of the occupation hazards may be summarized briefly as follows:

1. A campaign of education is needed, particularly among physicians, to direct attention to the importance of recognizing the early symptoms of the chemical poisons, a matter which heretofore has been much neglected. This is already being conducted by the State Labor Bureaus, the American Association for Labor Legislation, and an increasing number of instructive articles in technical medical journals.

2. The collection of accurate statistics regarding the extent and severity of the numerous chemical industrial hazards. This work is also in progress

under the auspices of the institutions above named and the State Factory Investigation Commission.

3. The interests of chemists in devising means to render dangerous chemical trades less hazardous. Already much has been accomplished in the modern improvements in the manufacture of phosphorus matches, the elimination of lead from pottery glaze and of arsenic pigments from the coloring of wall papers, artificial flowers, etc. In France, the compulsory substitution of zinc for lead white in the manufacture of paint has accomplished great good.

4. The education of manufacturers and employers in the knowledge of the economic efficiency which immediately results from the adoption of recognized methods of proper ventilation and cleanliness in foundries, mills or factories where toxic fumes, gases, vapors or dusts are generated.

5. The education of employees in hazardous chemical trades as to the special dangers involved and simple expedients to avoid them. Such a system of instruction as that practiced by the Illinois Steel Corporation, in methods of avoidance of accidents, if applied to the avoidance of disease hazards, would soon demonstrate an equal if not greater economic value. These measures, upon which this corporation finds it an economy to expend over $1,000,000 annually, comprise furnishing workmen with printed directions, display of special danger signs, offering of rewards for compliance with regulations, the formation of committees of safety among the workmen, and many other expedients.

I see no reason why there should not be warning labels attached to the containers of paints, varnish and volatile chemical irritants of all kinds, just as we now have compulsory labeling of the contents of all containers of dangerous drugs. Such labels should state concisely the name of the hazardous chemical, the chief symptoms it produces, and the means of avoiding the hazard. For example, such a label might read: "WARNING! *This paint contains lead. If the lead reaches the mouth by means of unclean hands, food or tobacco, poisoning may result with symptoms of colic, paralysis, hardening of the arteries, or chronic kidney disease.* BE CAREFUL!" or "WARNING! *This varnish contains wood alcohol, the fumes of which, if breathed in a confined space, may cause permanent blindness, or possible fatal paralysis of the heart. Use only where there is good ventilation, and never breathe the fumes directly.*" Of course, in this case the use of wood alcohol should be prohibited altogether, but such a label might have saved the lives and eyesight of those unfortunate men in the brewers' vats in Buffalo.

6. The periodic examination by physicians of workmen using dangerous chemicals, conducted at least as often as once a month, in order to detect incipient cases of poisoning and give proper suggestions as to prevention of further hazards.

I have presented only a brief review of a very broad and most important topic, which is just beginning to attract the study and interest in this country which it has commanded abroad for many years. It is a topic which appeals alike to humanitarian, scientific and purely economic interests, for there is no one among us who does not make use of some article of necessity, adornment or luxury which has in its process of manufacture been associated with possibility of disease hazard to the workman, from the match with which we strike a light, to the glaze on our porcelain coffee cup, or the felt hat which we "throw into the ring." The problem before us is to make first a rational study of the extent and gravity of the various occupational disease hazards, and then seek to deal with them through education, invention, common-sense precaution, and, where all else fails, through appropriate legislation.

THE PROGRESS OF THE WORK ON THE REVISION OF THE UNITED STATES PHARMACOPOEIA.[1]

By J. P. REMINGTON.

The American Chemical Society, having representation in the United States Pharmacopoeial Convention, should be kept informed of the progress made from time to time in the work of revision. The subcommittee on scope have been wrestling with the problem of admissions and deletions for over one year. Their labors cannot be said to be concluded, for, although they have presented a tentative list, some modifications will be required. The convention recommended publicity under Section 14 in the Abstract of Proceedings in the following words: "It is recommended that the General Committee of Revision make public, for comment and criticism, an abstract of new descriptions and standards and of changes in descriptions and standards proposed, before final adoption."

Inasmuch as admissions and deletions would be properly included, the Committee of Revision decided to give the lists to the journals for publication. The lists have excited considerable comment and the chairman has received many communications advising the admission of this, and that, and the other, or the deletion of this, and that, and the other. The committee itself, although reasonably harmonious, are divided on the scope of the Pharmacopoeia. A small but active minority have clearly expressed the view that the Pharmacopoeia contains a large number of articles which, in their opinion, are worthless. On the other hand, a large majority of the committee are opposed to dropping so many drugs and medicines because they say they are still used in the practice in various parts of the country, and as the Pharmacopoeia is now a book of standards, they believe that the doctor and the pharmacist are entitled to have the benefit of the best quality of drugs and preparations and that this consummation will be brought about most effectually by retaining the drug or preparation in the Pharmacopoeia and attaching definitions, descriptions, and tests, so that those who do use the article may have the protection of the National and State Food and Drug Laws. It seems difficult at times for some of the members of the committee to realize that the Pharmacopoeia is intended to represent all parts of the United States and that there always will

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[1] Chairman's address delivered before the Division of Pharmaceutical Chemistry, American Chemical Society, December, 1911.

be in the Pharmacopoeia many preparations which a doctor has never used and probably never will use in his life. It does not follow, however, that some other physician living in a different section of the country has not found the medicine rejected by Dr. A a most efficient remedy and Dr. B could argue with just as much force that he has no use for the pets recommended by Dr. A. This situation is a perfectly natural one and will not embarrass the committee.

So far, there has not been the slightest attempt on the part of the manufacturers of specialties protected by trade mark or copyrighted label or controlled by proprietary rights to have their goods introduced into the Pharmacopoeia. In former revisions there were slight evidences of the pride of a manufacturer to have his product paid the compliment of Pharmacopoeial recognition, but since the passage of the Food and Drug Laws it would seem that the manufacturer preferred to get along without official recognition, for this would mean that he must always maintain his product at the standard of strength and quality once established by the Pharmacopoeia.

This does not mean that he would like to lower the quality; he might want to improve it by raising the standard, or the Pharmacopoeial test for it might prove inadequate or faulty. In any event he would prefer freedom of action.

Analytical chemistry has proved to be one of the foundation stones in the building of reform structures. Without it, successful prosecution of offenders could not be maintained. The chemist has risen immensely in reputation in the eyes of the public. The labels of the manufacturer must now represent the *truth* in describing the contents of the container. False and misleading statements are no longer tolerated. This puts the honest manufacturer in the proper light. Advertising artists with imagination have prepared labels attractive to the eye in the past and they are still exploiting preposterous claims of remedies, but much more intelligence is being displayed by the public. Nowadays it is amusing to listen to the remarks of young people who ask their elders whether this or that statement in an advertising circular is really true or likely. The old idea that so many people used to have, that because a statement was in print it must be "gospel truth," is becoming obsolete. Probably no other influence has been so great in improving the quality of chemical preparations as the requirement of the Food and Drugs Act, that, if an article labeled with an official name differs in quality or strength from the standards laid down in the United States Pharmacopoeia, such difference must be distinctly printed on the label. A manufacturer in nine cases out of ten prefers to improve his product and bring it up to the official standard rather than place upon the label a qualifying statement.

The tests in the Eighth Revision of the chemical substances are undergoing careful investigation, and a number of the old tests will be deleted and new ones admitted. The sub-committee on organic and inorganic substances have their hands full at the present time in trying out the many suggestions which have come to them; it is this part of the work which will probably delay the issue of the book. Much time has been consumed in selecting the simplest and most effective methods for determining the physical factors, *i. e.*, melting points, boiling points, solubilities, specific gravities, saponification values, iodine numbers, etc. It is obvious that in a law book it is necessary to designate uniform methods for obtaining these physical factors. The figures given in the text of the book would show that they were obtained by the methods given in the book in the Introductory Notices. The question of solubilities seems to be the most difficult, as might be supposed, and the work of revising all the solubilities in the text according to the Official Method will call for much labor and time.

Every one of the sub-committee has been industrious and active, but so far, the sub-committee on nomenclature have not been called upon for their report. This is usually the last sub-committee to send in its recommendations. A number of letters have been received by the chairman urging the necessity for retaining the present system of nomenclature.

While there may be some members who desire to introduce changes, it is believed that the majority of the committee are opposed to radical changes. Of course, these members will listen attentively to all suggestions. When it is considered that millions of labels of official products are now in use and a large sum of money has been expended very lately in revising these to conform to the provisions of the law, it is believed that it would not be wise to make any change in the general form and style. But obviously any errors must be corrected, and new drugs, chemicals, or preparations introduced must have corrected titles which conform in style with those already introduced. Undoubtedly some of the names will be shortened for the sake of conciseness and convenience in printing. Abbreviations of the official titles will be introduced for the first time in the new Pharmacopoeia. These will serve as a guide to physicians and to pharmacists in labeling their stock bottles and containers.

Inasmuch as the Pharmacopoeia is now a law book, it has been proposed to print a small numeral on the left hand side of each line of the article completely down the page so that for convenience of reference one who quotes the Pharmacopoeia can indicate the page and the numbered line.

On the whole, it may be said that the work is being pushed most actively. A proper sequence and system is necessary if the valuable time of the members is not to be wasted. The immediate work of revision is entrusted to fifteen members selected by the general committee. This is called the Executive Committee of Revision and each member is chairman of a sub-committee. He and the other members of the sub-committees are chosen for their fitness to serve under their chairman. When a sub-committee is ready to make its report, the Executive Committee votes upon it and the text of the book will be framed upon the results as reported. It will be seen that, by this plan, the large number of facts accumulated in ten years will receive minute and careful consideration by the whole Committee of Revision and probably ninety per cent. of the final work will stand as reported by these experts. If the sub-committee should make a mistake or an error in judgment, it will be pointed out by some member of the Executive Committee and a reconsideration by the sub-committee asked for. If the whole Executive Committee and the special sub-committee should differ on any question, the Executive Committee has the right under the By-Laws to appeal to the fifty-one members of the General Committee of Revision for final statement. Then again, under the plan of publicity, any one interested in the Pharmacopoeia may comment through the journals or appeal to the chairman of the Committee of Revision for a reconsideration. This plan, which differs from that used in the previous edition, is working out satisfactorily: it is constructive work on a comprehensive plan. The new Pharmacopoeia will not represent one man's work, but the best judgment of men selected by a large convention for their special fitness to perform certain duties. A Pharmacopoeia should represent as accurately as possible the *present state of knowledge* and a committee should not delay the publication of the work because some one believes he has discovered a new test or an improvement and all must wait until such has been tried out.

In the past a number of tests were introduced into the Pharmacopoeia which *had not* been sufficiently tried out by many workers. The result sometimes proved to be unsatisfactory and an old test had been discarded in favor of a new one which had practically failed. Therefore it would seem to be common sense to "hold fast that which is good." A Pharmacopoeia should represent advanced knowledge of facts known and proved at the time the book is written. There should be no guess work or hope-so's. It is far better to take no chances on an untried test, no matter how promising it may seem to be; but now that the book is the standard for the country, it is of the utmost importance that the definitions, descriptions and tests should be selected from facts which are tried and true.

The members of the American Chemical Society are requested to send at once to the office of the chairman of the Committee on Revision, 1832 Pine Street, Philadelphia, any correction or suggestion which they believe will improve the present Eighth Revision of the United States Pharmacopoeia. These letters are referred first to the sub-committee having such subject in charge. They are then carefully treated under the plan outlined above and it is not likely that any comment or suggestion could be overlooked. Of course, no one can promise that every suggestion will be adopted, for many of the suggestions upon the same subject are opposed to each other. In some cases two tests for the same substance have been suggested, both of which are valuable. It then becomes the duty of the committee to choose between them, and this responsibility must be assumed by the committee. Outside assistance from experts will be freely sought. Some one who has made an especial study of an assay or the habitat of a plant, or some manufacturer, who is willing to disclose special information which he may have, will find the committee responsive and eager to accept whatever is tried and true.

Now is the time to send in all suggestions for improvement. Unfavorable criticism of the printed book will be shorn of its sting. If any one interested in the new revision holds aloof and deprives the committee of a valuable fact or hint which he has discovered, it will tend to depreciate the value of the Ninth Revision. The plan of revision is comprehensive and the system is the best that could be devised by representative convention in which no special interest has been recognized and which is not under the domination of any trust or clique.

The conclusions of the committee will be published in advance and no corporations or firms will have any privileges which would tend to give them any financial advantage over any other firm or corporation. Neither the chairman of the committee nor, as far as he knows, any other member has been approached by any one seeking such an advantage. This is undoubtedly due to the fact that advance information has gone abroad that it would be useless for any one to attempt to obtain special privileges which would be denied to others. Investigation will always prove that the confidence and the trustworthiness of the members of the Committee of Revision are well placed.

Finally, let me appeal to the members of this Society to cheerfully render every assistance in order that the new Pharmacopoeia may be the best book of its kind in the world.

CURRENT INDUSTRIAL NEWS

By W. A. Hamor.

THE INDUSTRIAL USES OF OZONE.

In a paper on the production and application of ozone, in a recent number of *Nature* (88, No. 2208, pp. 551-5), F. Mollwo Perkin states that the only method employed commercially to prepare this powerful oxidizing agent is to subject oxygen to the action of the silent electric discharge, the oxygen thereby receiving electrical energy and becoming converted into ozone. Since all the apparatus employed depends upon some method or other of obtaining such a discharge, very high electrical potential is necessary. In general, the silent discharge occurs between conducting plates separated by means of a dielectric. The original ozonizer of this type was the invention of W. von Siemens; it consisted of two concentric tubes, coated on their outside surfaces with tinfoil, the glass of the tubes acting as the dielectric. Berthelot employed glass as the dielectric and a liquid as the conducting material. Modifications of both these forms are now used commercially. The "Ozonair" apparatus consists of wire gauze as the conductor, separated by mica as the dielectric. When the ozone is to be produced for water sterilization—now actually employed commercially—the ozonizer is enclosed in an iron case; when it is to be required for the purification of the air or for ventilation, it is open, the air being drawn through the apparatus and distributed by means of a fan. The electrical tension used is about 7,000 volts. The Siemens-Halske type, used for water sterilizing, consists of concentric pipes placed one within the other; the inner one is of aluminum connected with the leads carrying a high-tension current; a glass cylinder, surrounded by water circulated for cooling purposes, and "alive," is the other pole. The water surrounding the glass cylinder receives its electricity from the iron-containing box, which is earthed, and consequently forms the negative pole, while the aluminum pipe is the positive pole. The annular space between the concentric pipes is where the silent discharge occurs. The complete apparatus is composed of a cast-iron box divided into three chambers: a lower chamber for receiving and conveying the air to the ozone tubes; an hermetically sealed middle compartment into which the ozone tubes are inserted by means of a stuffing-box gland; and an upper chamber for collecting the ozonized air. An alternating current at 8,000 volts is used. The Abraham Marmier apparatus is said to employ a potential of 40,000 volts; it is made up of a number of hollow cylindrical electrodes, insulated by glass and contained in a box. The Otto ozonizer consists of a series of transverse plates, so arranged that a dielectric plate is placed between the electrodes.

The "Ozonair" process is said to be used in England for the sterilization of water. The ozonization takes place in three stages—that is, the same water comes into contact with ozone three times. The Siemens-Halske system is said to be largely employed on the continent, the largest plant erected by them being at St. Petersburg. In this plant the ozonizers are worked with a three-phase alternating current at 7,000 volts and 500 periods; and 2,000 cubic meters of water can be dealt with per hour. Other places in Europe where ozone is used for sterilizing the public water supply are Paderborn, Wiesbaden, Paris, Hermannstadt, Florence, Nice, Chartres, Villefranche, Rovigo, and Chemnitz. Two new ozone plants are said to be under installation in Paris with a daily output of 45,000 cubic meters of water. In the United States ozone is employed at Philadelphia. Perkin states that the employment of ozone for sterilizing water is "not only efficient but also very cheap. In this country (England) to sterilize 1,000 gallons of water the cost is from one halfpenny to one penny, depending upon the size of the plant and the cost of the electrical power." Ozone apparatus has also been devised for fitting on to the ordinary water mains, the ozonizer only functioning when the water tap is turned on; and by means of petrol motors, ozone may be used for sterilizing water during campaigns. Comparing the ozone process with ultraviolet sterilization, Perkin says: "For small scale work the ultraviolet sterilization is very well adapted, but ozone is better for large scale operations."

Ozonized air is said to be very largely employed in the ventilation of theatres and other large public buildings; an ozone plant is now being employed in the ventilation of the London Tube Railways "with beneficial results." Perkin recommends that the House of Commons be supplied with an ozonizing apparatus.

Ozone is now used in the manufacture of vanillin from iso-eugenol; in the strengthening of weak yeast in brewing; in bleaching oils and fats; in blowing such oils as linseed oil; in bleaching delicate fabrics, and in bleaching flour. The maturing effect of ozone on wines and spirits is said to be remarkable, since spirit which requires years for aging is matured "in a remarkably short time by emulsifying with ozone." It has been suggested that ozone be used in tobacco factories to aid the maturing.

A study of the influence of ozone in ventilation has recently been published by Hill and Flack [*J. Roy. Soc. Arts*, 60, 344 (1912)]. These authors point out that for efficient ventilation, the chemical purity of the air is of relatively little importance, what is required being air of the proper degree of coolness and humidity, and movement of the air so as to vary continually the cutaneous condition of the body. The impulsion of hot air into a room is regarded as the most objectionable of all systems of ventilation. Hill and Flack consider that the chief value of ozone in ventilation lies in its effect on the olfactory nerves and those of the skin and respiratory tract. The concentration of ozone must be very low (less than 1 part per million).

Perkin failed to note that there is an ozone plant at Great Falls, S. C., which handles 80,000 gallons of water per 24 hours (*Eng. Record*, 64, 12); that there are various methods of applying ozone to ventilation, cleaning and sterilizing purposes in the brewery (Vetter and Moufang, *Wochschr. Brau.*, 28, 377); and that ozone has been tried as a sterilizing agent for milk, cream, butter and soft cheese, with hardly desirable results (Freund, *Chem. Ztg.*, 35, 905). Another discussion on the applications of ozone is contained in *L'Industria Chimica*, 11, 121–3. On the preservation of food and medicine by means of ozone, see Linder, *Chemical Engineer*, 12, 61.

NON-FREEZING MIXTURES.

The prevention of freezing in water pails and chemical fire extinguishers is discussed by Robinson in a recent paper (*Ind. Eng.*, 11, No. 4, 310), and some important data are given.

FAHRENHEIT FREEZING POINTS OF SOLUTIONS CONTAINING:

Lbs. per gal.	Sodium chloride.	Calcium chloride.	Lbs. per gal.	Sodium chloride.	Calcium chloride.
0.5	24°	29°	3.5	—8°	—8°
1.0	18	27	4.0	.	—17
1.5	12	23	4.5	.	—27
2.0	6	18	5.0	.	—39
2.5	1	4	5.5	.	—50
3.0	—3	—1	...	.	..

Calcium chloride is superior to sodium chloride in that it does not corrode steel tanks and barrel hoops. When calcium chloride is used, wooden barrels should first be well coated inside with asphaltum or a mixture of paraffin and resin, to prevent shrinkage of the staves. Calcium chloride attacks solder, and is therefore unsuitable for use in extinguishers of metal. A 40 per cent. solution (specific gravity 1.4) can be purchased on the market; when this is diluted with an equal quantity of water, the solution will not freeze at —9° F. It is recommended that when automatic sprinkler systems are installed in warehouses or other places of exposure during winter, a calcium chloride solution be used, as this will do away with the necessity of maintaining a dry-pipe system and its attending risks, due to leaky valves and possible failure of the air supply. The system should be filled with a solution of 1.225 to 1.25 specific gravity (3.36 to 3.76 lbs. of calcium chloride per gallon of solution), and a check valve installed to separate this from the source of the water supply.

Glycerine has been recommended for use in extinguishers, the addition of 3$^1/_2$ qt. to a standard extinguisher making a solution capable of withstanding —4° F., and 4 qt. a temperature of —10° F. It tends to disintegrate rubber, however.

Denatured alcohol—water solutions are stated to have the following values: 20%, 10° F.; 30%, —5° F.; 40%, —20° F.; 50%, —35° F.

A NEW LIQUID MIXER.

The liability to use an excessive quantity or an insufficient amount of solutions of chemical reagents for the purposes of precipitation, neutralization, or purification in manufacturing processes where the financial side of the matter is an important factor, renders the question of economy in weighing or measuring such reagents a point to be accorded careful consideration. It is reported (*Chem. Trade J.*, 50, No. 1299, 411) that an apparatus, which is self-acting and requires very little attention in its use, is being placed on the market by a London firm for the chemical treatment of water and trade effluents, in which the exact proportions of reagents are maintained, it is claimed, notwithstanding any change which may occur in the rate of flow of the liquid under treatment. The apparatus is said to be adapted to deal with large quantities of liquid, and if constructed on a small scale may prove useful in other ways. The crude liquid to be treated passes under slight pressure through a pipe leading to the purifying tank. A portion of the pipe being constricted at one point like the Venturi tube allows the liquid to flow at this point at a greater velocity than in the full-sized portion; consequently, as the velocity increases, there is a corresponding decrease of pressure in the narrower portion, which is connected with two vertical pipes, each containing a float of a material heavier than water. A cylindrical vessel containing the reagent is attached to these floats by a lever, and the change of pressure is used as the power for setting the apparatus in action. When the apparatus is at work, the liquid in the two vertical pipes stand at levels depending upon the velocities of flow in the two portions of the Venturi tube, the difference of these two levels determining the amount of reagent entering the main stream. It is claimed by the manufacturers that under the most extreme conditions, the error in use will not exceed 1.7 per cent.

THE STERILIZATION OF POTABLE WATERS.

In a paper on the "Sterilization of Drinking Waters by the Action of Ozonized Oxygen and of Chlorine Compounds in the Nascent State," presented before the Paris Academy of Sciences (*Compt. rend.*, 154, 447), Rouquette states that sodium hypochlorite was successfully employed for the sterilization of water during a recent cholera epidemic. Water containing 15,000 *B. coli* per liter was rendered sterile by the addition of 1 mg. of active chlorine per liter containing 1 mg. of organic matter. Rouquette states that the best form in which to use active chlorine for this purpose is as a mixture of one part of the salt $Na_2S_2O_9$ (obtained by mixing hydrogen dioxide and sodium hydrogen sulphate in concentrated solution) and two parts of the compound Na_2O_2Cl (prepared by the addition of sodium sulphate to calcium hypochlorite solution, the calcium sulphate being removed by filtration). The mixture is added in the proportion of 0.02–0.1 part per 100,000, according to the degree of bacterial contamination. It is said to be more rapid and intense in action than sodium hypochlorite, and the water thus treated is reported to be odorless and tasteless, and to contain no chlorine, hydrochloric acid or sulphuric acid.

PORTLAND CEMENT.

A review of the contributions of E. Leduc to the constitution and formation of Portland cement is contained in a recent number of (*Nature*, 89, No. 2216, 177), and many useful data, with few speculations, are given.

Concerning commercial cements, the fact recognized in practice, that the mechanical strength falls off rapidly as the content of clay is increased, is confirmed in Leduc's "Sur la Constitution et la Formation du ciment Portland," and it is also shown that the coarseness of grain of both clayey matter and of sand has at least as great an influence on the "falling" of clinker as has the amount of their constituents. A normal clinkering temperature is set down at 1400–1450° C. Leduc shows that cements in which the alumina is replaced by ferric oxide are mechanically weak, and found that those containing large amounts of magnesia (*e. g.*, 25 per cent.) went to pieces on exposure to steam. "It should be noted that Leduc took unusual pains to bring his raw materials to an extremely fine state of division, fully comprehending that in a mass which is almost plastic the occurrence and completion of the reactions concerned in the production of definite silicates, aluminates, and the like are dependent on the intimacy of admixture, as well as on the temperature and the time. Any one who has prepared Portland cement experimentally knows that particles of sand which may be only 0.1 mm. in diameter will each produce its small center of 'falling,' the dicalcium silicate oozing forth from the site of the grain. . . . , whereas the same raw materials, really finely ground, will not 'fall' at all."

In collaboration with Chenu, Leduc has shown that Seger cones, useful as they are for a number of purposes, are far from exact as temperature indicators; that they may well be used side by side with materials of the same class which are to be heated in the same way, but that in all cases they must be checked by whatever kind of pyrometer is best adapted for the temperatures to be measured.

BLEACHING POWDER AS A SOAP SUBSTITUTE.

According to *Scientific American Supplement* (No. 1897, 304), a German physician, Sacher, recommends the use of bleaching powder as a cleansing agent for the hands of workmen as a preventive agent against metal poisoning. Working men handling metals, such as lead, mercury, antimony, arsenic, bismuth, zinc, chromium, or manganese, either in metallic form or in the form of compounds, are constantly exposed to the danger of poisoning, through imperfectly cleaned hands. Small particles may thus be transmitted to the mouth in eating or using tobacco. To completely remove metallic impurities from the hands is sometimes difficult; soap alone is generally useless, especially since it forms insoluble compounds with most of the metals. Bleaching powder, however, is said by Sacher to be an ideal material for the purpose; it has no injurious effects, when properly used, and acts chemically as well as mechanically. It forms a saponaceous lather and has the further advantage of possessing strong disinfecting properties.

WATER-GAUGE GLASSES.

All users of steam boilers are familiar with the trouble which is occasionally experienced in connection with the glasses used in water-gauges as the result of the corrosion or wasting of the ends of the glass tubes inside the glands of the fittings. Efforts have been made to get over the difficulty, and many different kinds of glass have been tried, but only a partial measure of success appears to have attended the experimentation, while the rapidity with which the glass is attacked has increased as steam pressures have become higher. The corrosion is always worse at the steam end of the tube than at the water end, and has often led to accidents. According to *Engineering* (93, 499), in order to prevent this destruction of the glass, a Berlin concern has recently brought out a method for protecting the ends of the tubes. This is said to be accomplished by providing the tube, on the inside and outside of its ends, with a metal protective coating which yields to the expansion of the glass. This is united to the glass by means of a cement that forms a compact whole, which, it is claimed, can not be dissolved by water. For normal pressures, the glasses are provided with a metal sheath at the steam end; while for high pressures and for water high in alkalies, the tubes are provided with metal coatings at both ends.

PACKING IN STEAM PLANTS.

Packing for cylinder heads, steam chests, pipe-flange joints, valve stems, etc., is now regarded as indispensable, and the engineer has quite a large line of packings to select from. According to *Power* (35, 545), the development of the manufacture of packing has proceeded hand-in-hand with the utilization of steam. Up to 1850, for example, the commonly used material was a composition containing red lead, hemp and oil, made into a putty. About 1860, cloth insertion packing was introduced;

it consisted of rubber composition with insertions of duck or sheeting, and was used between 1860 and 1875, when the steam pressure did not exceed 80 pounds per square inch. Afterwards came plumbago and rubber compositions, termed "self-vulcanizing" packings; these were found to be more durable and satisfactory under the conditions then existing than the preceding, but had the disadvantage that they had to be baked into the joint. In 1886, several semi-vulcanized rubber-composition packings appeared on the market, and a composition of rubber and asphaltum, suitable for liquid conditions, was next introduced. During the period 1900 to 1910, steam pressures have increased from 80 to 200 pounds and over in stationary plants. This increase brought a corresponding rise in temperature, which was further increased by the practice of superheating. Then, too, the wider use of the air compressor, ice machines, gas engine, superheater, etc., created extreme temperatures demanding a packing which could meet exacting conditions. It is said that composition packings have been perfected which possess great resistance to extreme heat as generated under high pressure. The basis of the material is pure asbestos fiber, the fibers being treated with a waterproof compound to prevent the absorption of water. The treated fibers are compressed into sheets, pliable, resilient, and of high tensile strength.

DEVELOPMENTS IN STEAM GENERATION.

In the United States the employment of measuring instruments in the boiler room has rendered it possible to make the boiler conform more closely to the load curve than formerly. H. G. Stott points out in the *Electric Railway Journal*, 38, 781, that the Venturi meter for measuring the feed to the individual boiler; the Pitot tube in the steam pipe for giving a general indication of the relative amount of work done in different boilers; and a coal-measuring instrument in the chute or down-take coal pipe, have been used along with forced combustion. He studied the records of one-minute indications of steam and water-flow meters to show the variations in power due to variations in load. To meet these variations, it is recommended that the boiler room should be designed for maximum operating conditions and economy at average load, and to sacrifice slight economy at light loads by working only one of a pair of grates to each boiler, the other being banked; or to employ the auxiliary use of liquid fuel; or to have grates capable of working with natural draught up to a given power and thereafter with forced draught.

THE CONTACT PROCESS OF SULPHURIC ACID MANUFACTURE.

Wieland [*Ber.*, 45, 685 (1912)] has studied the catalytic conversion of sulphur dioxide into sulphuric acid. When palladium black is exposed to moist sulphur dioxide, air being excluded, and the excess of sulphur dioxide is afterwards removed by carbon dioxide, sulphuric acid is found in the palladium, which can only have resulted by the removal of hydrogen from sulphurous acid:

$$H_2SO_3 = H_2 + SO_3;\ SO_3 + H_2O = H_2SO_4$$

The equivalent hydrogen was not found, but, instead of it, sulphur; and Wieland has found that palladium-hydrogen does reduce aqueous sulphurous acid:

$$SO_2 + 2H_2 = 2H_2O + S$$

He therefore suggests that the ordinary contact-process of sulphuric acid manufacture is not a direct oxidation, but a reaction similar to the above, in which the function of the oxygen is to oxidize the hydrogen produced, forming the water which is itself necessary for the reaction to occur:

$$SO_2 + H_2O = H_2SO_3 = SO_3 + H_2;\ 2H_2 + O_2 = 2H_2O$$

FORTOLINE.

In 1910, K. Hadorff (French Patent 416,325, April 27, 1910) devised a fuel "for increasing the power of internal-combustion engines," consisting of "benzene picrate" (prepared by dissolving picric acid in benzene, heating for a prolonged period, and finally separating the excess of benzene by distillation) mixed with benzene or other liquid hydrocarbon. This fuel was said to burn without the formation of any deposit in the cylinder.

The fuel claimed in First Addition, dated September 25, 1911, to French Patent 416,325, termed "Fortoline," contains nitrobenzene in addition to "benzene picrate;" 10 parts of benzene are mixed with 0.5 part of nitrobenzene to which a small quantity of picric acid has been added, and the resulting mixture is boiled for a long time. The product is added to 10 times its amount of petroleum, naphtha, petrol, benzene, or other hydrocarbon, and is claimed to "increase the power of internal-combustion engines" when the treated fuel is used therein.

THE UTILIZATION OF STORAGE BATTERY SLUDGE.

The sludge of lead peroxide and sulphate which accumulates during long periods in lead batteries has a value on account of its lead content, but its transportation to lead smelteries has been expensive and difficult because of the associated acid. Moreover, washing and pressing are out of the question because of the fine state of division of the lead peroxide. In German Patent 236,343, it is claimed that these difficulties are overcome by mixing the sludge with slaked lime; the mixture quickly sets to a firm cake. An alternative plan is to mix the sludge with the sulphite liquor from sulphite cellulose works, the lead peroxide being thus converted into lead sulphate; molasses may also be employed for the reduction of the peroxide. So much heat is liberated during these reactions that considerable of the water is evaporated.

THE MANUFACTURE OF WHITE LEAD.

It is reported (*Chem. Trade J.*, 50, 386) that the West German Lead Color Works are now in the possession of a new process for manufacturing white lead which does away with the difficulties of dissolving the lead, encountered in the old Dutch process. Finely divided lead (readily obtainable now in a uniform state) is put into a chamber, acetic acid is added, and air is led through for agitation: a large amount of lead becomes soluble. The lead solution is then subjected to the action of carbon dioxide under pressure in another chamber, and the lead lye and white lead formed are removed by atmospheric pressure. The method can be worked in a few hours instead of weeks, and, furthermore, no lead residues are left and less acid is used.

In German Patent 244,509, recently issued, a novel process of making white lead is claimed. Litharge is treated with a boiling solution of amino acids, such as result upon the hydrolysis of albuminoid substances, and the lead is precipitated by a current of carbon dioxide. Since the organic acids remain in solution, the liquor can be used continuously for dissolving more litharge.

THE PURITY OF COMMERCIAL METALS.

Mylius (*Z. anorg. Chem.*, 74, 407) suggests that instead of the existing irregular nomenclature ("pure," "puriss.," etc.) for denoting the purity of commercial metals, a system of numerical classification be employed. According to this plan, the first degree of purity would represent a metal in which the total true impurity, with the exception of oxygen and the products of atmospheric corrosion, was from 1–10 per cent.; the second degree from 0.1–1 per cent., and so on to the sixth degree. It is stated that as technical products of the fourth degree and upwards (less than 0.01 per cent. impurity), the following metals may be obtained: cadmium, copper, gold, lead, mercury, platinum, silver and zinc. Zinc, cadmium and tin (Kahlbaum) have all risen from the third to the fourth degree since 1895. Redistilled zinc was found to contain from 0.007–0.0088 per cent. total impurity, whereas a sample of electrolytic zinc costing ten times as much contained 1.3 per cent. of zinc sulphate, about 6 per cent. of zinc hydroxide, 0.02 per cent. of insoluble silicate, and 0.04 per cent. of metallic impurity.

THE COST OF CHLORINE.

The following costs per ton of active chloride are compiled from a recent paper by Kershaw (*Chem. Trade J.*, **50**, 330, 385):

Method of preparation.	Form of combination.	Cost.	Remarks.
Chemical.	Calcium hypochlorite.	$68.82	Taking 3 tons 3.5% bleach and assuming 5% loss of chlorine.
Chemical.	Sodium hypochlorite.	98.62	Using sodium sulphate to decompose calcium hypochlorite.
Chemical.	Sodium hypochlorite.	$109.96	Using sodium carbonate, *ibid.*
Electrolytic.[1]	Sodium hypochlorite.	$106.33	6.07 kw. hrs. and 6.0 kg. salt per kg. chlorine; 15 kg. Cl per 10-hour day.
Electrolytic.	Sodium hypochlorite.	$112.13	Power at $0.008 per kw. hr.
Electrolytic ("Hermite" electrolyzer).	Sodium and magnesium hypochlorite.	$392.28	Actual cost at Poplar, England, where 50,726 gal. of hypochlorite solution were produced (1910).

SYNTHETIC ORGANIC DYES AND PATENTS FOR THE MANUFACTURE OF THE SAME, 1907-'11.

(Lehmann, *Chem. Ind.*, **35**, No. 7, 207.)

	1907.		1908.		1909.		1910.		1911.	
Groups.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.	Dyes.	Patents.
Nitro	..	..	..	..	..	1	..	1	..	..
Azo, substantive	54	5	123	14	85	23	92	13	72	19
Azo, acid	35	11	38	11	37	6	58	27	50	18
Azo, chrome	37	20	52	8	38	10	44	19	37	7
Azo, basic	1	2	..	..	..	..	..	1	..	1
Azo, varnish	5	6	19	9	11	11	13	15	8	7
Azo, "ingrain"	2	11	3	4	2	5	3	7	1	7
Triphenylmethane	8	5	7	5	3	9	11	10	9	14
Pyronine	4	..	2	2	4	1	..	..	3	1
Acridine	1	..	..	..	..	..	..	..	1	1
Nitroso	1	..	..	..	2	2	..	..	1	1
Anthracene	16	32	13	40	30	54	13	50	24	93
Indophenols	..	3	..	..	..	..	..	..	..	3
Oxazine	..	6	6	13	4	8	2	6	4	5
Thiazine	..	2	..	..	..	..	1	..	..	..
Azine	..	7	2	1	..	4	1	..	5	3
Quinoline	..	..	2	1	..	..	1	..	..	..
Indigo, Thioindigo	4	28	15	59	15	45	21	47	8	90
Sulphur	37	16	64	24	40	12	45	21	22	7
Constitution, unknown	2	3	1	1	..	2	..	2	..	3

THE MANUFACTURE OF ALUMINUM FOIL.

Aluminum foil is now being manufactured at La Praz and Charleville-sur-Andelle by a French company, and at Ludwigshafen a. Rh. by a German concern. The German product, termed "Alolit-foil," is being marketed as a substitute for tin-foil, and is said to be "from pure aluminum, and to be lead-free and non-poisonous."

Guillet [*Rev. Met.*, **9**, 147 (1912)] has given an account of the processes conducted in France for the manufacture of aluminum foil. The metal, delivered to the works in the form of ingots, 700 × 320 × 120 mm. (cast at 750°–775° C.), is first hot-rolled at 420° C. to a thickness of 3.5 mm. and then cut into strips 8 cm. wide, which, after being annealed at 420° C., are cold-rolled to 0.04 mm. in six stages, further reduction in thickness being then effected by continued rolling or by hammering. In the former case the metal bands are first greased, then rolled in pairs to 0.02 mm. and subsequently in fours to the desired thickness of 0.01 mm., the foil thus being had in lengths of about 16 m. In the latter case the bands are made into packets of 500 each and beaten by pneumatic hammers, each packet being placed between two thin sheets of zinc; when the thickness of the metal reaches 0.03 mm., the packets are hammered in pairs to 0.02 mm., and finally in fours to 0.01 mm. The waste in either case is considerable, only about 33–35 per cent. of the 0.04 mm. metal employed being obtained as good foil 1 sq. m. of which weighs about 27 grams. The waste foil is employed for the production of aluminum powder. Prior to trimming and cutting to size, the sheets of foil are mechanically separated. In the manufacture of aluminum powder, the comminution of the waste foil is conducted in stamp mills in which the closed mortar-box is provided with a circle of 12 stamps actuated from a central shaft.

SOME NEW "NON-CORROSIVE" ALLOYS.

The American market now affords a grade of sheet steel known as "Vismera," possessing the following composition: Iron, 99.542 per cent.; copper, 0.200; manganese, 0.190; carbon, 0.036; phosphorus, 0.004; sulphur, 0.018; oxygen, 0.009; and hydrogen, 0.001. Particular attention is called to the copper and manganese content, and to the low percentage of oxygen. It has been known for some time that the presence of a small amount of copper increases the resistance of steel to corrosion, and that cupreous steel is more resistant to acid mine waters than ordinary steel. It is said that another producer has succeeded in obtaining "an alloy steel that will successfully withstand tests with sulphuric acid, the chief enemy of tubing and sheets."

Gaston Jacquier, of Belgravia, Transvaal, has patented an anti-corrosive alloy said to be suitable for employment in the manufacture of tanks, piping, ropes, valves, pumps, etc. (U. S. Patent 1,019,963, 1912). It is made of the following metals: Aluminum, 92 per cent.; bismuth, 2 per cent.; copper, 5 per cent.; and silicon, 1 per cent. The composition may also be as follows: Aluminum, 91 per cent.; bismuth, 2 per cent.; copper, 5 per cent.; and magnesium, 2 per cent.

KUPRONIZING.

According to *Engineering* (93, No. 2411, 367), a London firm mainly concerned with copper-plating wood applies the name "kupronizing" to the process it employs. In the plating of wooden hand-rails, the wooden core is first impregnated with a preservative material and then flashed with either plumbago or a metallic salt. The actual copper deposition is then carried out in a bath in the usual manner. It is the present practice to deposit a layer about $^1/_{16}$ of an inch thick. Iron window-frames and iron pump-rams are now kupronized, and the process gives a copper layer which adheres so that the pieces may be machined after the copper is in place.

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[1] To produce one ton of active chlorine per day, with the cheapest of the electrolytic cells described by Kershaw, would require 50 electrolyzers and involve a capital outlay of about $37,500, while the more efficient and expensive types, wherein platinum-iridium electrodes are used, would cost double this amount.

NOTES AND CORRESPONDENCE

THE GERMAN PATENT SYSTEM.

The laws regulating the protection of intellectual property in the German Empire are of relatively recent date. Previous to 1870, some of the many Kingdoms and petty states, forming now the modern German Empire, had special laws to that effect. However, all these laws proved to be rather ineffective in view of the relatively small extent of each individual state. Only the peace of Frankfurt, which established the national unity of Germany, removed this condition of affairs, which had for so many years handicapped technical and scientific progress in Germany. The new constitution expressly provides that the protection of industrial property is under the jurisdiction of the Empire. Since then, a series of broader laws has come into force, among which the patent-law is undoubtedly the most important one. This law has had a predominant influence upon the unprecedented rapid development and high standard of German industries. The number of native and foreign inventors applying for patents, increases from year to year; it is a noteworthy fact that among foreign applicants, *American inventors predominate*. It may, therefore, not be without interest, for Americans, to know the broad outlines of the principles and rules of practice and procedure of the German Patent Law.

In Germany, a patent is regarded to be equivalent to a promotion of national knowledge by the disclosure of a heretofore unknown art. The inventor is judged to be a kind of teacher to the nation. Therefore, the Patent Office does in no way care for the real father of an invention. To the first applicant is allowed the patent, and lack of first and true inventorship does not invalidate or bar the grant of a patent unless the invention has been fraudulently obtained, or stolen. If in this case, the person from whom it was stolen files an opposition at the proper time, or starts an annulling suit against the granted patent, the patent is refused or annulled. Moreover, under certain conditions, a fraudulent patentee may be compelled, by a lawsuit, to assign the patent, or even the patent application to the original owner.

This broad principle regulates easily the status of persons who have actually carried out the invention previous to a patent application by another, as well as the question of interfering applications: Such persons are not affected by the patent, for they have not been instructed by the inventor; in other words, they have not derived any new or useful knowledge by the disclosure of the patent. Therefore, they have a legal right to use the patent for their own business, but this right can only be assigned to others, together with the transfer of their whole business. In other terms, they are entitled to a limited free license. Patents filed later on for the same subject matter, for which a former application was filed, are simply refused, if the earlier application results in a patent. So all the interfering applications are rejected in favor of the first applicant, even if they are based on inventions that have been conceived at an earlier date. This, of course, stimulates inventors to apply for a patent without delay, and gives the public the benefit of early disclosure; it excludes expensive and complicated interference proceedings, and prevents applications from being kept pending in the office, for endless years, as frequently happens in the United States. It, furthermore, prevents anybody engaged in a business which is based or not on patents, being threatened at any time with unexpected destruction of business, on account of some hidden or creeping patent applications which, several years later, develop into interference proceedings.

Every application for a patent is examined by an examiner just as in the United States, and substantially along the same lines; on the average, the requirements as to inventive quality are more rigid. If an application is in the proper shape, and patentable according to the examiner's opinion, he forwards it to a Board of Examiners for a preliminary decision. If the Board of Examiners, which is composed of at least three examiners, judges that the invention is not patentable, they reject the application, in about the same way as in the United States. Otherwise, they issue the so-called decision of publication; that is to say, they apply for a supplementary public examination by publishing the title, filing date, name and residence of the applicant in the "Reichsanzeiger," or official journal. Numerous technical periodicals reprint this publication for their readers, and thereby inform the public that the Patent Office is about to grant a patent on the published invention.

At the same time, the drawings, models, specification, and claims are rendered available to public inspection for a period of two months. During that time, anybody can file a written opposition against the grant of a patent. In this way, the inventor, as well as the public, is guarded against the issue of invalid patents. Anybody, in any part of the world can file such an opposition without any costs. The law prescribes only that the opposition be filed in German language and before two months and that it embody the necessary argument. In this way, no individual who can show that the grant of the patent is unjustified is withheld from formulating his arguments, unhampered by any other formality than the mere writing and stating of the argument,—all this without the necessity of passing through the intermediary of an attorney. Opponents who file their opposition too late are not considered in the further proceedings, though their information may be given consideration by the examiners in their final decision.

If no opposition has been filed within a two months' period, the Board of Examiners issues a second decision by which the patent is finally granted; thereupon the specification is printed and published, just as in the United States.

If an opposition has been filed in due time, the opponent thereby becomes a party of the further legal proceedings. He gets information of all the arguments of the applicant and, *vice versa*, the applicant is kept informed of all opposition arguments and the names of his opponents; after the situation has been cleared up, the Board of Examiners decides whether or not the opposition was justified and whether the patent shall be allowed as presented, or allowed with restricted claims, or refused entirely.

During the whole period of examination, up to the final grant of the patent, the Patent Office can, if it deems it necessary, hear witnesses. However, all testimony is taken by the office itself, or if the witnesses live at distant points, by the courts of justice in that district, at the request of the Patent Office, which prearranges and formulates all the questions to be put before the witnesses. No opponent or applicant can be a witness in his own behalf, nor has he any influence upon the decision of the office, and the latter alone decides what witnesses shall be heard and which not. All these questions are decided by the Board of Examiners as far as the interests of the applicant and the public may require, and no appeal is admitted against such a decision. Furthermore, no costs can be charged by the Patent Office for taking testimony, even if such testimony has to be taken in German colonies or in foreign lands, under the provision of the Convention of The Hague. Taking testimony by lawyers as in the United States, in the presence of a notary public, is unknown in Germany, and depositions of witnesses that are obtained in this way would be without any consideration whatever before the German courts.

This same way of taking testimony is followed in all proceedings whether they be for annulment, for compulsory license, or for revocation, as I shall describe hereafter.

If the grant or rejection of a patent has been agreed upon by the Board of Examiners, every applicant or opponent who feels himself injured by that decision can still file an appeal to the Board of Appeals, composed of five officials. The Chairman of this Board of Appeals is the Commissioner of Patents, or the so-called "Praesident," or in his absence, one of his legal representatives. The Board of Appeals reëxamines the whole case and its decision is final.

The life of a patent in Germany is 15 years, which begins with the day succeeding the filing day. The protection it confers becomes effective on the day of publication of the invention in the Reichsanzeiger; from that day on, the inventor can sue infringers, or the public can start a suit for a compulsory license against the inventor. It is obvious that the effective life of a German patent is therefore always shorter than 15 years, and can be badly shortened by any retardation in the issue of the final decision of allowance. In average, if no opposition is filed, and no other complications are met, about two years are absorbed, until the patent is finally granted. This represents one of the most serious defects of the German patent system, but very probably the next revision of the patent law which can be expected in 1914 will remove this deficiency.

The maintenance of patent rights depends, furthermore, upon the payment of certain yearly taxes, small during the first years, but increasing from year to year, and upon the nonpayment of which the patent lapses without possibility of reinstatement. A patent lapses at once if the patentee renounces to it by written declaration.

Other persons can remove a patent right only by a suit for annulment or for revocation; such suits are brought before the Annulment Board of the Patent Office. This provision represents one of the predominant differences over the American system, inasmuch as no court is entitled to discuss the validity of a patent, as long as the patent has not been annulled by the same Patent Office by which it was granted; the courts have to take the patent as it stands and it is only left to them to interpret it in a broad or narrow sense, if the scope of the claims is unclear.

Fraudulent possession of an invention is always a reason for annulling a patent, if the annulment suit is started by the injured party; suits for annulment on account of lack of invention can only be instituted within the period of five years after publication of the final grant of a patent in the "Reichsanzeiger." After expiration of this term, the patent stands valid and unassailable. Probably this latter provision will be canceled before long, in as far as it has caused many inconveniences and injustices to the public.

Appeals against the decisions of the Annulment Board are not decided by the Board of Appeal, but by the highest court in Germany, the Reichsgericht in Leipzig. In all the legal decisions in patent matters, the "Praesident" of the Patent Office has no other intervention than to act as the Chairman of the Board of Appeals and of the Annulment Board. He is never Chairman of the Board of Examiners, and his other official functions are more of an administrative character, at least as far as patent matters are concerned.

Apart from annulment suits, the Annulment Board and the Reichsgericht decide all the actions for the grant, of a compulsory license, or the revocation of patents. Up to May 1, 1911, a patent could be revoked if it were not worked in Germany, or if, in spite of the offer of reasonable royalties and deposit of a guarantee, the patentee refused the grant of a license, provided such a grant were advisable for the public interest. Influenced by the introduction of the new revocation practice in England, and since a decision of the Reichsgericht in a revocation suit against an American patentee, it was held by the court that by reason of the German-American treaty of February 23, 1909, no American could be compelled to work his patents at all in Germany; it even was decided, if the patent was assigned to an American after the revocation suit had been started, these compulsory working provisions did not apply to him.

Under later provisions, Germany has no longer compulsory working of patents, to whatever nationality the patentee may belong. But any patentee can be compelled by decision of the Annulment Board to grant a license in exchange of payment of reasonable royalties, and deposit of a guarantee, provided such a compulsory license is conducive to the public welfare, all this regardless of the actual working or non-working of the patent by the patentee or other persons. However, it has not yet been decided, and it is doubtful whether, in view of the above-mentioned American treaty, patents which are owned by Americans are met by the new provisions of the law. Revocation of patents on account of non-working is now possible only if the patent is worked exclusively outside of Germany, but even then this does not seem to affect American patentees on account of the existing treaty.

As the courts are not allowed to discuss the validity of patents, a suit against infringers is relatively simple. Unintentional or careless infringers can be sued for damage, but intentional infringers are moreover liable to fine and imprisonment on motion of the patentee or his representatives to the public prosecutor (Staatsanwalt). Preliminary and final injunctions can be issued, or an infringer can be sued first so as to compel him to acknowledge that he actually infringes a patent. On the other hand, a similar acknowledgment suit can, under certain conditions, be started against the patentee, so as to compel the latter to acknowledge non-existence of infringement by another party. The defeated party has to pay the expenses and costs of the winning party. All these infringement suits are decided in open court before civil courts. Upon appeal, they are finally decided by the Reichsgericht, so that practically all the questions of predominant importance are decided by one and the same court. Infringement suits are relatively rare, and by no means so frequent as in the United States. Furthermore, they are considerably less expensive. The time consumed for reaching a final decision in an infringement suit depends, of course, largely upon the complications of the subject matter, the necessity of making experiments, etc. Most of the courts in industrial districts in Germany have special departments to which are assigned all cases concerning the protection of patents and of intellectual property in general.

Herbert F. Wertheimer.

ORIGINALITY OF INVENTIONS.

Patent Law Reform is at present the subject of discussion in several foreign countries as well as in the U. S. The German Scientific Societies' Journals are full of criticisms and suggestions for improving the present status of the patent law. It should be interesting to Americans to watch the situation abroad as the American and the German Patent Laws are the best national laws to guarantee the rights of the inventor and to stimulate the progress of industry. The highly developed state of industry in both of these countries is the best proof that their Patent Laws rest on a sound basis.

Comments on the U. S. Patent Law by our leading inventors have shown that it is largely in matters of appeals, interferences, infringements and the like proceedings where reform is urgently needed. One extremely important complaint about the U. S. Patent Office has been overshadowed by the discussions and suggestions in regard to a U. S. Patent Court of Appeals.

American inventors who have had experience with German patents are usually much pleased with the strict impartiality and business-like methods of the German Patent Office in up-holding the rights of the inventor upon protests against final allowance of the patent. This is only conditional up to the publication as prescribed by the German Law analogue to our publishing of applications for trade marks.

The one point alluded to above represents a shortcoming peculiar to both the American and German Patent Practice. Our information indicates that German inventors have to suffer just as much from certain Patent Office proceedings as the American inventor. The rock on which the hopes of many an inventor with a meritorious proposition are wrecked is the examiner's decision:—*Lack of novelty, or lack of invention.* Such a decision dooms nearly any application to an untimely death, for on appeal the examiner's opinion is usually sustained.

It has recently been amply shown that the examiners and the staff of the U. S. Patent Office are altogether too overburdened with work to make a very far-reaching search of the prior art, and that they very often, after finding some prior patents, give the same such a broad interpretation as to negative a new application. These shortcomings have been very heavily felt by the American industry for it happens relatively often that a patent is denied because in view of some former often irrelevant arts the examiner denies the application the dignity of invention. Just such "microscopical" inventions, for which protection by patent letters was denied or could be obtained only under great difficulties, have later on become splendid industrial successes. We hope that such inventions may find salvation with the future U. S. Patent Court of Appeals, where any party aggrieved by adverse decisions may have due redress.

Things are similar in Germany. The very same trouble in overcoming the resistance of the examiner to applications apparently bare of inventions was lately the matter of many and hard complaints at the meeting of the Berlin Section of the Association of German Chemists. We learn from the *Zeitschrift fuer angewandte Chemie* (March 29, 1912, pages 636–7) that several speakers severely criticized the Examiners of the German Patent Office especially for reading too much between the lines and for incorporating into literature certain information from a new application, thereby interpreting said literature in a broad sense which never would be done by an unprejudiced reader without knowledge of the new application. The practice of combining several quotations from literature by a certain order of reasoning in order to prove existence of the subject matter previous to the new application was also clearly pointed out. Much complicated reasoning and quibbling is often resorted to which more than anything else is sufficient proof of invention in behalf of applicant. Some other complainants pointed out that the requirements of the German Patent Office for "originality" of invention are too far reacting in view of the present high development of industry. For this reason most inventors can only submit improvements of the present art, such improvements being entitled to protection if they bring the art nearer to the goal of perfection. A high official of the German Patent Office was present at this meeting and was in a rather tight place for the tone of the complaints was rather bitter.

The same complaints must be made against the American Examiner. It may be said in behalf of both the American and German Patent Examiners that the severe standpoint in adjudging new applications is taken with the best intentions for protecting the interests of older patentees but the echo we hear from abroad is another proof that this shortcoming is really existing to the chagrin of inventors and that we should strive for proper means to repair a too broad interpretation of the prior art as detrimental to the justifiable claims of an inventor.

Suggestions to this effect were lately made in Germany, and it is interesting to note that one of them consisted in recommending the provision of funds to send every Examiner and the Sub-Examiners of the staff once in two to three years on a six weeks' tour for inspecting industrial works. He would then gain thorough information about the latest developments of industry, and get a better view on the exigencies of business by making the personal acquaintance of the men who keep things moving.

REPORT OF THE DELEGATE TO THE JOINT CONFERENCE ON THE PATENT SYSTEM.

The Committee delegated to attend the conference on the Patent System held in Washington, April 15th and 16th, attended the conference and advocated the appointment of a Board of Experts to which all matters relating to Patent Legislation should be referred for report before action is taken by Congress in formulating and enacting changes in the present laws governing the issuance, scope and regulation of patents.

After consideration and discussion of the various bills now before Congress the following report was agreed upon by the Informal Joint Conference.

INFORMAL JOINT CONFERENCE.

At a meeting of representatives from the following associations held at Washington on the 15th and 16th of April, 1912, over forty bills affecting the patent system of the United States were considered to such extent as time permitted. Many of these bills are obviously of a radical character—aimed at fundamental principles of the patent system—and others deal with such complicated matters as Patent Office procedure and practice.

After extended discussion, in view of the importance of careful consideration of the said bills, to the end that the patent system of the United States, to which in so large a measure our industrial prosperity is due, may not be unduly affected, it was unanimously resolved that the representatives of the several associations there represented agree to recommend to their respective associations:

(1) That the committee of Congress be respectfully urged to defer action on said bills until the associations represented at the conference, and the public generally, have had ample opportunity to study the bills and determine what may be the full effect of the changes contemplated by them.

(2) That a recommendation be made to the respective associations to appoint members of a joint Standing Committee with power, subject to the call of the Chairman of the Patent Law Association of Washington, to study the pending bills and the whole patent situation and adopt means for such action as may appear expedient.

Subsequently, the conference, to carry out the purpose of the concluding clause of the preceding resolution, unanimously adopted the following:

RESOLVED: "That the associations here represented, and such associations as shall be hereafter added thereto, shall appoint, each, three delegates, each association to have one vote, and that a committee, consisting of Mr. Rogers, Dr. Baekeland and Mr. Mershon, shall be appointed, which may add at its discretion associations and members to meet in future joint conferences."

AMERICAN CHEMICAL SOCIETY.
AMERICAN ELECTROCHEMICAL SOCIETY.
AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.
AMERICAN INSTITUTE OF MINING ENGINEERS.
AMERICAN SOCIETY OF MECHANICAL ENGINEERS.
CHEMISTS' CLUB OF NEW YORK.
INSTITUTE OF CHEMICAL ENGINEERS.
INVENTORS' GUILD.
PATENT LAW ASSOCIATION OF CHICAGO.
PATENT LAW ASSOCIATION OF WASHINGTON.

New York County Lawyers' Association and Non-resident Members Patent Law Association of Washington.

The various organizations were represented as follows:

American Chemical Society.—Clinton P. Townsend, Washington; Professor Charles E. Munroe, Washington.

American Electrochemical Society.—Dr. L. H. Baekeland, Yonkers, N. Y.; A. B. Marvin, Marquette Bldg., Chicago.

American Institute of Electrical Engineers.—A. W. Berresford, Milwaukee; F. P. Fish, Boston; Dugald C. Jackson, Boston; M. I. Pupin, New York.

American Institute Mining Engineers.—Capt. A. F. Lucas, Washington.

American Society of Mechanical Engineers.—W. H. Blauvelt, Syracuse, N. Y.; B. F. Wood, Altoona, Pa.

Chemists' Club of New York.—Carleton Ellis, New York.

Institute of Chemical Engineers.—Dr. Wm. M. Grosvenor, New York; Maximilian Toch, New York.

Inventors' Guild.—Ralph D. Mershon, New York; H. Ward Leonard, New York.

Patent Law Association of Washington.—Walter F. Rogers, Washington; William W. Dodge, Washington.

Patent Law Association of Chicago.—Thos. F. Sheridan, Chicago.

New York County Lawyers' Association and Non-resident Members Patent Law Association of Washington.—Wm. H. Kenyon, New York; Alfred W. Kiddle, New York; E. W. Bradford, Washington and Indianapolis; Robert C. Mitchell, New York; Odin Roberts, Boston; George O. G. Coale, Boston.

Yours very truly,
Charles E. Munroe, *Delegate.*

REPORT OF THE COMMITTEE ON QUANTITATIVE METHODS.

During the past six months your committee has done some work on volumetric and gravimetric methods of assay for the various zinc salts official in the Pharmacopoeia, and begs to submit herewith a report of this work together with a bibliography of various articles dealing with the quantitative estimation of zinc which have appeared from 1890 to the present date.

The results of co-operative work on zinc assays follow and comments of the various members of the committee are appended to this report.

The gravimetric method was referred to in report of July last and is the well-known Ammonium Phosphate Precipitation Method. The volumetric method is that published by E. Rupp, *Chemiker Zeitung,* 33, 3 (1909), which is as follows:

"Prepare a solution of the zinc salt containing the equivalent of 0.1 gram of metallic zinc, using dilute sulphuric acid to make the solution if necessary, as with zinc oxide, and subsequently exactly neutralizing the solution with $N/1$ NaOH. This solution should measure about 10 cc.

"Dilute exactly 20 cc. of approximately 5 per cent. solution potassium ferrocyanide to 50 cc. with water and dissolve in this 5 grams of potassium sodium tartrate. To this solution add the zinc solution and let stand for 30 minutes, in order that the zinc ferrocyanide as precipitated may be transformed into potassium zinc ferrocyanide.

"Now add 30 cc. of $N/10$ I and let stand for one hour whereby the excess ferrocyanide is converted into ferricyanide quantitatively. Titrate the excess $N/10$ I with $N/10$ sodium thiosulphate.

"At the same time a blank test may be run in exactly the same manner, omitting the zinc solution so as to determine the iodine value of the potassium ferrocyanide solution. The difference between the amount of iodine consumed as an oxidizing agent in the blank and that consumed in the actual assay corresponds to the quantity of zinc present:

$$3\text{Zn} = 2\text{I}.$$

$$0.00981 \text{ gm. Zn} = 1 \text{ cc. } N/10 \text{ I.”}$$

Zinc Estimations.

Volumetric.		Gravimetric.	
Zinc oxide. Per cent.	Zinc phenolsulphonate. Per cent.	Zinc oxide. Per cent.	Zinc phenolsulphonate. Per cent.
Mr. Briggs.			
97.54– 97.54 99.84–101.29	103.12–102.14	98.9 98.2	99.3 99.2
Av. 99.05	Av. 102.63	Av. 98.55	Av. 99.15
By using more for assay.			
96.5 – 96.9	91.8 – 92.6		
Av. 96.7	Av. 92.2		
Mr. Engelhardt.			
Standing 1 hr. with $N/10$ I. Per cent.		As NH_4ZnPO_4. Per cent.	As NH_4ZnPO_4. Per cent.
100.5 –104.8 101.7	No proper results could be obtained with this salt.	101.2 –100.9 100.1	101.6 –101.6 101.6 –102.1
Av. 102.33		Av. 100.73	Av. 101.7
Standing over night.		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
97.9 – 98.2		99.5 – 99.9 99.6	100.01–100.03 100.05–100.2
Av. 98.05		Av. 99.73	Av. 100.08
Mr. Brown.			
Per cent.		As NH_4ZnPO_4. Per cent.	As NH_4ZnPO_4. Per cent.
92.54– 97.13 96.53– 99.4 100.53– 97.89 98.95	No satisfactory results.	99.99–100.29 99.86–100.12	100.4 –100.71 98.16– 97.73
Av. 97.56		Av. 100.06	Av. 99.25
		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
		99.51–100.03 99.40– 99.60	100.09–100.45 97.12– 96.68
		Av. 99.63	Av. 98.58
Mr. Taylor.			
Per cent.		As NH_4ZnPO_4. Per cent.	
101.1 – 98.58 98.77– 98.58	No reliable results obtained.	100.73–100.95	
Av. 99.23		Av. 100.88	
		As $Zn_2P_2O_7$. Per cent.	As $Zn_2P_2O_7$. Per cent.
		99.95–100.16	99.34–99.18
		Av. 100.05	Av. 99.34–99.04

Mr. Briggs: "The Gravimetric Method is more accurate and preferable."

Mr. Engelhardt:

As to the Volumetric Method, says: "This method, although somewhat shorter than the Precipitation Method, gives unreliable results when carried out according to instructions."

As to the Gravimetric Method:

"This method which is used exclusively in the laboratory here works very well. I prefer estimating the zinc as pyrophosphate, although if the precipitate of the ammonium zinc phosphate is washed thoroughly as directed, the results are too high, probably due to the presence of ammonium phosphate.

"The high results obtained with the zinc phenolsulphonate may be due to the salt having lost some of its water of crystallization."

Mr. Brown: "The Volumetric Method does not appear to be reliable. This objection may be removed by a further study of the method, allowing more time for the reaction between the iodine and ferrocyanide to take place, also to determine whether the reaction proceeds better in a neutral solution slightly acid or strongly so, etc."

"The Gravimetric Method: "It appears to be very satisfactory in point of accuracy and speed. However, I think the amount of wash water called for in the method is entirely too much as there are no difficultly soluble salts to wash out and such a large volume of wash water dissolves an unnecessarily large amount of the precipitate.

"There appears to be a slight loss of zinc on ignition to the pyrophosphate. I think more work should be done along this line to determine whether this is true, also to determine whether more accurate results are to be obtained by weighing as the zinc ammonium phosphate or as the pyrophosphate."

Mr. Taylor: "The Volumetric Method gives fair results with zinc oxide but requires a larger sample than given in the assay processes used to be at all sure of results. Four assays by this method on the phenolsulphonate give results about one-fourth of the theoretical for no apparent reason. The method is entirely unsatisfactory for this salt, and because of the fact that the least variation in the results makes a considerable difference in the percentage of the zinc salts found, the method is not desirable."

"The Gravimetric Method is almost as rapid and decidedly more accurate than the Volumetric Method, and it seems preferable to estimate directly as pyrophosphate. The entire assay can be run within a period of three hours, and on the whole it seems that this is the most desirable method for the assay of all zinc salts."

The high percentage obtained on the zinc oxide by most of the members of the committee is probably due to the distinct trace of some calcium salt, evidently the carbonate present in the zinc oxide sample which was sent out. This, of course, does not show in the solubility of the zinc oxide unless sulphuric acid is used for its solution as directed.

The chairman of the committee would suggest for the consideration of the division during the next six months or year, if necessary, a very careful survey and testing out of methods of assay for capsicum and cantharides be taken up by the committee as two substances of considerable interest for which there is neither a standard in the Pharmacopoeia nor a method assay. If, however, the division prefers the committee to continue in exactly the manner that has been done on the zinc and mercury salts, we shall be glad to follow out these instructions.

Respectfully submitted,

Linwood A. Brown,
C. H. Briggs,
H. Engelhardt,
L. D. Havenhill,
B. L. Murray,
A. P. Sy,
Frank O. Taylor, *Chairman.*

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THE TECHNICAL ANALYSIS OF BRASS AND THE NON-FERROUS ALLOYS: AUTHOR'S NOTE.

Editor of the Journal of Industrial and Engineering Chemistry:

My attention has been directed to a review of "The Technical Analysis of Brass and the Non-ferrous Alloys," which appeared in the March number of your excellent Journal. This review contains so many misleading statements and shows evidence of such careless reviewing that I am forced to call attention to the same.

First.—In discussing the first part of the book, in which it is stated that "it is liable to confuse the reader when he finds two entirely different analysis of, for instance, Delta metal," I am unable to see how any reader could be confused, in view of the fact that one Delta metal is placed in Table No. 1, dealing with bearing metals, while the other Delta metal is placed in Table No. 3, under foundry and rolling mill alloys. One would not be likely to take a metal containing 92.4 per cent. copper to be one and the same with an alloy containing 55.94 per cent. of copper.

Second.—The reviewer states: "The authors do not mention the fact that precipitates of the hydroxides, especially if precipitated by ammonia, are almost certain to contain silica, and often phosphoric acid, in sufficient quantity to cause serious error." In this connection, the reviewer evidently speaks from the standpoint of iron and steel, as brass and the general run of non-ferrous alloys contain such minute quantities of silica, that they would have no effect on the accuracy of the determination.

Third.—The statement, "under lead they advise washing the precipitate of sulphate with a mixture of water, sulphuric acid and alcohol; this is apt to give high results, as few sulphates are readily soluble in alcohol. The precipitate should first be washed free from sulphates with dilute sulphuric acid, and after this has drained off, with alcohol." If these directions were carried out, lead results would be low, as lead sulphate is soluble in dilute sulphuric acid, and it is for this very reason that the alcohol is added to render the lead sulphate insoluble, and it has been repeatedly shown that the solubility of the copper and zinc sulphates, after having been dissolved in hot water, are not effected by the amount of alcohol used in the washing solution as recommended.

Fourth.—"For the volumetric determination of manganese, they give the old Williams method, apparently not knowing that it has been shown that it is incapable of giving correct results as the precipitate is not MnO_2 but a lower oxide. They also give the method of Metzger and McCrackan but do not give the Volhard method which most analysts have found the simplest, quickest and most accurate." While the Volhard method, it is true, may be superior to the Williams method for iron and steel, for the analysis of brass and the non-ferrous alloys, the combined Williams and Ford method, as described on page 103, has been found to be vastly superior to the Volhard method. Two of the largest brass laboratories in the country are using the Williams and Ford method in preference to the Volhard, after having made a long series of tests with both methods.

Fifth.—"They advise the use of aluminum for the reduction of iron, but do not mention that commercial aluminum usually contains enough iron to cause a serious error." More careful reviewing would have made it evident that the authors specifically mention this fact under Iron, page 83, line 1: "To the solution in the six-oz. flask, add 2 grams of pure aluminum sheet or drillings. Weigh this fairly accurately, as *all aluminum contains a little iron which must be deducted from the total iron found*," and, again, on page 84, line 8: "A small correction must be applied to the burette reading to allow for the amount of permanganate used to produce a pink tint in a blank solution containing the same amount of aluminum and the same amount of acids and water used but without any iron wire." "Dissolve two grams of aluminum, etc.;" "Subtract the correction thus obtained from every burette reading."

Sixth.—"In the description of the volumetric method for zinc, they do not lay enough stress on the necessity of keeping all conditions uniform. Variations in the temperature, acidity, and amount of ammonium chloride present, all affect the end point." In this connection, it did not seem necessary to burden the reader with all of Waring's different experiments and results connected with the temperature, acidity, and amount of ammonium chloride present, especially as the amounts of hydrochloric acid, ammonium chloride and temperature, as given on pages 141 to 145, inc., are exactly the same as the conditions given by Waring to insure accurate results after he had investigated the effect of temperature, acidity, and amounts of ammonium chloride on the end point.

It is to be regretted that this book could not have been reviewed with more care. WM. B. PRICE.

SCOVILL MANUFACTURING CO.
May, 1912.

VOLATILITY OF METALS OF THE PLATINUM GROUP.

During the reading of a paper on "The Volatility of Metals of the Platinum Group," read before the members of the British Royal Society in March, Sir William Crookes narrated some observations which indicate that platinum is not so entirely fixed at temperatures well below its melting point as has been universally accepted by chemists and physicists.

In using an electric furnace consisting of a coil of platinum ribbon contained in a porcelain tube he found that in time the ribbon grew thinner till it melted at the weakest part. When that happened he noticed that the porcelain tube was coated with a fine dust of beautifully formed crystals of brilliant metallic luster, which on analysis proved to be platinum. It therefore seemed of interest to subject a platinum crucible to a temperature approaching that to which the platinum resistance coil had been exposed. A crucible was heated to 1,300° C. in the electric furnace for 30 hours when the loss of weight amounted to 0.245 per cent. Palladium, treated in the same way, lost 0.745 per cent. in 30 hours. An iridium crucible lost over 7 per cent. in weight after 22 hours at 1,300°, and at greater heat, loss of weight for equal periods of time was proportional to temperature. After this severe treatment, the crucible, which had taken on a crystalline appearance over the whole surface when the series commenced, began to show disintegration along its edges and pieces began to crumble when touched with the forceps. With rhodium, a metal intermediate in fusibility between platinum and iridium, the loss in 30 hours was 0.13 per cent., not far from that of platinum.

Experiments were then made at 900° by heating the metals in a flame of a good Méker burner. Platinum and rhodium after heating for 20 hours showed no loss of weight, but palladium in 10 hours lost 0.0919, and iridium in 20 hours lost 0.091 per cent.

In an experiment to see whether iridium would volatilize at a high temperature in a vacuum, a fused silica tube had a bulb blown on the end. In the bulb were put 27.619 grains of clean iridium; the other end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length till all moisture and occluded gases had been removed; it was then sealed off, and placed in the furnace in such a position that the iridium would be at the point of greatest heat. The bulb was kept at a temperature of 1,300° for 30 hours. On examining the silica tube when cold it was seen that the long-continued high temperature had caused the bulb and the upper part of the tube to devitrify and become white and translucent and that it had an irregular black deposit on the lower part, which proved to be metallic iridium.

LONDON, March 13, 1912.

CHEMISTRY AND THE LITHOGRAPHIC INDUSTRY.

Editor Journal of Industrial and Engineering Chemistry:

The article in the January number by Mr. W. H. Watkins strongly appealed to the writer, who may be classed as a chemist in one of the industries in which "there are almost no chemists." A few years ago my attention was directed to the lithographic industry as one involving chemical processes to a large extent. These processes, almost without exception, had developed by rule-of-thumb methods and were entirely without technical control. A given operation would be successful one day and unsuccessful the next, depending on the "luck" of the operator.

After carrying on research work for some time to convince myself that the rule-of-thumb man was not always correct in his methods and deductions, I laid some of the laboratory results before a lithographic firm for its consideration. The work of demonstrating the advantages of chemical control in this particular line of manufacture, although somewhat slow at the beginning, was eventually convincing. A laboratory was installed in the plant, and actual work begun. Changes were made in the processes one after another. Not only in the testing of raw materials but more especially in modifying some of the time-honored practices, the work met with considerable opposition from the "practical" man who had done it the old way for so many years. The attitude of some of the men concerned in these changes was well described by Mr. A. D. Little in his recent lecture on "The Earning Power of Chemistry." They certainly took no pains to conceal their "militant skepticism." To-day this laboratory, with its system of control, is an integral part of the factory and is regarded as one of the essential departments.

It is of the utmost importance in work of this character for the chemist to familiarize himself as rapidly and as completely as possible with the details of the manufacturing processes. While often wrong from the standpoint of the theory-shrouded technical graduate, the practical man may be nearly correct as far as he goes, but the chemist, or chemical engineer, can investigate the problem more thoroughly and by properly classifying the data at his disposal obtain the desired results. The work of both these men can be materially lightened by consistent coöperation. In the lithographic industry, as well as in industries where chemists are more generally employed, the chemist should bear in mind that in addition to his more specific duties he must endeavor to become an efficiency expert. This feature of his work is sure to attract the attention of the manager of the varnish, ink, or paint works, as the case may be, whereas the more technical details would pass unnoticed. Whether it be the mere routine testing of finished products or the perfection of methods for the profitable utilization of waste, the progressive manufacturer is not going to rely upon "the fellow who doesn't know any better." He is realizing more each year the need for technically trained men. Men trained in chemistry should force their way into *new* industries if this "century of chemistry" is to be realized. To use an expression of Prof. Wm. Ostwald, it behooves us to "put more brains into the goods" and into a greater variety of goods, if the chemist's hopes are to end in fruition. B. P. JAGGARD.

SAN FRANCISCO.

CONTAMINATION OF LABORATORY SAMPLES BY IRON DERIVED FROM CRUSHING MACHINERY.

By VICTOR LENHER.

The article by George A. James on the "Contamination of Laboratory Samples by Iron Derived from Crushing Machinery" in *The Chemical Engineer*, 14, 380, Sept., 1911, calls attention to the too often neglected fact that in the preparation of samples for analysis the crushing or grinding apparatus employed may introduce material in such kind and quantity as would render the analysis worthless. Dr. Hillebrand, in *Bull.* 422, U. S. Geol. Survey, p. 50, lays stress on this point. Too much emphasis cannot be laid on the choice of grinding apparatus used in the preparation of samples for analysis. Recently a series of samples of quartzite were collected by the writer for analysis. Inasmuch as the quartzite beds, from which the samples were taken, were being valued for the purpose of being used in the manufacture of silica brick, it was desirable to obtain an accurate determination of the content of silica and particularly of iron.

Sample No.	Metallic iron introduced from crusher. Per cent.	Iron content of quartzite. Per cent.
1	2.92	0.49
2	2.74	0.49
3	2.73	0.23
4	2.61	0.63
5	2.82	0.25
6	2.59	0.29
7	1.86	0.55
8	2.46	0.16
9	2.65	0.75
10	2.67	0.12
11	2.81	0.16
12	1.87	0.06
13	1.98	0.20
14	2.01	0.68
15	2.62	0.11

The samples on being brought to the laboratory consisted of chips of the rocks, approximating in size $^3/_4$ inch square by $^1/_4$ inch thick. After being broken somewhat smaller by means of a hammer, they were reduced in a Braun crusher to pass a 120-mesh screen. The material in the original beds is of a light pinkish cast, while the powdered material was distinctly gray. Tests by the magnet revealed the presence of metallic iron in the powdered quartzite, but owing to the fine state of division of the powder, it was found to be impossible to satisfactorily remove the iron by mean of the magnet.

Treatment of the powder with dilute sulfuric acid and subsequent analysis of the remaining quartzite is shown in the accompanying table.

The variation in the amount of metallic iron abraded from the crusher is, of course, dependent on the length of time of crushing.

It is interesting to note in connection with the above results that a similar set of samples were sent to one of the largest iron laboratories in the northwest, and reports were made showing an apparent iron content of the quartzite to be from 1.42–2.97 per cent. iron.

It has been the frequent experience of the writer in the analysis of igneous and metamorphic rocks to find the sample contaminated by iron from the bucking board, crusher, or such grinder as may have been used in reducing the sample. As a rule this metallic iron can be removed and at the same time determined by treatment with dilute sulfuric acid and subsequent titration with permanganate. As a matter of fact, the more common material which will materially abrade iron or steel in crushing is not appreciably attacked by dilute sulfuric acid during the few minutes contact that is requisite to dissolve the finely divided iron. On the other hand, the general type of ores and products, which will themselves lose part or all of their iron to dilute sulfuric, will not appreciably abrade steel from the types of grinding apparatus on the market.

It cannot be too strongly emphasized, however, that the chemist is called upon to report on the constituents sought for, and when the common danger of contamination in the preparation of his sample presents itself, great care must be exercised to eliminate such errors.

UNIVERSITY OF WISCONSIN,
MADISON.

COMBATING MINERS' DISEASES.

An arrangement has been made with the Public Health and Marine Hospital Service by which one or more surgeons connected with that service will carry on jointly for that service and for the Bureau of Mines investigations looking to the improvement of mine conditions. These inquiries and investigations have already shown the prevalence of tuberculosis and hookworm as miners' diseases in a number of different localities in the United States. It is important that this work should be extended more rapidly, because of the fact that the health conditions, as well as the risk of accidents, may be influenced by conditions susceptible of easy improvement. Furthermore, the large and continuous influx of foreigners into the mining regions of the United States will bring to an increasing extent the hookworm and other diseases that abound in mines in parts of certain European countries.

Various questions that concern the health of workers in mines, quarries, and metallurgical plants can not be answered finally without investigations and inquiries that are national in scope. Among such questions are the most efficient methods of preventing the diseases peculiar to certain industries, the most effective sanitary precautions to be observed in and about coal mines and metal mines, and the relative healthfulness of occupations pertaining to mining and metallurgical industries. The investigations and inquiries that are essential to the gathering of reliable information on these questions can be undertaken by the Bureau of Mines, in connection with its collection of accident statistics, in a prompt and efficient manner and at minimum expense.

BOOK REVIEWS

Strength of Materials. By S. E. SLOCUM AND E. L. HANCOCK. New York. Ginn & Co. Revised edition. 1911. xxxvi + 372 pp. Price, $3.00.

The present volume is a revised edition of a previous publication appearing in 1906. It consists of two parts dealing with Mechanics of Materials, Part I, 262 pages, and Physical Properties of Materials, Part II, 110 pages.

The subject matter of Part I relates to the elastic properties of materials, the evaluation of and relation between the elastic constants, stress distribution in straight and curved beams, under different systems of loading and support, columns and struts, shafting, thick and thin cylinders, flat plates, springs, hooks, arches of concrete and masonry, foundations and retaining walls. A most rigid and satisfactory analysis is applied to each of the above cases, and comparisons with less rigid analyses are given, to the end that a study of the text will enable one to clearly understand the fundamental and complex relations of stress and strains in a wide range of formulative conditions. A number of problems at the close of each chapter are helpful to an appreciation of the extent to which the theories are applicable.

Part II relating to the physical properties of materials is given to the reports of experiments on engineering materials of which are selected: Iron and steel of varying compositions and heat treatments, lime, cement and concrete, brick and building stone, timber, rope, wire, leather and rubber belting. From these experiments are derived the constants and relations necessary to a quantitative treatment of the preceding part of the text.

Throughout the whole text many references to original sources and more extensive treatments are given.

The notation is very consistent. The printing, illustrations and binding are all that could be desired.

WALTER RAUTENSTRAUCH.

Fertilizer and Fertilizer Hints. By JAMES EDWARD HALLIGAN. 155 pages. 11 illustrations. The Chemical Publishing Co. 1911. Price, $1.25.

This book is an abridged edition of the author's "Soil Fertility and Fertilizers." The author has succeeded well in his endeavors to produce a volume which will be within the reach of the farmer, student or other persons interested in the subject of fertilizers.

The different subjects are only briefly discussed and yet by reading this volume one can get a very clear understanding of the usually accepted views concerning soil fertility and the composition and functions of fertilizers.

The work is divided into fifteen chapters as follows:

Chapter I: Chemical Elements needed by Plants and the Composition of Plants.

Chapter II: The Fertility of the Soil.

Chapter III: Maintaining Soil Fertility.

Chapter IV: Farm Manures.

Chapter V: High-grade Nitrogenous Materials.

Chapter VI: Low-grade Nitrogenous Materials and Functions of Nitrogen.

Chapter VII: Phosphates.

Chapter VIII: Superphosphates and Effect of Phosphoric Acid.

Chapter IX: Potash Fertilizers.

Chapter X: Miscellaneous Fertilizer Materials.

Chapter XI: Lime, Gypsum and Green Manures.

Chapter XII: Commercial Fertilizers.

Chapter XIII: Valuation of Fertilizers.

Chapter XIV: Home Mixtures.

Chapter XV: A Few Remarks about Fertilizers.

In addition to the subject matter indicated by the index, there are many tabulations giving valuable data with reference to the composition of different farm products, etc.

The book is a useful one as a brief general treatise on the subject and is well adapted for the purpose which was intended.

F. B. CARPENTER.

Die Chemie der Cellulose with Particular Reference to the Textile and Cellulose Industries. CARL G. SCHWALBE, Ph.D., Berlin. 1911. 2nd half, 8vo. 392 pp., with preface and index to complete work.

The second half upholds the excellent standard of the first. It contains the consideration of the esters of cellulose, probably not as much in detail as the author's intimate knowledge of the subject might lead one to expect, but undoubtedly as comprehensively as the space prescribed to it permits.

The general consideration of cotton cellulose (I) is concluded by reference to its decompositions, its constitution and its colloidal character. Under II is considered natural compound celluloses, the ligno-celluloses, the pectocelluloses, mucocelluloses, cuto- and adipocelluloses, and peat and humus. Section III treats of the technical manipulation of the plant sources of compound celluloses, subdividing the subject into lignocelluloses and into pectocelluloses; and Section IV deals with different forms of cellulose so prepared. Under Section V is briefly described and considered mercerization, artificial silk manufacture, rag cooking, and manufacture of parchment and vulcanized fiber. The concluding section (VI) is on analytic methods of cellulose chemistry and is subdivided into qualitative and quantitative analysis.

The entire work is a distinctly useful contribution to the literature on cellulose and its chemistry. H. S. MORK.

Chemiker Kalender. By DR. RUDOLF BIEDERMANN. Thirty-third year. In two volumes. Vol. 1, pp. 400; Vol. 2, pp. 641. Berlin: Julius Springer. 1912. Price: Cloth, M. 4.40; leather, M. 5.40.

The universally-known Chemiker Kalender now in its thirty-third year appears for 1912 with the number of pages somewhat augmented and with the very distinct advantage of having both volumes bound. Instead of naming the second part of the work "Beilage" as in former years it is now simply Volume 2 of the Chemiker Kalender, which is quite satisfactory. Vol. 1 now has 400 pages instead of 389 as in 1911 and Vol. 2 has 641 pages instead of 608. The regular increase from year to year indicates that this most useful work is constantly in a state of active revision and is not permitted by its author and editor to fall behind the times. A useful extension for future years would be the addition of more equilibrium diagrams and tables for water-salt solutions to replace in part or extend the present solubility tables in Vol. 1. W. D. RICHARDSON.

The Manufacture of Varnishes, and Kindred Industries. By J. G. MCINTOSH. Three vols., 1904, 1908, 1911. pp. 153, 209, 482. Scott, Greenwood & Co. Price, Vol. III, $4.50.

This book is said to be based on and to include Livache's "Drying Oils and Varnishes"; in fact, McIntosh originally published what was practically a translation of Livache, a book of no great interest to the English-speaking public; but the present book is by McIntosh: readable, more than fairly accurate, and full of good sense and practical knowledge.

Vol. I is on linseed oil; from a technical standpoint it is not equal to Ennis' book though, as it shows English practice instead of American, it may be regarded as supplementary to that; but as a chemical book it is by far the best on the subject.

The common and commercially important (at least in America) method of bleaching oil with Fuller's earth is nowhere mentioned, nor the "break" of raw oil, which is one reason for refining; but it gives much historical matter and European practice up to the date of publication, as well as considerable analytical and other chemical data.

Vol. II is on oleo-resinous varnishes, and contains especially much apparently accurate information about amber and copals, not to be found elsewhere, so far as the present writer's knowledge extends; it includes recent German and French investigations. The part on varnish-making contains much good historical matter, and European experiments.

Vol. III is on spirit varnishes, and is complete and up to date. It has a large amount of data on resins as well as solvents, and is the most satisfactory treatise yet published on the subject. It is better than either of the other volumes, because larger and fuller. A. H. SABIN.

Technical Methods of Chemical Analysis. By DR. GEORGE LUNGE and many others. English translation by Dr. Charles A. Keane, with a large number of collaborators. Vol. II in two parts. Part I, pp. xxvii and 610; Part II, pp. xii and

611 to 1252. New York: D. Van Nostrand & Co. 1911. Net price, $18.00 set. Not sold separately.

Analytical and technical chemists will welcome this English translation of the latest (6th) edition of Dr. Lunge's well-known work. The earlier German editions of Dr. Lunge's "Technical Methods" have been in use by chemists so long that it is unnecessary to go into the merits of this excellent work at this time, except to indicate its scope and list the material embodied in this volume.

To quote from the translator's preface, "The sections comprised in this second volume of the English edition are included in the second and third volumes of the new German edition which is being issued in four volumes." Again, "The section on Organic Dyes from Vol. IV of the German edition has been included in this volume, as it forms a suitable sequel to the section on Coal Tar."

The topics covered in Part I are: Iron, Metals other than Iron (including 22 of the more important metals), Metallic Salts, Artificial Manures, Feeding Stuffs, Explosives, Matches and Fireworks, Calcium Carbide and Acetylene.

In Part II are found: Illuminating Gas and Ammonia, Coal Tar, Synthetic Organic Dyes, and Naturally-occurring Organic Dyestuffs. Numerous references are given throughout the book, and at the end of each section, under the heading "Literature," is a well selected list of the important books dealing with the subject.

It is impossible, even in a work of this size, to give all of the methods of analysis which might be considered as good, and the authors are to be complimented on the selections they have made. The subject matter has been brought up to date remarkably well.

The appearance of this work in English will undoubtedly greatly extend its field of usefulness, and give it the recognition it so fully deserves. F. J. Metzger.

Cocoa and Chocolate, Their Chemistry and Manufacture. By R. Whymper. 327 pages. P. Blakiston's Son & Co., Philadelphia. Price, $5.00 net.

The present volume, divided in 3 parts, describes the agricultural, technical and chemical sides of the cocoa and chocolate industry.

In the first part of the book the history and development of the industry are reviewed, the botany and nomenclature discussed, and the agricultural operations of planting, pruning, picking, fermenting, and preparing the cocoa beans described.

In the second division of the work the manufacture of chocolate and cocoa powders from the raw beans is taken up. The operations of cleaning, roasting, nibbing, milling, etc., are described, and details given for the manufacture of plain, milk, and fancy chocolates and numerous cocoa preparations.

In the third part of the volume a comprehensive survey is taken of the composition of cacao and its preparations; methods for their analysis are described. The chemical data are very complete and as the author states: "For the first time the chemical composition of cacao has been traced from the fresh bean through various stages of manufacture, so that the changes which occur during fermentation, drying, roasting, etc., may be followed. The most recent methods of analysis have been discussed, and the author has only recommended those which he himself has found to give accurate and consistent results."

The author limits the term cacao to the raw material and cocoa to the powder manufactured from the nibs. The confusion which so frequently attends the use of these two terms is thus largely avoided, although it seems that the distinction cannot always be sharply drawn; the coloring substance of chocolate for example is listed in the index both as cacao-red and cocoa-red.

The new volume is well printed and splendidly illustrated with 12 full page photographs giving views of the agriculture of cacao in Trinidad. Other cuts show machinery, microscopical sections of pure and adulterated cocoa, etc. A useful appendix gives the provisional definitions of standards of cacao and its preparations and a very complete bibliography.

Of the numerous works which describe the manufacture and chemistry of foodstuffs, Whymper's cocoa and chocolate is one of the best which has come to our notice.

C. A. Browne.

A Manual of Fire Assaying. By Chas. H. Fulton. Second edition. pp. xvi + 209. McGraw-Hill Book Co., New York. Price, $2.00.

The second edition of this book retains all the commendable features of the previous edition, and is improved by the elimination or correction of questionable matter and the addition of new material.

The chapter on furnaces deals with the various types to date, their advantages, application, and the cost of operation under definite conditions.

There is little change in the chapter on reagents except for a more complete discussion of the action of boric acid and borates and somewhat greater attention to the cyanides.

The chapter on sampling has been slightly modified, but could stand considerable improvement to be truly useful to the student. However, this chapter and the book as a whole contain sufficient of the best references to make up for anything lacking in the text.

The subject of reduction and oxidation is extensively considered, and the points that affect the amount of lead reduced well discussed. In this connection it is surprising that the temperature effect was not brought out.

Slags have been considered from the silicate basis of the metallurgist. This method has been adopted by other writers but its value is doubtful. The author states that slags are solutions; they are more than this, in the fluid state they are electrolytes. He also states that the different bases require different silicate degrees for the best results. It is a fact that certain charges for Fe_2O_3 which will give good slags, if calculated for MnO_2, would be absolutely worthless and unsatisfactory for $CaCO_3$. There is positively no chemical relation, that we know, by which we can calculate the required silica irrespective of the base. From these facts it is difficult to see wherein this method of giving charges is scientific or what benefits are to be derived from a series of calculations, when the empirical method of stating directly the charge for a given mineral or compound is much simpler and makes no ambiguous pretentions.

The subject of cupellation has been handled in a masterly manner, and considerable new matter has been added from the author's investigations. All phenomena have been very carefully noted with their cause and effect. There are but two points on this subject open to criticism: (1) the failure of PbO to volatilize being assigned the cause of low temperature freezing (generally this is due to the cupel becoming too cool to absorb litharge); (2) that it is necessary to remove cupels from the furnace directly the beads have finished. As cupellation is properly finished with a furnace temperature below the melting point of silver, the bead sets shortly after the lead is removed, and as silver is not readily sublimed immediate removal is not necessary. This has been proved by test.

Under the headings of the assay of ores containing impurities and special methods of assay, various schemes of assay and the treatment of impurities are well considered. The latest methods and experiences are treated and the underlying principles explained.

The book as a whole is the most complete and reliable on the subject, but it could be more conveniently arranged. Subject matter directly related is treated under different heads. This relates especially to methods of assay.

That the author's efforts have been appreciated is indicated by the fact that the first edition appeared in the fall of 1907 and was reprinted before this second edition. E. J. Hall.

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian, Chemists' Club, New York.

Acetone; The Direct Production of— from Wood-waste. By J. Otto. Thesis, Technical High School, Dresden. (German.)

Alloys; The Binary Metal—. By K. Bornemann. $2.25. Wilhelm Knapp, Halle. (German.)

Analysis; Commercial Organic—; Vol. VI. By A. H. Allen. 4th Ed. 8vo. $5.00. P. Blakiston's Son & Co., Philadelphia.

Brass; Principles and Practice of Burnishing, Lacquering and Bronzing— Ware. By W. N. Brown. 2d Ed. 8vo. $0.75. Scott, Greenwood & Co., London.

Carbon Monoxid; The Testing for and Determination of—. 8vo., 69 pp. Thesis, Munich. (German.)

Coals; Steaming Tests of—, and Related Investigations. By L. P. Breckenridge, Henry Kreisinger and Walter T. Ray. 8vo., 380 pp. U. S. Bureau of Mines, Bulletin 23.

Emery and the Emery Industry. (Translation.) By A. Haenig. Cr. 8vo., 104 pp. $1.50. Oil and Colour Trades Journal, London.

Engineering Valuation of Public Utilities and Factories. By Horatio A. Foster. 8vo., 350 pp. $3.00. D. Van Nostrand Co., New York.

Explosives; The Use of Permissible—. By J. J. Rutledge. 8vo., 34 pp. U. S. Bureau of Mines, Bulletin 10.

Food, The Pure— Laws of Germany, Including Methods of Analysis. By K. von Buchka. 2d Ed. 8vo., 294 pp. $1.25. Julius Springer, Berlin. (German.)

Hydrogen; The Production of— from Carbon Monoxid and Lime. By W. H. Engels. 8vo., 55 pp. Thesis, Karlsruhe. (German.)

Metal and Iron Casting with Special Reference to Alloys for Machine Construction. By H. Wachenfeld. 8vo., 104 pp. $1.25. Halle, 1912. (German.)

Mines; First Annual Report of the Director of the Bureau of—. By Joseph A. Holmes. 8vo., 57 pp. Bureau of Mines, Washington, D. C.

Refractory; Production of— Substances. By G. Benfey. 8vo., 144 pp. $1.00. Hanover, 1912. (German.)

Refrigerating; The Absorption— Machine. By G. T. Voorhees. Cr. 8vo. $2.25. Spon & Chamberlin, New York.

Refrigerating Machinery, its Principles and Management. By A. R. Leask. 5th Ed. Cr. 8vo., 310 pp. $1.25. Simpkin, London.

Sewage; Practical Sewerage and— Disposal. By H. C. H. Stenton. 12mo., 148 pp. $1.00. Rogers, London.

Sewage Sludge. By A. Elsner, *et al.* Roy. 8vo. $2.75. Hill Publishing Co., London.

Smoke. A Study of Town Air. By Julius B. Cohen and A. R. Ruston. 8vo., 86 pp. $1.25. Edwin Arnold, London.

Smokeless; The— Combustion of Coal in Boiler Furnaces. 8vo., 188 pp. U. S. Bureau of Mines, Bulletin 40.

Soap; Manual of Toilet— Making. (Translation.) By C. Deite. Demy 4vo. $3.75. Oil and Colour Trades Journal, London.

Steel; Sampling and the Analysis of Iron and—. By O. Bauer and E. Deiss. Lex. 8vo., 258 pp. $2.25. Julius Springer, Berlin. (German.)

Sugar; Methods for— Analysis and Allied Determinations. By Arthur Given. 8vo. $2.00. P. Blakiston's Son & Co., Philadelphia.

Tables; Hering's Ready Reference—. By Carl Hering. New Ed. 16mo., 196 pp. $2.50. John Wiley & Sons, New York.

Textile; The German— Industry. By A. Oppel. L. 8vo., 167 pp. $1.50. Leipzig, 1912. (German.)

Water Analysis for Sanitary and Technical Purposes. By Herbert B. Stocks. 8vo., 102 pp. $1.25. Chas. Griffin & Co., London.

Smoke; The— Problem at Boiler Plants. By D. T. Randall. 8vo., 31 pp. U. S. Bureau of Mines, Bulletin 39.

Spectra; The— of the Elements at Normal Pressure. By F. Exner and E. Haschek. L. 8vo., 332 pp. $7.00. Vienna, 1912. (German.)

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Ammonium Sulfate; The Binding of Ammonia alone or together with Hydrogen Sulfid by Sulfurous Acid with the Simultaneous Formation of— and Free Sulfur. By Walther Feld. *Zeitschrift fuer angewandte Chemie,* Vol. 25, 1912, No. 15, pp. 705–711.

Cements; The Theories of the Hardening of the Hydraulic—, Based on the Latest Observations. By Ferdinand M. Meyle. *Zeitschrift fuer angewandte Chemie,* Vol. 25, 1912, No. 15, pp. 711–718.

Corrosion; The Influence of Carbon on the— of Steel. Anonymous. *Engineering Record,* Vol. 65, 1912, No. 16, pp. 426–427.

Iron; The Mineral Sulfides of—. By E. T. Allen, J. L. Crenshaw and John Johnson. *American Journal of Science,* Vol. 33, 1912, No. 195, pp. 169–236.

Oils; Action of Sulfur Dioxid upon— and their Fatty Acids. By S. A. Hird and L. L. Lloyd. *Journal of the Society of Chemical Industry,* Vol. 31, 1912, No. 7, pp. 317–319.

Oils; Methods for Testing Lubricating—. By T. D. Simpson. *Journal of the American Leather Chemists' Association,* Vol. 7, 1912, No. 5, pp. 235–243.

Paint; Recipes for the Colour, —, Varnish, Oil, Soap and Drysaltery Trades. Anonymous. New Ed. Demy. 8vo., 330 pp. $3.00. *Oil and Colour Trades Journal,* London.

Pulp; The Technical Development of the Manufacture of Sulfite—. By Spiro. *Chemiker Zeitung,* Vol. 36, 1912, No. 53, pp. 494–496.

Rare Earths; Bibliography of the—. By C. Richard Boehm. *Zeitschrift fuer angewandte Chemie,* Vol. 25, 1912, No. 16, pp. 758–761.

Soap; Modern Development of the— and Crude Glycerin Industry. By Franz Goldschmidt. *Zeitschrift fuer angewandte Chemie,* Vol. 25, 1912, No. 17, pp. 808–816.

Sugar; Comparison of the Methods of Heating and Evaporation Developed in Beet and Cane— Factories. Anonymous. *International Sugar Journal,* Vol. 14, 1912, No. 160, pp. 199–210.

Tar; The Determination of— in Generator Gas. By A. Gwiggner. *Chemiker Zeitung,* Vol. 36, 1912, No. 50, pp. 461–462.

Turpentine; The Determination of Benzine and Benzol Hydrocarbons in—. By J. Marcusson. *Chemiker Zeitung,* Vol. 36, 1912, Nos. 45 and 46, pp. 413–414 and 421–422.

RECENT INVENTIONS

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

PROCESS OF WELDING METALS.

U. S. Patent No. 1,021,318, to Anton Mucas, of New York, N. Y. Assignor to Goldschmidt Thermit Company, of New York, N. Y.

This is a process of uniting two metals (one of which is solid) by the action of cast metal.

The feature which distinguishes the process from other processes of uniting metals by the action of molten cast metal upon one or more solid pieces of metal is the employment in conjunction with ordinary molten metal of thermit and the superheated molten metal resulting from the thermit reaction for raising the temperature of such molten cast metal sufficiently to cause the melting of the solid metal or metals acted upon and the consequent union of all three kinds of metal into a substantially homogeneous body metal.

Fig. 1

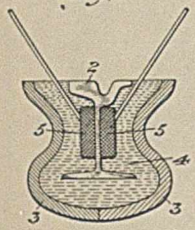
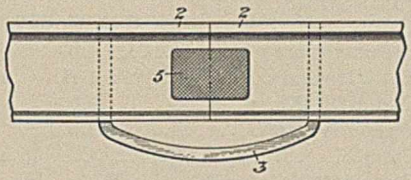


Fig. 2

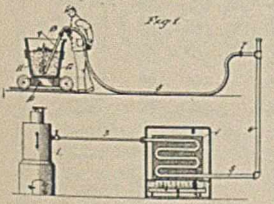


The illustration shows the application of the process to the welding of the railroad rails, the ends of the rails to be joined being placed in a mold, 3, and the thermit mixture 5, consisting of oxid of iron and finely divided aluminum, being held in position on each side of the joint by rods.

TREATMENT ON METALS.

U. S. Patent No. 1,019,965, to William H. Kelly, of Los Angeles, California.

This is a process of effecting the purification of molten metals from sulfur, phosphorus and other like impurities by subjecting them to the action of partly dissociated steam, such steam containing nascent hydrogen and nascent oxygen.

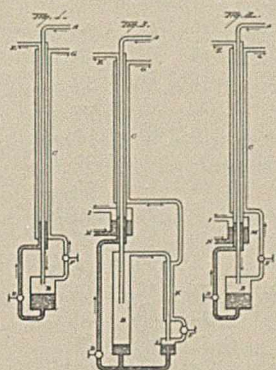


The steam is produced in the boiler 1, shown in the accompanying illustration, and partly dissociated in the retort 2 from which it is conducted to the nozzle 9 immersed in the molten metal.

PROCESS FOR THE PRODUCTION OF HYDROGEN FROM GAS MIXTURES CONTAINING HYDROGEN.

U. S. Patent No. 1,020,102, to Carl von Linde, of Münich, Germany.

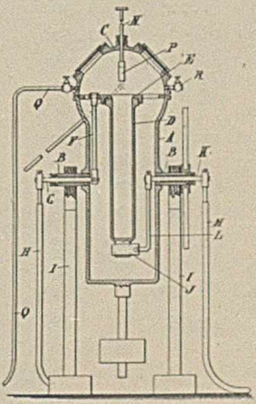
In the use of the apparatus illustrated the compression gas mixture enters at A after it has been previously freed from such constituents or impurities which can bring about stoppages in the liquefying apparatus, *e. g.*, carbonic acid and sulfur compounds. In its passage through the apparatus to the vessel B, the gas mixture reduced in temperature to such a degree in the temperature-interchanger C, that the greater part of the constituents of the gas mixture are liquefied and collected in the vessel B. The liquefied portion flows out of this vessel through the expansion mechanism D into the interchanger C, evaporates and thereby removes heat from the compressed gas mixture flowing through the apparatus. The products of this evaporation, *e. g.*, carbon monoxid, escape at E, after an interchange of temperature with that of the compressed gas mixture passing through the apparatus and can be applied in any manner desired. The portion of the gas mixture which is not liquid (hydrogen and the remaining constituents) after passing through the expansion mechanism F flows through the temperature interchanger C in an opposite direction to that of the compressed gas mixture and escapes out of the apparatus at G at normal temperature.



APPARATUS FOR MELTING AND MIXING METALS IN VACUUMS.

U. S. Patent No. 1,015,091, to Wm. Speirs Simpson, of London, England.

This invention relates to apparatus for melting and mixing metals *in vacuo* of the kind in which electrical heat is used for melting the metals, and the object is to construct an improved apparatus for removing volatilizable impurities from certain easily oxidizable metals, such as aluminium, magnesium, calcium and the like with which it is desirable for forming useful alloys; the hitherto unavoidable oxidation of these metals while in a molten state is prevented and effective mixing and alloying under the most favorable conditions is accomplished; the result affords a purified metal or alloy of uniformly superior quality and strength.



The invention is carried out in a receptacle or chamber of suitable size and dimensions wherein a comparatively high vacuum may be created and maintained by means of a vacuum pump in any convenient manner. Inside the chamber is placed a crucible made of refractory or carbonaceous material for containing the metals to be treated: these are heated by means of an electric current applied to the top and bottom of the crucible.

The apparatus consists of a vacuum chamber with a body portion having trunnions for mounting it tiltably; a cover removably applied to its upper end and adapted to form a fluid-tight connection; a crucible contained within and carried by the body portion; an interior chamber to contain a charge to be treated and having its mouth arranged toward the top of the body portion; means for conducting a heating medium to the crucible through the trunnious of the tiltably mounted body portion.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MAY.

ORGANIC CHEMICALS.

Acetanilid	Lb.	20½	@	23
Acetone (drums)	Lb.	17	@	18
Alcohol, grain (188 proof)	Gal.	2.56	@	2.58
Alcohol, wood (95 per cent.)	Gal.	50	@	52
Alcohol, denatured (180 proof	Gal.	40	@	42
Amyl Acetate	Gal.	2.90	@	3.00
Acetic Acid (28 per cent.)	C.	2.00	@	2.15
Aniline Oil	Lb.	10¾	@	11½
Benzoic Acid	Lb.	23½	@	28
Carbon Tetrachloride (drums)	Lb.	10	@	15
Carbon Bisulphide	Lb.	nominal		
Chloroform	Lb.	20	@	30
Carbolic Acid (drums)	Lb.	16	@	18
Citric Acid (domestic), crystals	Lb.	38½	@	39
Camphor (refined in bulk)	Lb.	44	@	—
Dextrine (imported potato)	Lb.	6	@	7
Dextrine (corn)	C.	3.30	@	3.66
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19	@	21
Oxalic Acid	Lb.	8½	@	8½
Pyrogallic Acid (bulk)	Lb.	1.35	@	1.45
Salicylic Acid	Lb.	32	@	34
Starch (corn)	C.	2.55	@	2.85
Starch (potato)	Lb.	5¼	@	5¾
Tannic Acid (commercial)	Lb.	35	@	35½
Tartaric Acid, crystals	Lb.	30½	@	31

INORGANIC CHEMICALS.

Acetate of Lime (gray)	C.	2.50	@	2.60
Acetate of Lead (brown, broken)	Lb	7¾	@	8
Alum (lump)	C.	1.75	@	2.00
Ammonium Carbonate, domestic	Lb.	8	@	8¼
Ammonium Chloride, gray	Lb.	6⅛	@	6¼
Aluminum Sulphate	C.	90	@	1.75
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	4	@	4⅛
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Barium Chloride	C.	1.40	@	1.55
Barium Nitrate	Lb.	4¾	@	5
Borax, crystals (bags)	Lb.	3½	@	4
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Bromine, bulk	Lb.	25	@	30
Bleaching Powder (35 per cent.)	C.	1.22½	@	1.30
Barytes (prime white, foreign)	Ton	18.50	@	22.50
Blue Vitriol	Lb.	5½	@	5¾
Calcium Chloride	C.	65	@	90
Chalk (light precipitated)	Lb.	4½	@	6
China Clay (imported)	Ton	11.50	@	18.00
Feldspar	Ton	7.00	@	9.00
Fuller's Earth, powdered	C.	80	@	85
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18^b)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	2.60	@	2.65
Lead Nitrate	Lb.	8⅜	@	8½
Lithium Carbonate	Lb.	65	@	70
Magnesite (raw)	Ton	7.50	@	8.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphorus	Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75	Lb.	22	@	26
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bromide	Lb.	31	@	34
Potassium Permanganate (bulk)	Lb.	9¾	@	10
Potassium Cyanide (bulk) 98–99 per cent.	Lb.	19½	@	21
Potassium Iodide (bulk)	Lb.	2.10	@	2.15
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Nitrate (crude)	Lb.	4½	@	4¾
Potassium Bichromate, 50°	Lb.	6⅞	@	7
Quicksilver	Flask	41.00	@	43.00
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	39	@	40
Soapstone in bags	Ton	10.00	@	12.00
Sodium Acetate	Lb.	4¼	@	5
Sodium Chlorate	Lb.	8¼	@	9½
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	5	@	5¼
Sodium Hydroxide, 60 per cent.	C.	1.70	@	1.75
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot	C.	—	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
Sulphur, Roll	C.	1.85	@	2.15
Sulphur, Flowers (sublimed)	C.	2.20	@	2.60
Sulphuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	13¼	@	13½
Tin Oxide	Lb.	47	@	51
Zinc Chloride (granulated)	Lb.	4¼	@	4½
Zinc Sulphate	Lb.	2¼	@	2½

OILS, WAXES, ETC.

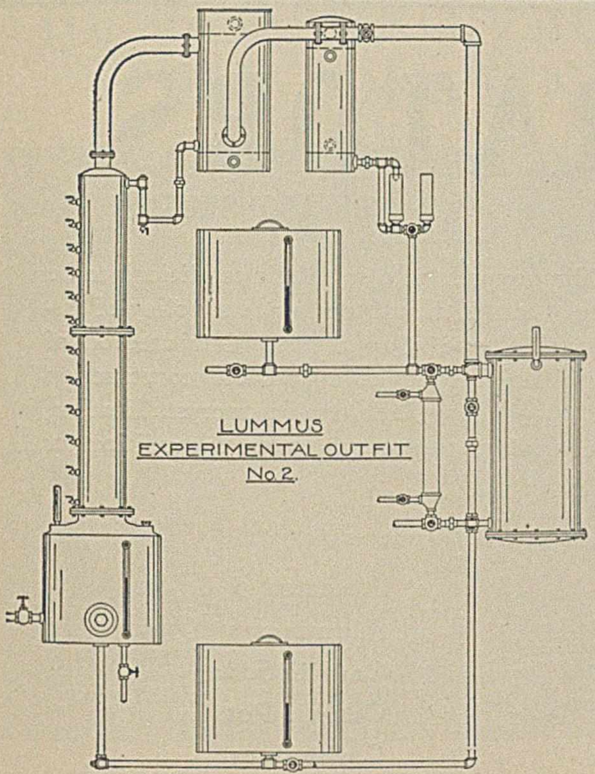
Beeswax (pure white)	Lb.	36	@	40
Black Mineral Oil, 29 gravity	Gal.	12	@	12½
Castor Oil (No. 3)	Lb.	9½	@	10½
Ceresin (yellow)	Lb.	9	@	15
Corn Oil	C.	6.15	@	6¼
Cottonseed Oil (crude), f. o. b. mill	Gal.	46	@	48
Cylinder Oil (light, filtered)	Gal.	19½	@	20
Japan Wax	Lb.	9½	@	10
Lard Oil (prime winter)	Gal.	85	@	90
Linseed Oil (double-boiled)	Gal.	75	@	78
Paraffine Oil (high viscosity)	Gal.	25½	@	26
Paraffine (crude 120 & 122 m. p.)	Lb.	3	@	3⅜
Rosin Oil (first run)	Gal.	38	@	40
Spindle Oil, No. 1	Gal.	16	@	16½
Sperm Oil (bleached winter) 38°	Gal.	74	@	76
Stearic Acid (double-pressed)	Lb.	9	@	10
Tallow (acidless)	Gal.	60	@	63
Tar Oil (distilled)	Gal.	30	@	31

METALS.

Aluminum (No. 1 ingots)	Lb.	20	@	20½
Antimony (Hallet's)	Lb.	7¾	@	8
Bismuth (New York)	Lb.	2.10	@	2.15
Copper (electrolytic)	Lb.	16¼	@	16⅜
Copper (lake)	Lb.	16⅜	@	16½
Lead, N. Y	Lb.	4.20	@	—
Nickel	Lb.	40	@	45
Platinum (refined)	Oz.	45.50	@	46.00
Silver	Oz.	61⅜	@	—
Tin	Lb.	46½	@	46¾
Zinc	Lb.	6.85	@	—

FERTILIZER MATERIALS.

Ammonium Sulphate	C.	3.40	@	3.45
Fish Scrap, domestic, dried	Unit	2.75	@	10
Blood, dried	Unit	2.75	@	2.80
Tankage, high grade	Unit	2.65	@	10
Bone, 4½ & 50, ground, raw	Ton	27.00	@	—
Potassium, "muriate," basis 80 per cent.	Ton	38.55	@	—
Phosphate, acid, 16 per cent.	Ton	7.25	@	7.50
Phosphate rock; f. o. b. mine:				
Florida land pebble 68 per cent.	Ton	3.70	@	3.80
Tennessee, 68–72 per cent.	Ton	4.25	@	4.50
Pyrites, furnace size, imported	Unit	0.13½	@	—
Castor meal	Unit	2.75	@	—
Mowrah meal	Ton	8.50	@	9.00



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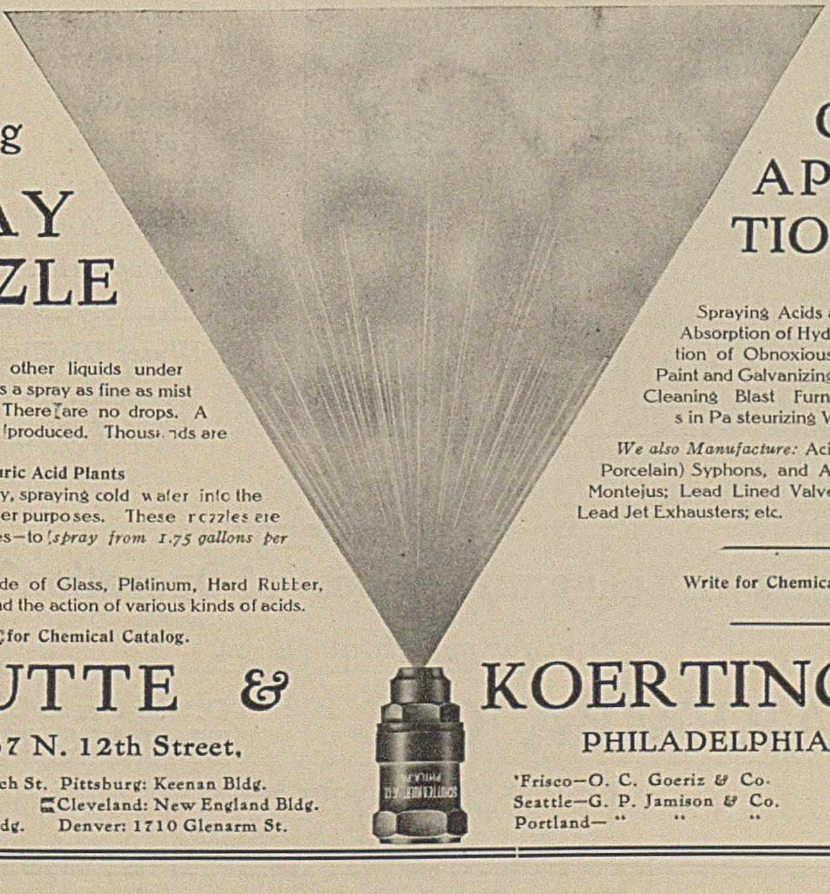

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Carbonates
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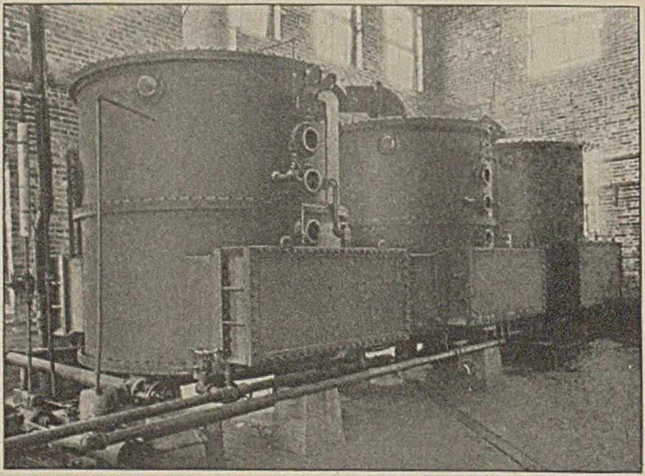

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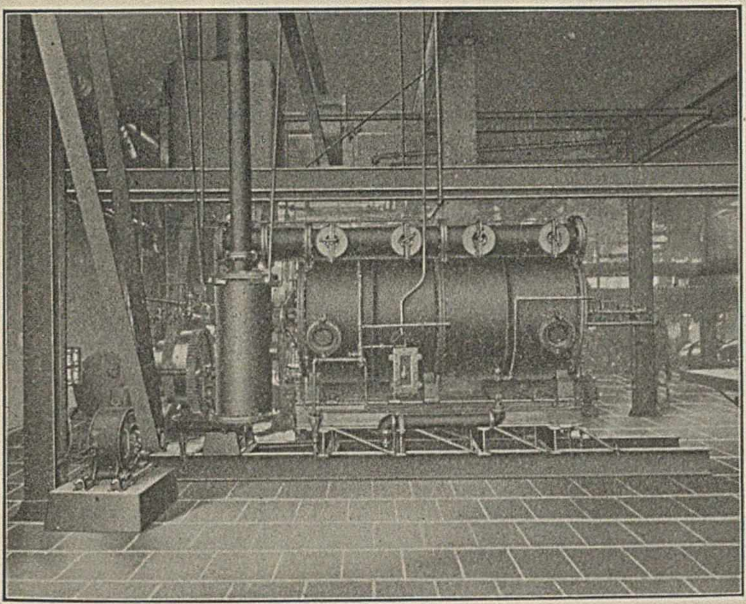

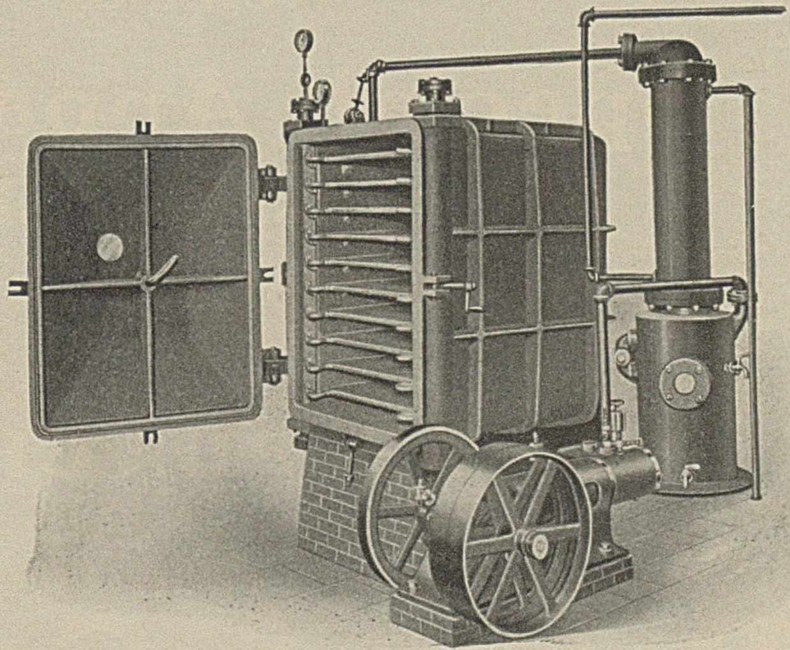

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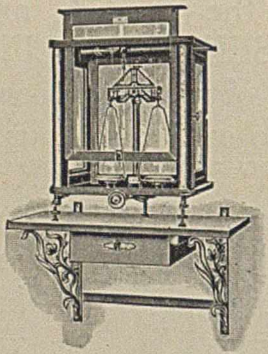

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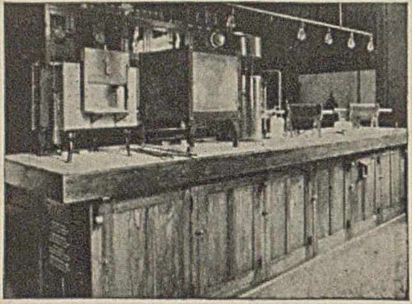

Twenty-six Hoskins Electric Furnaces of six different types are in use by the steel company in whose laboratory the above picture was taken. Three of these Furnaces are shown here.

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"I wish to say we have our "Hoskins" Electric Furnace in operation each day, and it gives us satisfaction in every respect."—From the Chief Chemist of an Ohio steel company.

"The furnace, which is of the small crucible type, has been very satisfactory, having been used a great deal in the determination of melting points of lead silicates. The furnace has been heated for hours at a time around 800° C."—From a member of the Department of Chemistry of an eastern university.

"This Furnace (Hoskins Type FA No. 301) works out very nicely indeed and has been running night and day at a temperature which we hold very close to 940° C.

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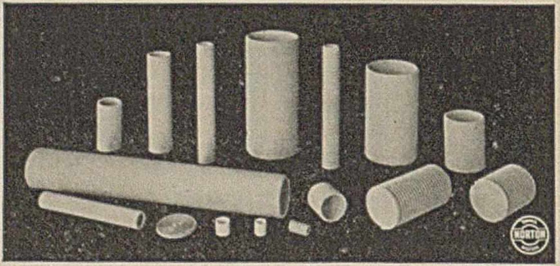

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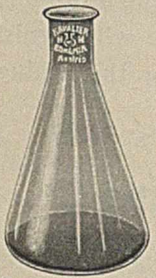

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Bohemian KAVALIER H NS H BOHEMIA Austria **Glassware**

Each Piece Bearing the Kavalier Trademark

Up to the latter part of 1909 the Kavalier factories had no trademark, and for this reason other ware has often been sold for genuine Kavalier's. To obviate this we urged upon them the necessity of a trademark until they finally adopted one, which is now etched on each piece of glassware, except on small glass tubing, by the Sazava and Neu Sazava Kavalier factories. Both factories have been under the same ownership and management for several years, and the mode of manufacture, material used and the product are identical, though the factories still do business under the old firms, Eduard Kavalier and Josef Kavalier.

It is a known fact that Kavalier glassware has at all times been recognized as the highest type of chemical glassware and that no other make has ever approached it in alkali-resisting quality, uniformity and elegance of shape, as well as property of resisting sudden changes in temperature.

Though Kavalier glassware is somewhat more expensive than other glassware, we recommend its general use knowing that our customers will be highly pleased with it and that they will find it the most profitable in the end.

Be sure to see to it that each piece of glassware sold to you as Kavalier's bears the trademark.

Prices will be quoted cheerfully on application to

Henry Heil Chemical Co.

The House of Quality

210 to 214 South 4th Street, St. Louis, Mo.

Headquarters for Laboratory Supplies

KAHLBAUM'S "Certified for Analysis" REAGENTS

KAHLBAUM BOTTLE

C.A.F. KAHLBAUM BERLIN

CHEMISCHE FABRIK
C.A.F. KAHLBAUM
BERLIN C.25.

Bleioxyd

Zur Analyſe, mit Garantieſchein

In 10 Gramm:	
Kohlensäure	0
Chlorid	Spur
Rückstand nach Bleifällung (Erden, Alkalien)	12 mg
Kupfer	0
Thonerde u. Eisenoxyd	0
Nitrat u. Nitrit	0
Löslichkeit in Essigsäure:	vollkommen

Dr. C. Bischoff.

KAHLBAUM LABEL

The firm of C. A. F. KAHLBAUM, of Berlin, have just put upon the market a new line of high-grade reagents under the title of "zur Analyse, mit Garantieschein" which we are listing in our new catalogue under the designation "CERTIFIED FOR ANALYSIS" abbreviated to C. f. A."

The material used in these reagents is identical with that used in the line designated "zur Analyse" in previous editions of Kahlbaum's catalogue. Each chemical is, in addition, subjected to the most rigid possible analytical control in the Kahlbaum research laboratories at the time of packing in the original packages in which we sell them, each package being marketed under lead seal. The result of this analysis is embodied in a signed certificate made a part of each label on every package as illustrated in the specimen label printed above.

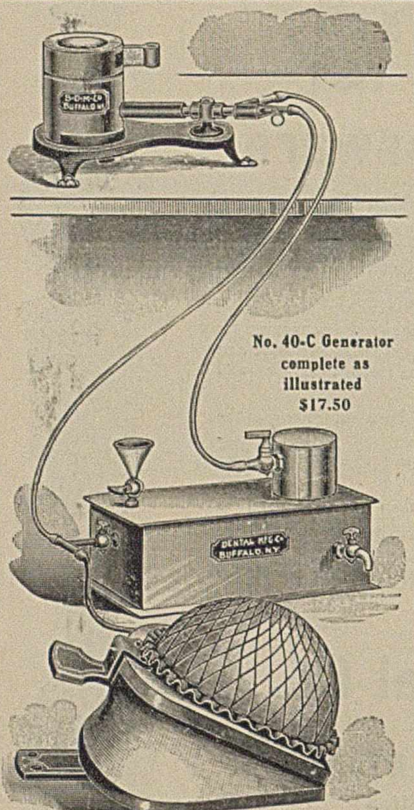
SEND FOR A COPY OF THE NEW, 1912, EDITION OF OUR CHEMICAL CATALOGUE.

ARTHUR H. THOMAS COMPANY

IMPORTERS AND DEALERS

MICROSCOPES, LABORATORY APPARATUS AND CHEMICALS

1200 WALNUT STREET, PHILADELPHIA



No. 40-C Generator
complete as
illustrated
$17.50

Generate Your Own Gas

The large number of enquiries for catalog "B" describing in full our gasoline gas generator outfits, resulting from our "ad." in the April number of this Journal, leads us to think there may be numerous other chemical laboratories without the convenience of a regular City gas supply and we therefore offer the same subject for your perusal this month, illustrating however our smaller generator. One of the largest iron foundries in the United States has used this outfit in its laboratory with great success, for many years. Why not you? Our largest generator will give you a regular piped supply of gas in your laboratory from which you can operate blast lamps, furnaces, or burners, of which we make a full line. Let us know what you wish to accomplish, and we will furnish the proper heating apparatus. Catalog is free for the asking. What's your address?

Buffalo Dental Manufacturing Co.
Buffalo, N. Y., U. S. A.

DE LAVAL CENTRIFUGAL Clarifier and Filter

Performs economies that have never before been approached by any other system

The 1911 improvements place the DeLaval Clarifier and Filter in a class by itself.

The improved machine embodies all the good points of other clarifiers and filters, and, in addition, advantages not offered by any other system of filtration.

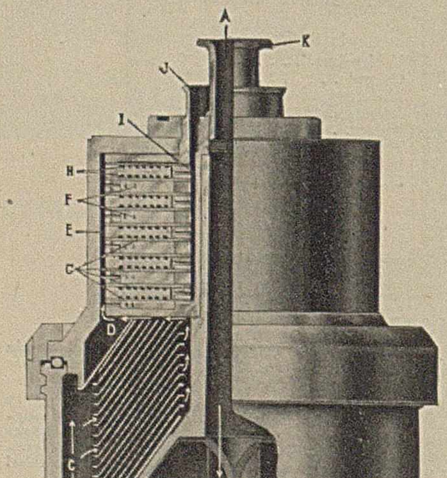
It removes the finest flock and all suspended dirt, as well as the coarsest sediment from varnishes, patent medicines, spirits, etc., and makes a saving of at least 90 per cent. in filter paper and cloths, and many other big savings impossible by any other process.

Note bowl illustration on the left—it has two distinct compartments—one clarifies, the other filters, all at one continuous, and practically instantaneous, operation. Easily and quickly adjusted for any and all products. Simple and inexpensive to operate and always ready. Exceptionally durable and saves its cost many times over each year of use.

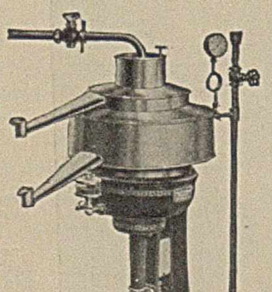
Made in four sizes for the smallest as well as the largest use.

Our Bulletin No. 125 tells more about this labor- and money-saving machine, and is free for the asking.

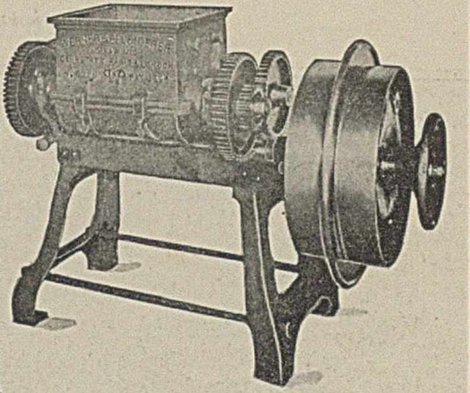
The DeLaval Separator Co.
Sole Manufacturers
165 Broadway, New York 29 E. Madison St., Chicago

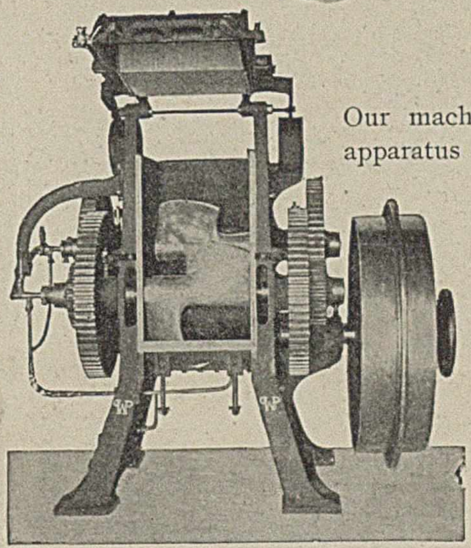


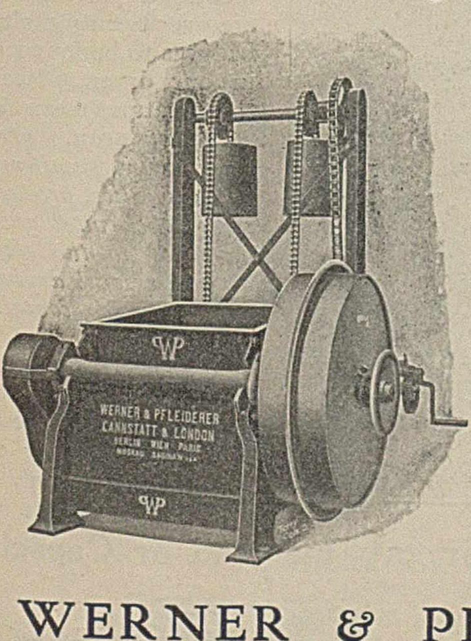
The Bowl—The Heart of the Machine



The Machine



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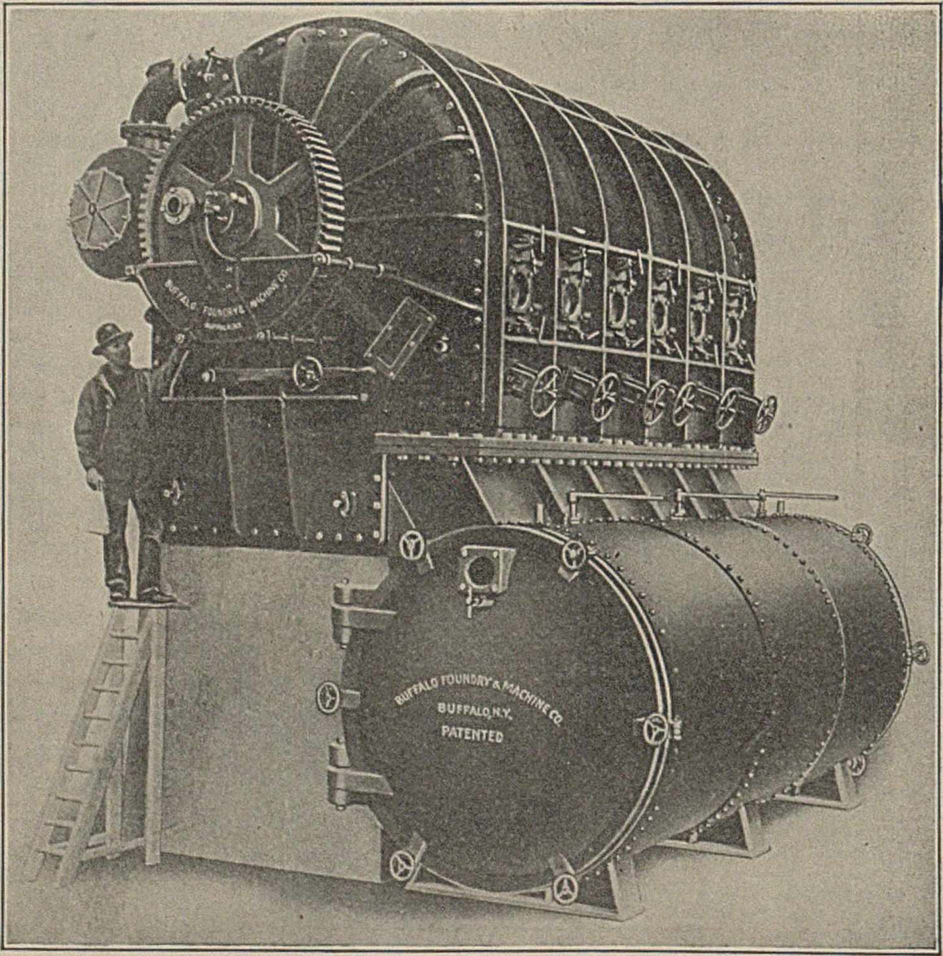
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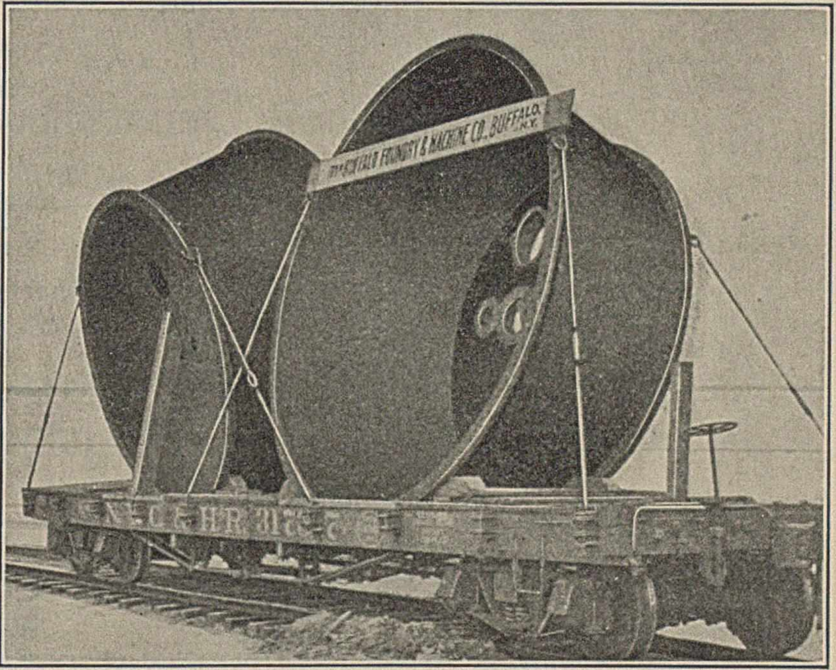
Chemical Castings

Do YOU Buy Metal, or Service?

When you buy
Chemical Castings

Your Primary Requirement is Service

rather than so many pounds of
iron at a certain price per pound—



You want ultimate value rather than extremely low first cost.

Now *ultimate value* is determined by dividing *service* by *cost.*

And many of our customers have told us that our castings give more than five times the service that they were able to obtain elsewhere, either in this country or in Europe.

This at an advance in first cost that becomes insignificant when compared with the savings effected.

Remember that when a chemical casting does fail in service, it often involves a three-fold loss—first cost of the casting itself, a part or all of the material being treated, and the investment (often quite heavy) represented by the setting. The unusual length of life shown by B. F. & M. Chemical Castings is largely due to our careful methods backed by experience, making up our metal mixtures, etc. All metal used in our foundry is both chemically and physically analyzed in our laboratories.

This service is one which few, if any other, foundries are in a position to render—but our long experience in this work qualifies us to make castings which will give excellent results.

Send us sketches or blue prints for estimate.

We make Castings up to 200 tons in weight each

MACHINE COMPANY

Buffalo, N.Y.

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¶ In specializing in the laboratory supply business as we do, we found it more efficient to have certain departments concentrate on special branches of this large field. We call the attention of all scientific men to the following departments and their scopes, and invite correspondence in relation to their particular problems.

Import Department

¶ Wherein are filed all the catalogues of every foreign manufacturer of apparatus for Chemical, Biological, or Metallurgical laboratories and lists of materials used in connection with the latest scientific discoveries.

¶ This department also handles all duty-free importations for universities and colleges.

Glass Blowing Department

¶ Employing expert glass blowers, engravers, and grinders, and maintained for the manufacture of all special glass apparatus of most complex design, and volumetric apparatus, thermometers, and hydrometers of precision.

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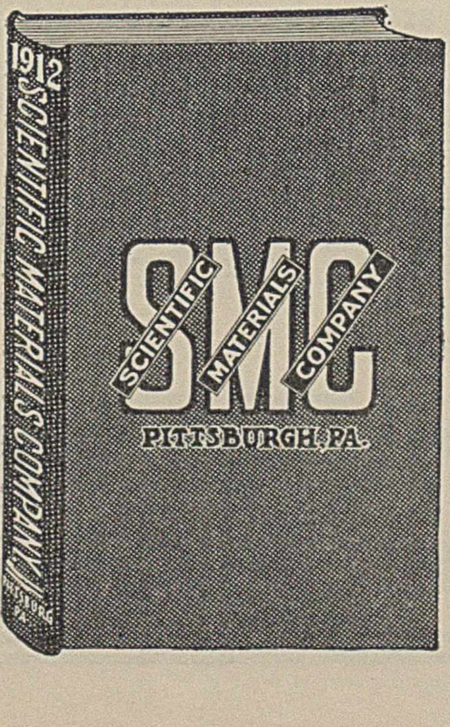
¶ Conducting all experiments with new apparatus before offering for sale, and trying out fairly all new improvements offered to us.

¶ This department also designs special scientific apparatus for particular purposes, and has the services of an Electrical Engineer, a Mechanical Engineer, a Physicist and a Chemist.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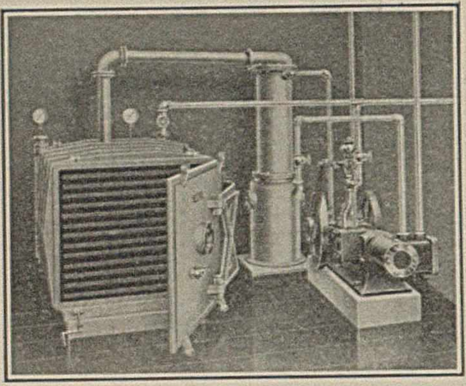
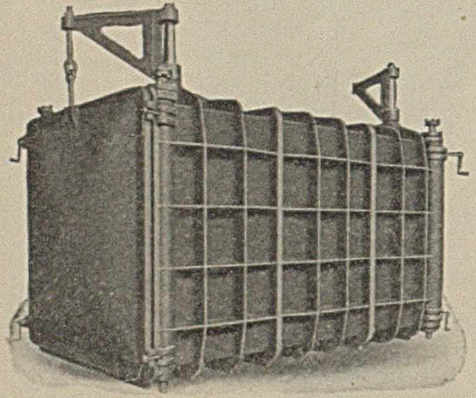


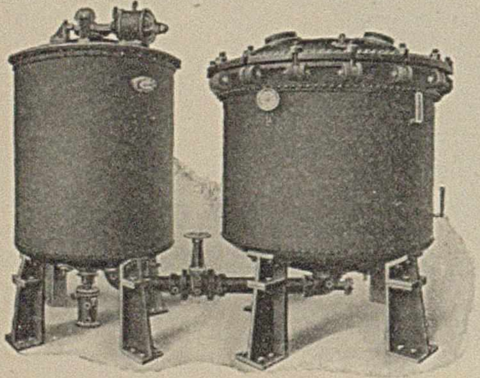
Drying and Impreg

J. P. DEVINE CO., BUFFALO, N. Y., are the pioneers of Vacuum Drying and Impregnating of material under vacuum in this country.



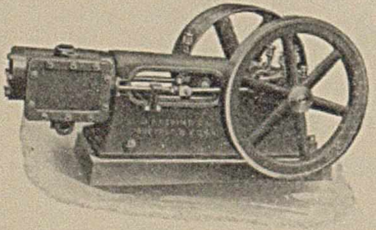
Over three thousand apparatus in daily operation.

The reason for our success is our ability to supply the *most scientifically constructed* and *economically working* apparatus for any given requirement based upon practical experience of upwards of *thirty years* in originating and designing Vacuum Apparatus and their auxiliaries exclusively.



Our shops are equipped with special tools and appliances for the economical manufacture of Vacuum Apparatus.

Our success naturally attracted others to *imitate* our apparatus



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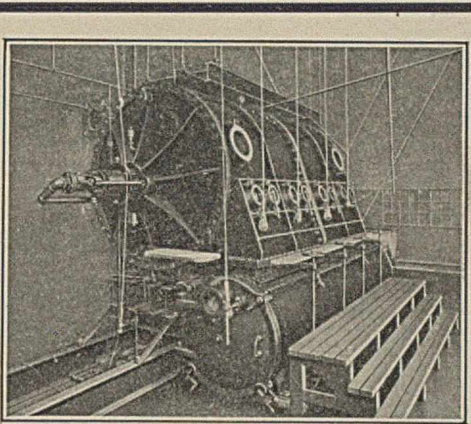

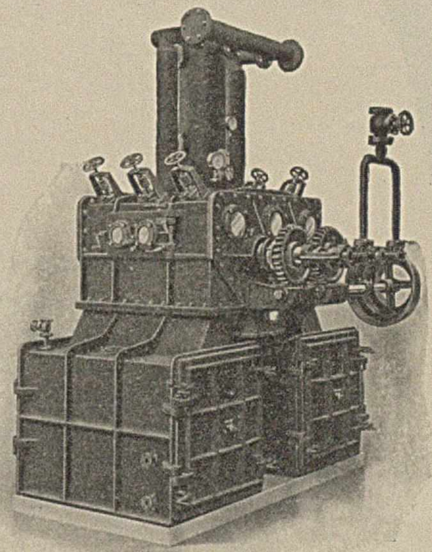

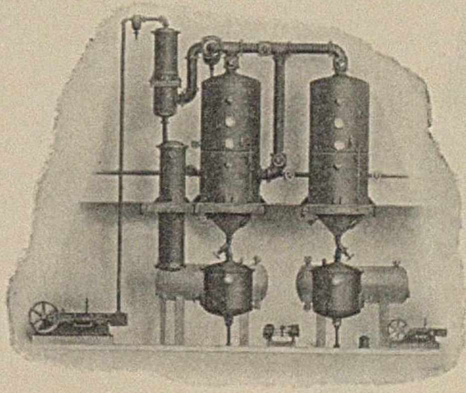

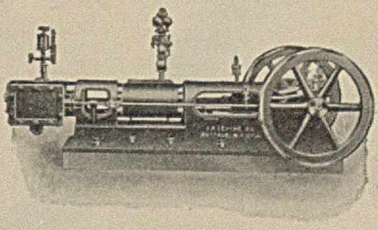

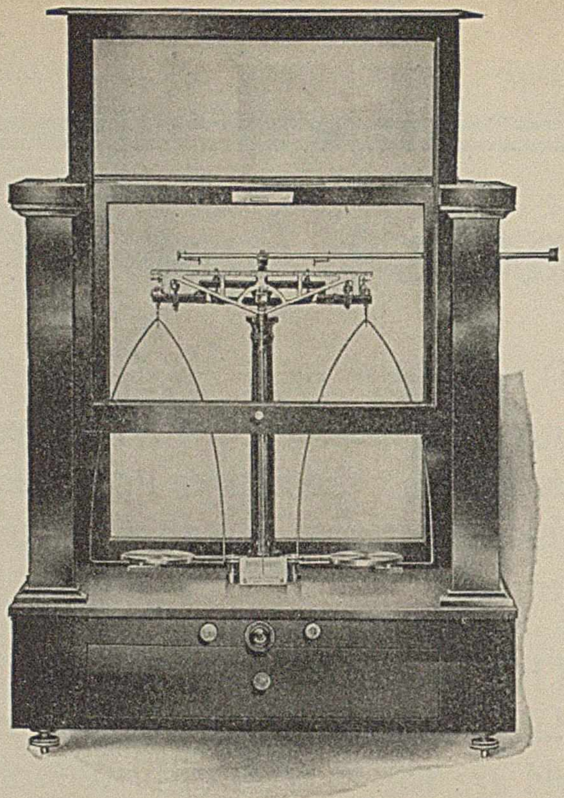

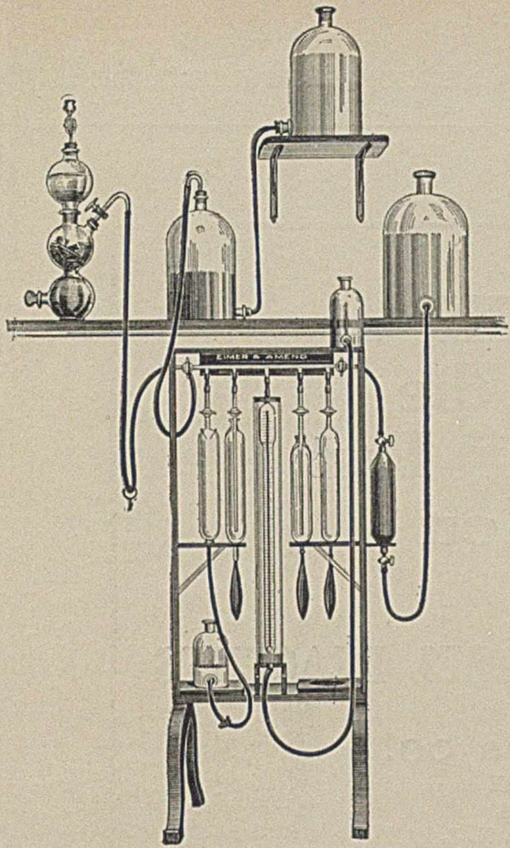
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