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# EDITORIALS.

## CHEMICAL ENGINEERS IN THE TEXTILE INDUSTRY.

In the textile industry there is a considerable need of the services of chemical engineers with some special training along the lines of textile manufacturing. For the usual type of analytical chemist, such as is turned out in such large quantity by so many of our colleges and technical schools, there is very little future in a textile mill.

In the various operations of manufacturing textiles, there are many occasions where the knowledge and advice of a trained chemist would be desirable. This is especially true in operations involving dyeing, bleaching, mercerizing, carbonizing, finishing, printing, sizing, scouring, etc. But something considerably more than a general knowledge of chemistry is required: even skill in analytical chemistry will not be of much avail. A textile chemist needs to be adept in engineering, to have a knowledge of machines, their principles of construction and operation, to be able to solve problems in the application and distribution of power, to devise methods for the handling of large quantities of liquids, and the preparation and conveyance of solutions, to be able to follow up main products and by-products, and to be able to work out problems involving economy and efficiency and the utilization of waste products.

This seems rather a broad curriculum, when it is also understood that at the basis of all this there must be a broad and substantial knowledge of both general and applied chemistry, and furthermore there must be a specialized knowledge of the textile fibers, and the various operations and treatments to which they may be subjected.

In this country, there does not seem as yet to have been a successful affiliation of studies in chemistry and engineering as evidenced by the courses offered in classes in chemical engineering at a number of our colleges. Why these combinations of studies are not popular among the students and why such branches do not draw the efforts of the best type of student is hard to say. Probably the fact that chemical engineers are not a factor in the teaching force has much to do with this lack of development of this branch of study in this country.

In our textile schools, while considerable teaching is offered in the specialized subjects of textile chemistry, with more or less attention paid to practical instruction, there is, on the other hand, a lack of thorough and broad training in the general principles of chemical science. The product of the textile school, therefore, has a short-sighted chemical vision, and this produces lack of initiative in after life. While some of the textile schools affect to train their students in the principles of engineering, the courses they offer are more or less amateurish and raw, a result which is more inclined to give the student a good opinion of himself than to turn him out an efficient chemical engineer.

The best course for a student to pursue, who desires to become a highly developed and efficient textile chemist, would be to pass through as good a course in chemical engineering as it is now possible to obtain at college, then specialize for a year or more at a textile school, taking not only in this connection the studies in dyeing, bleaching, textile chemistry, etc., which may be available, but also studies relating to the grading and selection of stock, and the principles underlying the processing of the fibers in the preparation of the finished fabric, such as carding, spinning, and weaving. After such theoretical knowledge is thus acquired, the prospective textile chemist should seek employment in a mill where he may have access to as wide an experience as possible. He should not be content to go into the mill laboratory (if there is one) and perform routine analyses merely; such work should be only a part of his functions. He should work out in the various departments of the mill, put on overalls and get his hands soiled, but acquire a knowledge of the practical manufacturing operations all through.

With such an equipment and experience, a man may become a highly efficient textile chemist. For such there are plenty of excellent opportunities for rapid advancement and high salaries. For the young man who is content to remain in the laboratory at the routine practice of analyses and thinks the dye-house is too nasty a place to work in, there is seldom any place beyond twelve to fifteen dollars a week salary. For the other kind of man, however, his future is only limited by his personal initiative and energy.

J. M. MATTHEWS.

## ORGANIZATION FOR ROUTINE WORK.

No more careful and painstaking work is required in any branch of chemistry than in the design and organization of the laboratory which turns out large numbers of routine analyses, requiring skill and accuracy, in a short period of time. On such control analyses the successful operation of innumerable large industries depends and the more accurate the work and the more rapidly it is turned out, the better the control will be. It appears that any chemist of average ability can make one or a small number of analyses and report reasonably correct results. But with the multiplication of samples and the making of hundreds or thousands of analyses, it appears almost unavoidable that a certain percentage of incorrect results are reported. In the abstract one might expect that the more samples analyzed, or the more determinations made the less would be the chance for error in any individual case. Practically this is seldom true. The steel-works laboratory probably takes first rank as a routine laboratory and will continue to do so, but the fertilizer laboratory has become a close second on account of the immense increase in fertilizer manufacture. In these laboratories, the organization for routine work has reached a rare degree of refinement, but perfection and even a perfectly satisfactory condition of affairs has not yet been attained. The average chemist, upon leaving college, looks upon routine work as a thing to be shunned or at most as a line of work to be followed only temporarily, and used as a means to other ends. Great emphasis has been laid on this view of the case recently by college professors and industrial chemists. It is needless to say that there is a posssibility if not a danger of overemphasizing this side of the argument. Let us pause for a moment to say a good word for the skilful, painstaking analyst whose results can be relied upon for the control of large manufactures. In spite of the view taken of routine chemical work by the profession at the present time, such work is highly appreciated by at least one man—the works manager or superintendent. We believe that as time goes on this sort of work will receive greater recompense than it does now, recompense more in proportion to its importance in the operation and control of great industries.

In passing we may say that whatever our views on the subject may be, we can be permitted to admire the excellent equipment, organization and management of such a routine laboratory, as the nitrogen laboratory in the Bureau of Chemistry at Washington. It is a pleasure to inspect this laboratory and to see under what satisfactory conditions routine work can be conducted.

## THE FERTILIZER INDUSTRY.

The steady and consistent growth of the fertilizer industry and the greatly increased use of fertilizers during recent years indicate a very large future for this branch of manufacture. The new soils in this country have for the most part been taken up—many farms have been "used up," many farms abandoned. As the old farmer explained to the Professor of Agriculture who was lecturing in his district: "You can't tell me anything about farming. I've used up three farms."

One of the most important practical facts in regard to the use of fertilizers is that they are used chiefly in the older settled parts of the country and where the same crop is raised year after year. Be the explanation what it may, the facts and the experience of many different individuals appear incontrovertible. The tendency now appears to be toward an increased use of fertilizers even on the newer soils, and all must agree that this tendency is a wholesome one. In the meantime the large fertilizer manufacturers are constructing factory after factory and mixing plant after mixing plant and the growth in output year by year is enormous. The old and tried sources of nitrogen, phosphorus and potassium are the ones chiefly drawn on for the increased consumption. In spite of the agitation for raw phosphate rock as a source of phosphorus, acid phosphate continues to be the principal phosphatic fertilizer. Air-nitrates and cyanamide are making headway slowly on account of the large supply of Chili saltpeter. Conservationists have issued a warning on the subject, but there appears to be no immediate danger of a shortage in the supply of fertilizer raw materials. The large increase in the use of commercial fertilizers is the more interesting, because of the fact that there has been a corresponding large increase in the use of green crops, legumes and barn-yard manure on the farm. The increased use of commercial fertilizers has come in addition to a largely increased use of the natural fertilizer resources of the farm. We are, beyond question, progressing gradually toward permanent systems of agriculture.

## INDUSTRIAL RESEARCH.

Since the first metallurgist, by making such simple tests as were in his power, investigated the suitability of various earths for making iron, or since the ancient Egyptian glass-maker examined various alkaline salts which might be adapted to his art, industrial chemical research has ever been the guiding light of chemical industry. Called by various names at various times, whether it rested upon ungeneralized empirical knowledge, or whether through the vitalizing force of science, it assumed the voice of prophecy, fundamentally it has always been the same. Like the pillar of fire of old its purposes has been to lead and guide. It has guided all-conquering industry out of the bondage of tradition and led it from goal to goal and conquest to conquest until the observer, with any knowledge of the history of industry, can scarcely conjecture whither the next advance will lead. This progress can not properly be compared to finite geographical explorations and discoveries; it is more like the exploration of space and the infinite worlds of space.

The chemical investigator connected with the industries has been likened to the exciter on an electric generator, while the superintendent or works manager, the driving force, has been compared to the generator itself. There appears to be much truth expressed in the simile. Each is necessary for the development of the power required to operate the plant. There is an implied truth also apparent, namely, that the scientific imagination is not usually accompanied by the capacity to organize and to operate a large industry.

The present age is one of industrial transition, wherein the scientific man is beginning to have a more prominent place in industry than previously. That he does not come to the front more rapidly and take the place to which he believes he is entitled is sometimes a cause for complaint on his part. However, it has been demonstrated again and again, that so far as the mere traditional operation of a plant is concerned, the accumulated experience of years or hundreds of years, is of more value than the theoretical contributions of the scientific man. The chemist, for example, must usually spend a number of years in studying present-day practice in an industry, before he can really be of much service to that industry. The training of most superintendents and works managers is such that the development of their imagination is neglected or retarded. They lack the imagination necessary to carry the operations of their factories beyond present-day practice. On the other hand, the college-trained chemist usually has too much imagination and too little common sense and knowledge of present-day practice. Possibly, also, he has too little desire to investigate thoroughly present-day practice before undertaking to revolutionize it, and herein are the sources of the eternal conflict between the practical man, educated by experience, and the college-educated man. Once in a blue moon comes the chemical engineer—that rare combination of chemical and engineering instincts. And rarer yet is the college-trained man who makes a satisfactory chemist, engineer and superintendent. Most plants must be satisfied now and probably in the future with a separation of these offices, and perhaps the highest results may be accomplished by a proper coördination of the work of chemist, engineer and superintendent.

Whatever the solution of the much tortured question, industrial research will go on. Such research may be far removed from immediate application. As Dr. W. A. Noyes has suggested, Kekulé's ring formula for benzene lies at the bottom of much of the coal-tar industry. Or it may directly start into being a new industry, like Acheson's discovery of carborundum. Again it may result in improving or revolutionizing the old methods of an industry, like Bessemer's discoveries in steel-making.

To foster such work in every possible way and to spread among scientific co-workers and mankind generally the knowledge of such inventions is the best work that a scientific society can perform.

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## CRYOLITE AND ITS INDUSTRIAL APPLICATIONS.[1]

By Alfred S. Halland.

Received December 1, 1910.

While the mineral cryolite has become almost indispensable in certain branches of the chemical industry, yet it cannot be called one of the important minerals in a commercial sense. It is, however, of interest in a chemical and geological sense. In the following paper the writer will try to outline its general characteristics, its applications in the arts, and finally the methods used in bringing it from its crude state into the almost chemically pure condition in which it is brought on the market.

*I. Source.*—The only place in the world where cryolite has been found in considerable quantities is at Ivigtut, an esquimaux hamlet on the southern coast of Greenland at 61° northern latitude. Minerals of a similar composition have been found at Pike's Peak, Colo., but not in quantities to pay mining. Cryolite was first introduced to the scientific world about the year 1800. The esquimaux at Ivigtut had for centuries back known and valued the beautiful white mineral; they used to grind it and use it for snuff. The first imperfect analysis of it was made by the Danish chemist, Abildgaard, who gave it as containing acid of fluorspar, alum and some plant ash (potash). Its true constitution as a double salt of sodium fluoride and aluminum fluoride, $3NaF.AlF_3$, was first established by the analysis made by Berzelius in 1823. The first crystallographic description of the mineral was given by the Portuguese mineralogist, D'Andrada e Silva; he gave to the mineral its present name, cryolite, which is Greek for ice stone, because pieces of cryolite when viewed under water show a strong resemblance to ice. The crystal form is monoclinic and the hardness relatively low, 2.5. Cryolite is difficultly soluble in water (about 1:3000) but quite soluble in warm solutions of aluminum salts, preferably aluminum chloride. This furnishes an excellent means of separating it analytically from quartz. When finely powdered cryolite is stirred in water it appears to dissolve therein; this is due to the fact that cryolite has almost the same refractory index as water. In its natural state cryolite is more or less heavily intermixed with other minerals, mostly ironspar (siderite), zinc blende, galena, chalcopyrite and hagemannite. The color of the cryolite itself is generally a pure white but sometimes smoke-colored pieces are found, and it never fails that in the smoke-colored parts are found well-developed crystals of red fluorspar. This red fluorspar was first examined by Julius Thomsen, who obtained interesting results. He found that it contained a small quantity of yttrium

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[1] Paper read before the Western New York Section of the American Chemical Society at the University of Buffalo, Nov. 3, 1910.

fluoride and further that by heating it gave off helium while emitting a yellow light. Radium was not known at that time, but after its discovery this red fluorspar was tested for radioactivity and found to possess it in a much smaller degree, however, than pitchblende. This explains why helium is obtained by heating the fluorspar. The dark color of the surrounding cryolite is the effect of the emanation on the mineral. Both the coloration and the radioactivity disappear on heating to a low red heat.

The foreign minerals following the cryolite are shortly described. Its constant companion is the ironspar which at times makes up 20 per cent. of the entire weight. It is found in very well-developed, beautiful brown crystals, at times very large. Next in quantity follow galena, zinc blende and chalcopyrite. Quartz is always found in small quantity and is, of course, hard to distinguish from the white cryolite.

The cryolite deposit at Ivigtut is practically one solid mass, located right under the surface of the earth. The length of the deposit is about 600 feet, running parallel with the coast, and the width about 200 feet. The depth of the mine which is nothing but an open cut is now about 150 feet. While the surface extension of the deposit as seen is comparatively small, the deposit fortunately widens, the deeper one descends; and the depth of the deposit is unknown. There is therefore no reason to fear that the mine will become exhausted for a long time. Considerable discussion has been going on as to the origin of this extraordinary deposit. The theory now generally accepted is that the cryolite is of volcanic origin and at one time was fluid. This idea is strongly supported by the fact that big pieces of granite from the surrounding rock occasionally are found embedded in the cryolite. This excludes the possibility of the cryolite having been separated out of a watery solution, as the granite boulders would have fallen to the bottom in that case. On the other hand, it is difficult to explain the presence of crystallized ironspar, ferrocarbonate, which decomposes entirely at a temperature below the fusing point of cryolite (about 900° C.). One must assume that the cryolite, like other eruptive masses, contained water and carbonic acid gas and was subjected to an enormous pressure. It is therefore reasonable to suppose that the fusing point of the cryolite was considerably lower, and the decomposition temperature of the ferrocarbonate higher. That the cryolite originally solidified at a great depth and later came to the surface can be judged by the nature of the surrounding rock of granite and porphyry.

*II. Cryolite Soda.*—The first successful attempts to utilize cryolite were made by Julius Thomsen in 1852. He tried to win from it soda and alum—two materials which were at that time considerably higher in price than now. Thomsen found that by heating cryolite with limestone the following reaction took place:

$$Na_3AlF_6 + 3CaCO_3 = 3CaF_2 + 3CO_2 + Al(ONa)_3.$$

When the mass is extracted with water, the sodium aluminate goes into solution, while the calcium fluoride remains undissolved. Now by conducting carbonic acid gas into the sodium aluminate, hydrate of aluminum and soda are formed.

$$2Al(ONa)_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2CO_3.$$

This, the cryolite soda process, was carried out on a large scale in the following manner: The finely ground cryolite which need not be pure (in fact the presence of sulphur compounds which by the subsequent treatment would form glaubersalt would make the soda crystals come out hard and distinct) was mixed with lime and heated in a sort of reverberatory furnace. The mass was leached with water systematically, finally giving a solution of aluminate 33° Bé. strong, into which carbonic acid gas from the flues was led. The hydrate fell out in a granular condition, which made filtration possible. The solution of soda was evaporated to crystallization. Originally the aluminum base was transformed into aluminum oxide but was later worked into sulphate of aluminum. The by-product, calcium fluoride, was dried and sold to the bottle-glass factories. Several cryolite soda plants were built in Europe on the plan of the mother factory in Copenhagen. They were operated with several ups and downs for about 15 years. At that time the Solvay process came into use and soon triumphed over the other soda processes. The rights for the United States were acquired by the Pennsylvania Salt Mfg. Co., which built a plant at Natrona, near Pittsburg, and here the process was worked much longer than in the old world on account of the heavy duty on alkalies in the United States.[1]

*III.* While the use of cryolite for production of soda and alum, therefore, must be said to be a thing of the past, other important applications developed, *viz.*, for opaque glass (so-called milk glass), for the enameling of iron ware and in the metallurgy of aluminum.

In order to produce white opaque glass, several materials, mainly bone ash (calcium phosphate), fluorspar and tin oxide, have been and are still used as an addition to the molten glass. Superior to them all in producing a pure white and uniformly opaque glass is cryolite. The amount necessary is about 10 per cent. of the weight of the glass; it is added to the flux in which it dissolves easily. On cooling the glass the cryolite separates out in minute crystals throughout the mass, which causes the opaqueness.

The enamel industry consumes a great deal of cryolite. While it is useful as an ingredient of the enamel for cast-iron goods it is mostly used for pressed steel articles. The enamel for this purpose is made up from feldspar, quartz, soda, borax, etc., which are mixed together, fused, ground, and stirred to a fine paste with water; this is now applied to the object and fused on in an oven. The above-mentioned materials, however, will produce a transparent enamel through which the dark color of the steel is visible, making the enamel appear a bluish gray (well-known from the "granite" household ware), but if 5–10 per cent. cryolite is added to the enamel flux a pure white, totally non-transparent enamel results. By adding smalt to the flux the well-known

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[1] The writer believes that pure aluminum oxide for the manufacture of aluminum is still manufactured at Natrona by the cryolite soda process.

blue, non-transparent enamel is obtained. Cryolite enamels are not poisonous; this is a feature which strongly recommends their use for kitchen utensils. Fluorspar will, to some extent, produce a similar effect but it renders the enamel difficultly fusible. An interesting substitute for cryolite for use in enamels has lately appeared in Germany. It is sodium fluosilicate, $Na_2SiF_6$, which now can be obtained very cheaply as a by-product from the phosphate fertilizer works. When treating certain natural phosphates with sulphuric acid, silicon fluoride, $SiF_4$, escapes. The German factory law would not permit this gas to escape into the air and the fertilizer works were compelled to absorb it in water. From the watery solution of $H_2SiF_6$ thus formed the sodium salt is obtained by neutralization with caustic soda. The sodium fluosilicate mixed with bauxite is sold as a substitute for cryolite. It does not do as good work, however, and does not effect any considerable economy as it loses 30–40 per cent. of its weight on fusion.

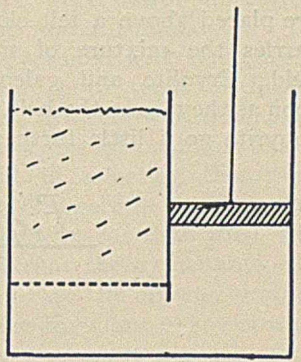
The role of cryolite in the aluminum production after Héroult's method is well known. Here the fused cryolite forms the dissolving bath for the bauxite, which is the actual electrolyte. As the electrolysis proceeds, bauxite is added to the bath. The amount of cryolite used for the production of 10 kg. aluminum is about 1 kg. It is important that the cryolite for this purpose should be as free from quartz as possible as the electric current separates silicon from any silica present which alloys itself to the aluminum, making it brittle.

One more application of cryolite should be mentioned, namely, for the production of white Portland cement. The following is an extract from the *U. S. Geological Survey Report*, **1909**: "The white cement.... is not used as a structural cement, but rather for ornamental purposes. Raw materials suitable for white cement are not widely distributed and must be selected with great care; silica and alumina must be properly proportioned and iron oxide must not be present to exceed 0.2 per cent. ....With the use of materials low in iron it has been found essential to add an iron-free fluxing material which shall perform the function of the iron in effecting combination between the silica and the alumina. In one of the white non-staining cements manufactured in the United States under patent rights, 2 to 5 per cent. of cryolite .... is the material used as a flux."

*IV. Purification of the Cryolite.*—It is obvious that the cryolite as it comes from the mine must be freed from the accompanying minerals before it can be used for any of the purposes mentioned. A rough idea of how this is done will be given in the following:

The first operation consists in breaking with a plain sledge hammer, and already at this point a great deal of pure white material is sorted off. The mass of impure pieces is conveyed to vibrating screens which sort it into 4 different sizes, from the size of a hand to that of a wheat grain. The big pieces down to the size of a walnut are now treated separately; they are placed on a circular anvil, 1 dcm. in diameter, on top of which a mechanically driven chisel is working. Several such chisels are placed in a battery along the same desk. The pure parts are separated in this manner, while the impure parts, still containing considerable cryolite, are mixed with the small material from the vibrating screens and brought onto another set of screens which separate the mass into two sizes, from 14 mm. to 1 mm. and from 1 mm. down to the finest dust. These two products are now worked up separately, but according to the same principle, which is first a separation according to specific gravity and next a magnetic separation.

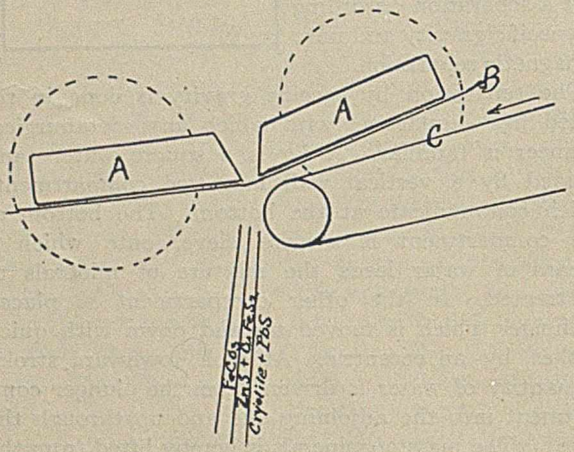
Fig I.



The separation by specific gravity is done in so-called jigs—appliances with which any metallurgical engineer is familiar. A jig is a square water tank divided by a vertical wall into two compartments which communicate at the bottom. The bottom of one compartment is a wire sieve, onto which a stream of water leads the mixture of minerals to be treated. In the other compartment is placed a plunger which is moved up and down with quick strokes by an eccentric. At each downward stroke a quantity of water is driven from the plunger compartment into the adjoining one and up through the sieve. The mass of minerals is hereby lifted from the sieve and left in suspension for a short period, and after a number of strokes the heavy minerals will settle to the bottom while the lighter ones, in our case the cryolite, will gather on top. Several jigs are placed in steps in series and the running water brings the material from one jig to the next and finally off the jig. Two products are ultimately obtained in this manner, one containing almost entirely cryolite and one the gangue minerals with some cryolite. They are both dried and are now ready for the magnetic separation.

Magnetic mineral-separation is based upon the fact that different minerals show a different permeability for magnetic lines of force. If a mass of mineral fragments of approximately the same size is made to drop through a magnetic field the lines of force will concentrate in them in varying intensity according to their permeability (or their "magnetism") and they are consequently attracted more or less towards the poles of the magnet. This causes the curve of their fall to deviate more or less from that of the vertical line determined by gravity, and a separation and collection of the different minerals is thereby made possible. The magnetic ore separators were originally devised and are still mostly used for the enrichment of low-grade magnetite ore. For this purpose a comparatively weak magnetic field is employed on account of the great permeability of the magnetite, but in the case of cryolite-separation a very strong field is necessary. Cryolite, galena and pyrites are totally inpermeable; chalcopyrite and zinc blende possess a very small permeability and ironspar a considerably greater, although much smaller than that of magnetite. The arrangement used in cryolite-separation is roughly sketched in Fig. 2. The two leveled poles A of a very strong electromagnet are placed above a felt cloth, B. An endless belt, C, carries the mixture of minerals into the magnetic field. Cryolite and galena drop straight down as soon as they leave the belt, while zinc blende and chalcopyrite go a little further and drop into a separate slit. The ironspar goes still further and is gathered through a third channel. There is always a small amount of magnetite present, which by and by would stick in a solid mass to the felt cloth and interrupt the work if not removed. This is done by passing the mass of minerals previously through a *weak* magnetic field. The first product from the jigs yields after this separation a pure cryolite, while the second product yields a mixture of cryolite with some galena. A following jigging separates them completely.

Figure 2.



The purified cryolite is either sold in lumps or ground to a fine powder on a chaser mill. A careful grinding allows here a separation from a small amount of quartz still present, as the quartz is not ground so easily and can be removed by a subsequent sifting.

The separated gangue minerals possess some value. The ironspar is sold to steel plants and the galena and chalcopyrite which contain traces of silver and gold respectively go to a smelter.

It would probably not pay to subject a cheap mineral to such a complicated treatment as that above described, but cryolite is relatively high-priced—it sells around $160 per ton. The cryolite-separation as described is to the writer's knowledge only carried out at the "Oresund Chemical Works," Copenhagen, Denmark.

# ON THE INTERPOLATION METHOD OF OIL ANALYSIS.[1]

By J. J. Kessler and G. K. Mathiason.

Received December 14, 1910.

The methods of analyzing oil mixtures may be reviewed under three divisions:

*First.*—Those methods which depend upon a separation of the constituent oils, or their derivatives.

*Second.*—The qualitative identification of one oil in the presence of another, by means of color reactions, odor, etc.

*Third.*—The determination of some of the physical constants of the mixture of oils and the use of such data in drawing conclusions as to the percentage of each constituent present.

Of these three general methods, the first one, by far the most satisfactory in principle, has unfortunately very limited application. A separation of the constituent oils is many times either impossible or impractical.

The constituent oils of a mixture are generally soluble in one another in all proportions at ordinary temperatures, and separation by fractional crystallization is not possible. Again, the oils are more or less decomposed by distillation, and a clean separation is, except in very special cases, impossible.

As an illustration—hydrocarbon oils may be separated from ester oils by saponification, but, of course, the method is limited to those cases where hydrocarbon oils are present.

The second set of methods, the qualitative identification of one oil in presence of another, by means of reactions producing characteristic colors, while of the very greatest qualitative value, has very limited application. Many such color reactions will be recalled.

Among the most valuable are the Liebermann-Storch reaction for the identification of rosin oil, rosin and cholesterol, the Bechi, Halphen and Brullé tests for cottonseed oil; the Villavecchia test for sesame oil, etc., etc.; of very limited usefulness are the color tests with nitric and sulphuric acids.

The only method of perfectly general application, the third set of methods, may be called interpolation methods, because one calculates a percentage composition from certain physical constants of the mixture, after assuming values of the corresponding constants for the pure oils. The inherent weaknesses of such procedure need only a rapid review. The first and greatest difficulty lies in the fact that a commercial oil, whether a mineral, a seed, an animal or a fish oil, has an individual character, depending upon the condition of the source of the oil, the method of obtaining the oil, method of refining, of storing, the age and the conditions under which the oil is kept. The fundamental necessity of exact interpolation is, therefore, lacking. We ought to know the particular constants of the particular oils in the mixture in order to obtain exactness, and this is impossible.

Our literature does not give us the assistance that it should in this respect. It is too general. Lewkowitsch, for instance, will give us constants from

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[1] Read before the St. Louis Chemical Society, May 9, 1910.

different observers, working at widely different periods, on oils of continental or British origin, and which have been obtained by methods differing widely in details. We ought to have, on the other hand, tables showing constants for the oils actually on the American market, which constants have been obtained by standard methods. We are now beginning to get such information.

The cottonseed oil literature is very extensive; so is that of linseed oil, and the government bulletins are of the very greatest service both as to standardization of methods and the compilation of up-to-date analytical results. No doubt, the time is near at hand when we will be able to get the best of such work collected together and easily available.

A second difficulty lies in the fact that the constants of many oils have approximately similar values, while the precision of an interpolation of any sort depends partly upon the condition that one variable changes rapidly for a correspondingly small change of the other.

A third difficulty lies in the very generality of the method. The physical constants obtained may apply equally well to many different mixtures. A gravity of 0.920, for instance, does not define any particular oil or mixture of oils. It must be used with other data in enabling the oil chemist to proceed with the logic he uses in reaching his results.

From the foregoing is seen the difficulty of obtaining an exact analysis by the interpolation method.

On further consideration of the requirements for exact interpolation, we must not forget one very important point, a point next in importance to the requirement of having exact end points. This point is not mentioned nor discussed in works on oil analysis, and while we cannot believe that it does not occur in many places in some of the many papers that have been written on the subject, it is certainly not a part of the general literature.

The requirement referred to is that the form of the functional relationship between composition on the one hand and property on the other shall be known.

Geometrically this means, of course, the determination of the shape of the curve joining the two end points, or, if three oils are present in the mixture, the shape of the surface joining the three end points. As stated, we do not find any explicit statement on this question in the general works on oil analysis. The inference of the chemist is, we believe, that the curve is a straight line.

Stillman[1] gives a formula for calculating the composition of a mixture of two oils, after assuming the kinds of oils present, their Maumené test, and using the observed Maumené test.

This formula is based on the assumption that the temperature rises of a mixture of oils is proportional to the temperature rise of the constituent oils, and the relative amounts present. It is assumed here, therefore, that the relationship is additive, that the law of the mixture of oils, as far as this test is concerned, is a straight line.

We wish to present some experimental data on this point. Our plan of work has been to take certain commonly used oils, make mixtures of them, obtain constants on these mixtures, and plot the results against the composition, in order to obtain an insight into the law of the mixture.

The oils used in this work were castor oil, cottonseed oil, linseed oil, a rosin and a mineral oil. The rosin and mineral oils were selected with reference to their having viscosities similar to those of linseed and cottonseed oils, such oils, in other words, as might be used in the adulteration of linseed or of cottonseed oils. Some care was used in selecting these oils, in order to be sure that the oils were in the first place pure oils, and in the second place, that they were representative oils; that is, that their constants were average constants. In each case the oil was obtained in a barrel quantity, and bore the name of the crusher, or refiner.

The castor oil was a No. 1 castor oil, and was obtained from the Waters-Pierce Oil Company. The barrel bore the label of the Robert B. Brown Oil Company. The linseed oil was obtained from the American Linseed Co., direct from their warehouse. It was designated as "Pure Pressed Raw Linseed Oil—Old Process." The cottonseed oil was obtained from the Proctor & Gamble Co. It was designated as "White Clover Cooking Oil," and was a summer-bleached oil. The mineral oil was obtained from the Waters-Pierce Oil Co. It was designated as "Paraffine Oil." The rosin oil was obtained from the American Naval Stores Co., and was shipped to us direct from Savannah. It was designated as "No. 2 Rosin Oil."

Our method of working was to make up approximately 1000 gram samples, by direct weighing of the constituents. We made seven different mixtures of each set of two different oils. The percentages chosen were 2, 5, 20, 50, 80, 95 and 98 per cent. It will be noticed that our observational points were chosen unevenly along the composition line, in order to crowd our observations near the end points. This was for the purpose of enabling us to study the influence of a small quantity of one oil in another. We made up, therefore, combinations of five oils, two at a time, each of which were made up in seven different mixtures, or seventy different samples in all.

The tests that were studied were as follows: The acid No., saponification No., density, flash test, together with the fire test, Maumené test, and viscosity at 70° F. The saponification No. and viscosity were made in duplicate in each case, and the other tests in duplicate where the results showed a larger accumulation of experimental error than was considered allowable. In some instances where the acid number was very small in both members of a mixture, the determination was omitted for that particular mixture.

The methods used for making the tests named were as follows:

*Acid No.*—Ten grams of the sample were weighed into an eight-ounce oil bottle. 20 cc. 95 per cent. ethyl alcohol were added and the mixture shaken thoroughly. The mixture was titrated with *N*/10

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[1] Edition 1900, "Engineering Chemistry."

potassium hydrate solution, in water, using phenolphthalein as an indicator. Blanks were run on the alcohol and the amount of caustic potash required for neutralization subtracted from the reading for the sample. The blanks did not require more than 0.1 cc. potassium hydrate for neutralization.

The end point taken was that obtained when the pink color persisted after vigorous shaking. The acid number calculated from the burette readings was the number of milligrams of potassium hydrate required to neutralize the acids present in 1 gram of the sample.

*Saponification No.*—Approximately $1^1/_2$ grams of oil were weighed into an eight-ounce oil bottle, the oil being accurately weighed on a chemical balance, using the pycnometer used in the determination of density as a weighing bottle. Duplicate samples were weighed out in each case. 20 cc. alcoholic potash were added and the mixture heated on a water bath at 80° C., from 30 to 40 minutes. The samples were thoroughly shaken several times while saponification was going on. After cooling, the mixture was titrated with $N/2$ hydrochloric acid, using phenolphthalein as an indicator. Two blanks of 20 cc. each of alcoholic potash were run through with the samples each time and the mean of the results used in calculating the potash used in the saponification. The alcoholic potash solution was made up with 30 grams KOH dissolved in a small amount of water, and made up to 1 liter with 95 per cent. ethyl alcohol, and allowed to stand over night. The saponification No. calculated from the burette readings was the number of milligrams of caustic potash required to saponify one gram of the sample.

*Specific Gravity.*—Specific gravity determinations were made in all cases with the commonly used form of pycnometer, holding in each case between 25 and 30 cc. of oil. All determinations were made at 21° C. within a degree on each side.

*Flash Test.*—An open iron cup was used in making this test. The cup held 75 cc. of oil and was filled to within $^3/_8''$ of the top of the cup. The oil was heated at the rate of 3° C. per minute, over a Bunsen burner.

*Fire Test.*—The fire test was taken at that temperature at which the oil first began to burn continuously upon application of the small flame. Both flash and fire tests are recorded in degrees centigrade.

*Viscosity.*—The viscosity was measured in a standard Tagliabue instrument. Readings were made at 21° C., and the temperature of the oil kept in all cases to within $^1/_2$° C. on a side. The figure for viscosity given is that obtained from the number of seconds required for 70 cc. of the oil to run out multiplied by two, this being the amount of oil and the standard method of calculating recommended by the makers. 70 cc. of distilled water ran through this instrument in 23 seconds, at a temperature of 70° F., making the viscosity of water at this temperature 46, with this instrument and method. The temperatures were regulated by pouring warmer or colder water into the jacket surrounding the instrument. All figures given are the mean of two different readings made on the same sample.

*Maumene Test.*—Fifty grams of the sample were weighed into a No. 3 beaker which was placed inside a No. 4 beaker. The larger beaker was prepared by filling the space between the two beakers with a mixture of plaster of Paris and asbestos. After drying, the inside beaker may be removed and replaced by another of the same size. Since many of the samples tested frothed badly, particularly the cottonseed oil and linseed oil mixtures, a much higher form of beaker was used in these cases. Ten cc. sulphuric acid were added to the oil from a burette, during one minute. Stirring was effected by using a simple device, the object being to use the same conditions of stirring as possible during all of the tests. Instead of noting only the maximum temperature reached by the thermometer, we read the temperature each half minute until the thermometer showed a falling temperature. In this way we were certain of the actual maximum rise of temperature in all cases, and were able to observe some interesting facts with reference to the development of heat, by the mixture. The Maumené test is the maximum temperature rise obtained, subtracting from the thermometer reading the temperature of the oil and acid, which was kept at the temperature of the room. In some cases we found that a higher temperature rise may be obtained if the stirring is discontinued after the oil and acid are mixed. We attempted to use in all cases that condition of stirring which would give the maximum temperature rise.

## DISCUSSION OF RESULTS.

*Acid No.*—The acid No. was determined on these mixtures of oils principally as a check upon the composition of the samples. They have not been made in a few mixtures, since some of the oil mixtures contain practically no free acids. These tests bring out the fact that the acid number is accurately determined by the method shown for all combinations of oil, whether they contain large amounts or small amounts of free acids.

*Saponification No.*—These tests were carried out in order to determine principally whether the saponification of a small amount of saponifiable oil is completely effected under the ordinary conditions of the test, when a large amount of unsaponifiable oil is present. The tests indicate that such is the case, and that the saponification number is readily obtained in all sorts of mixtures.

*Gravity.*—Specific gravity determinations were made as a further check upon the composition of the sample. Since the samples were made up by weight, and not by volume, it would not be expected that the curve showing gravity plotted against composition by weight would be strictly a straight line, although it plots nearly as a straight line, since the density of the oils were nearly unity. This is a simple illustration of the fact that additive relationships may not be found in some cases from purely algebraic reasons.

*Flash Test.*—The results on flash tests show very clearly that this phenomenon is not necessarily an additive one. In those cases where there is any great difference between the flash points of the constituent oils, a very considerable curvature is to be found. In the cottonseed-linseed, and cottonseed-castor oil mixtures, where the flash tests of the constituent oils are nearly the same, the curvature is not apparent, and if it exists, lies within the range of observational errors.

*Fire Test.*—These results have not been plotted, but are similar to those obtained from the flash test.

*Viscosity.*—The curves of viscosity show considerable deviations from the additive relationship. We obtained indeed such curves even in these cases where the viscosity of the constituent oils is nearly the same. Nor do we obtain straight lines when we plot fluidity against composition. We believe those results are of interest, as an indication of the fact that neither the viscosity nor the fluidity of such solutions are necessarily additive, even though there is no evidence to indicate that either chemical or molecular compounds are formed.

*Maumene Test.*—Our results on Maumené tests indicate, on the whole, that the results are not additive, but that in mixtures containing a high Maumené test oil and a low Maumené test oil, that the results are greater than calculated from the law of averages at the upper end of the curve and lower than that calculated from the law of averages at the lower end of the curve. In no case were we able to duplicate the Maumené test on any given mixture within a degree, or even within several degrees, when tests were made time after time, or day after day, upon the same sample. We have tried to use every possible precaution with reference to duplicating the conditions of the test time after time, but we have found this test to give most unsatisfactory results, and we consider it almost useless as a quantitative method.

Of the different factors which determine the rise in temperature of a mixture of oil and sulphuric acid, there seems to be quite a few which are beyond the control of the operator, and the result is that the different samples of the same oil mixture will give temperature rises that differ between themselves as much as 5° and even 10° centigrade.

We have found that the rate of stirring has an important influence upon the result, and our experience has been that a method of stirring must be used which differs with different mixtures, in order to get the highest temperature rise.

This seems to be due to the fact that the stirring has two different effects: it tends to mix the oils intimately with the acid, and it also assists in the cooling of the mixture. Consequently, after stirring has mixed the oil and the acid thoroughly, further stirring only assists in the loss of heat by the mixture. This carries with it, of course, the assumption that the oil and acid stay mixed.

The more viscous the oil the greater the tendency to stay mixed. Oils containing castor oil do not require more than a certain amount of stirring. Mixtures containing a large amount of oils of low viscosity require constant stirring in order to keep the acid in contact with the oil.

There are other important factors, however, which influence the development of heat in a mixture of oils and sulphuric acid. The reaction appears to be a function of the temperature itself, which is in its turn a function of the velocity of the reaction. Any condition which influences the initial velocity of the reaction, therefore, has an influence upon the quantity which is under observation, which is the maximum temperature rise.

If the reaction starts off briskly the total rise will be correspondingly higher than is the case where, for some reason, the velocity of the reaction is slower at the beginning.

We think it probable that it is this dependence of the quantity of the reaction upon its own velocity that interferes so seriously with its yielding results which may be duplicated within satisfactory limits.

## SUMMARY OF RESULTS.

Certain tests commonly used in oil analysis (the viscosity, flash test, fire test and Maumené test) have been shown to follow a law of mixtures which is not an additive one, and hence if interpolations are made from the data obtained from such tests, the results will be in error, to a very considerable amount in some cases.

These results call attention to the possibility of many other physical tests being non-additive. They also suggest the possibility that certain chemical tests, in which a complete chemical reaction does not occur, may not be additive.

The saponification No. is shown to be an additive relationship even for small percentages of one oil in presence of another.

The Maumené test as carried out at the present time is incapable of yielding results which can be used in making a quantitative analysis by the interpolation method.

Work is being done at the present time upon the iodine Nos. of these oil mixtures.

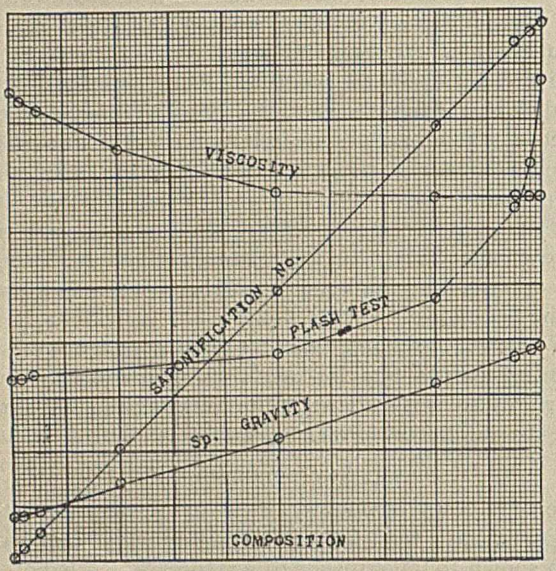
## NOTES ON THE TABULATED RESULTS AND CURVES.

The tabulated results show the figures obtained on all of the tests made.

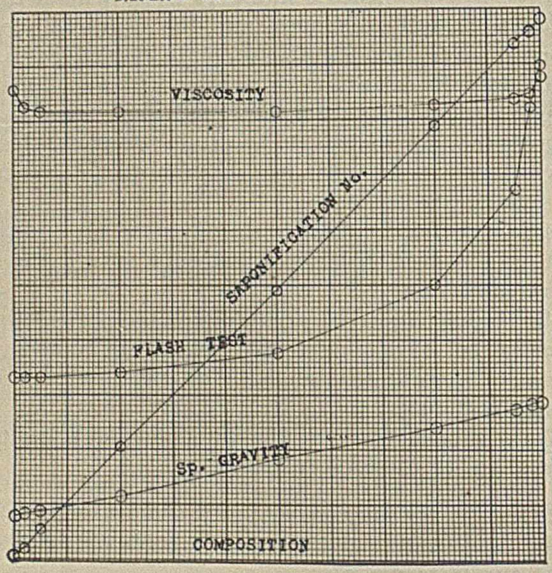
In the case of some of the mineral oil-castor oil mixtures the constituent oils are not soluble in one another at ordinary temperatures. These mixtures were analyzed, however, together with the rest of the samples, the mixture being very thoroughly shaken before the sample for the test was taken out of the bottle. These mixtures are marked in the tables with a star.

The viscosity, saponification No., flash test and specific gravity have been plotted in the curves. Observational points are shown by small circles. In the case of the saponification Nos. the diameter of this circle indicates a difference of saponification No. of 4; in the case of specific gravity the diameter of the circle indicates a difference of specific gravity of 0.0020; in the case of the flash tests the diameter of the circle indicates a difference of temperature of 4° C. In the case of viscosity the diameter of the circle indicates a difference of 4 when castor oil is absent and a difference of 40 when castor oil is present.

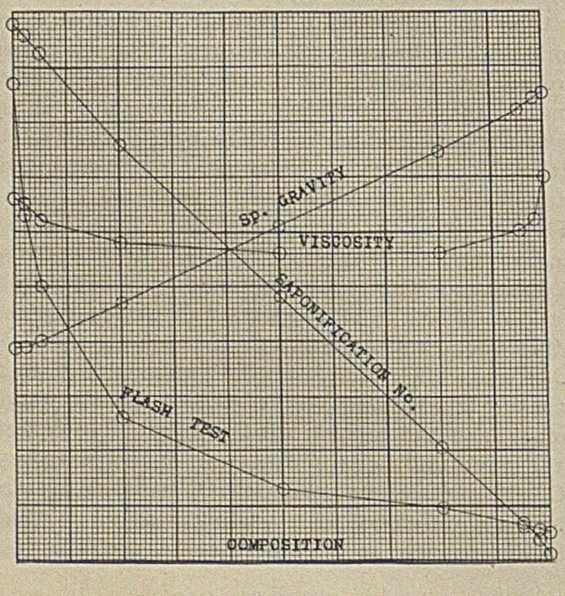
MINERAL OIL-LINSEED OIL



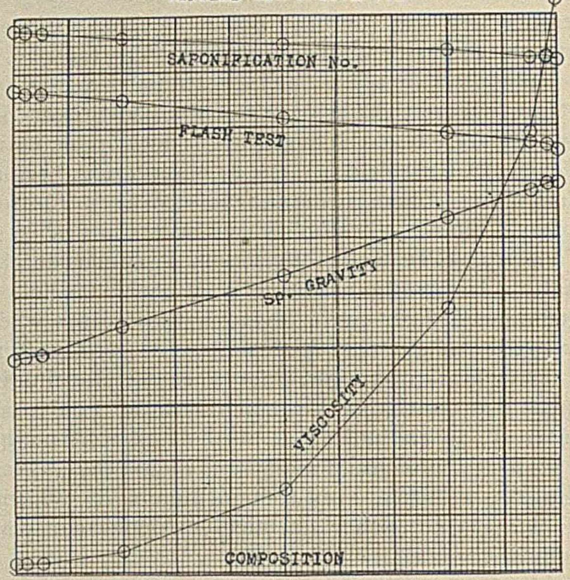
MINERAL OIL-COTTONSEED OIL



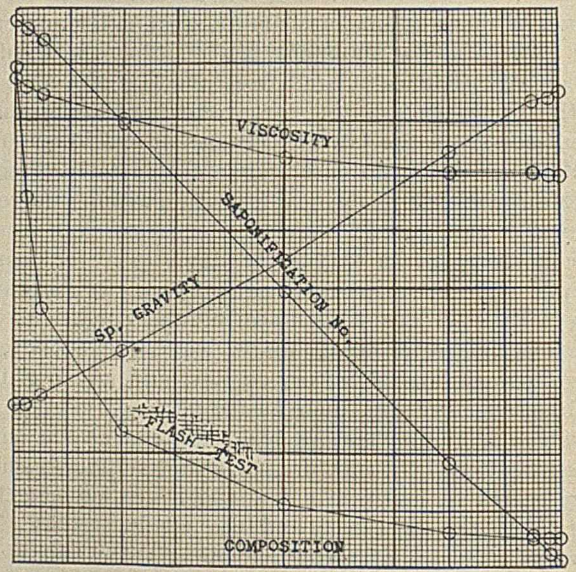
LINSEED OIL-ROSIN OIL



LINSEED OIL-CASTOR OIL



COTTONSEED OIL-ROSIN OIL



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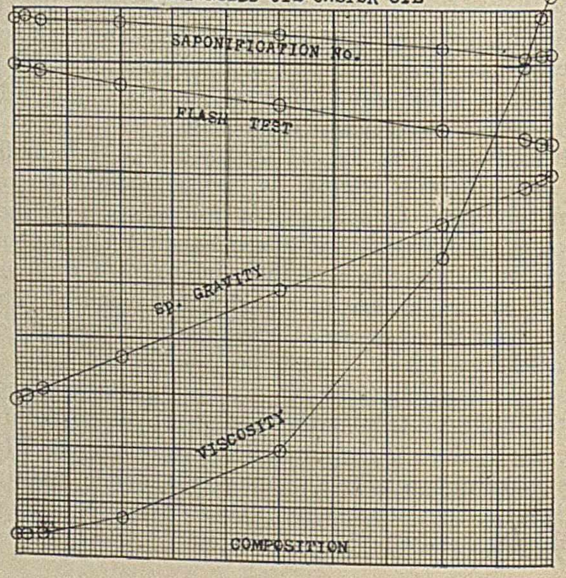

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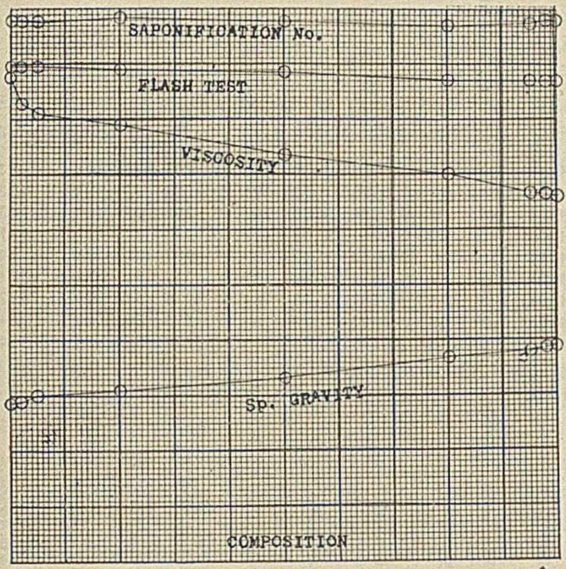
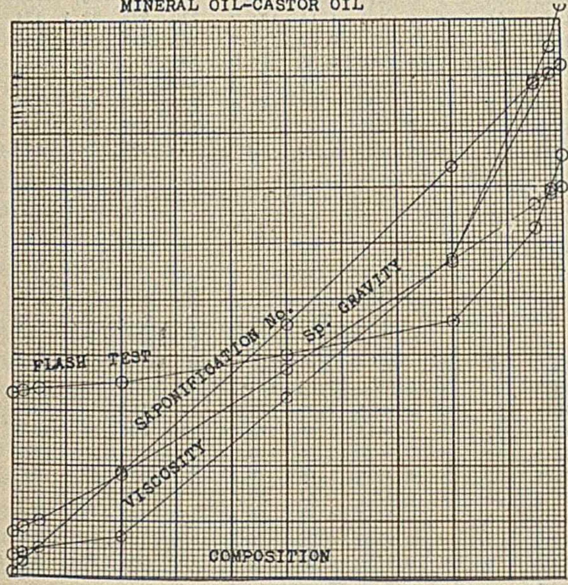
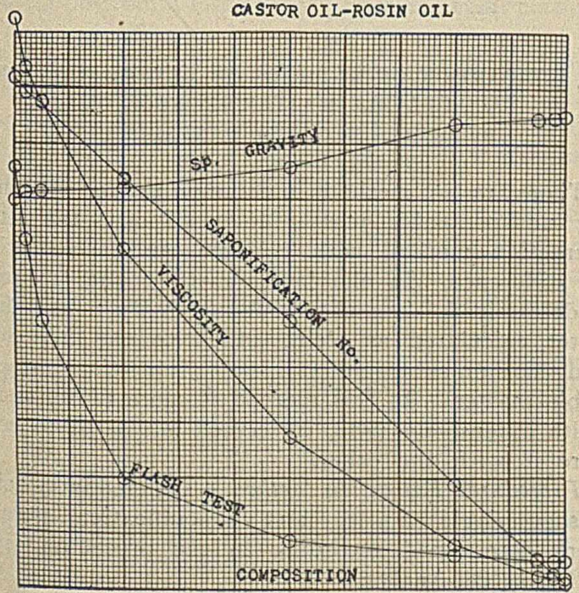


MINERAL OIL-CASTOR OIL



CASTOR OIL-ROSIN OIL



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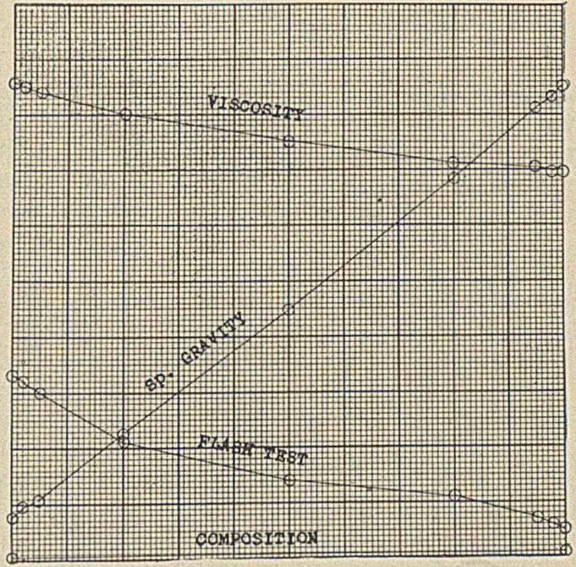

Mineral Oil-Cottonseed Oil.

| Lab. No. | Per cent. mineral. | Per cent. cottonseed. | Specific gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4921 | 100 | 0 | 0.8977 | 0.03 | 1.0 | 186 | 217 | 6.2 | 171.6 |
| 4990 | 98 | 2 | 0.8981 | .. | 3.6 | 186 | 208 | 8 | 164.8 |
| 4989 | 95 | 5 | 0.8986 | .. | 10.5 | 186 | 210 | 11 | 163.6 |
| 4988 | 80 | 20 | 0.9016 | .. | 40.6 | 188 | 213 | 25 | 163.2 |
| 4987 | 50 | 50 | 0.9084 | 0.06 | 98 | 195 | 225 | 50.5 | 162.6 |
| 4986 | 20 | 80 | 0.9140 | .. | 156.8 | 220 | 257 | 63.5 | 165 |
| 4985 | 5 | 95 | 0.9173 | .. | 187.3 | 254 | 330 | 63 | 167 |
| 4984 | 2 | 98 | 0.9183 | 0.08 | 191.4 | 284 | 338 | 68 | 169 |
| 4983 | 0 | 100 | 0.9184 | 0.08 | 196.1 | 299 | 340 | 71 | 175 |

Mineral Oil-Linseed Oil.

| Lab. No. | Per cent. mineral. | Per cent. linseed. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4921 | 100 | 0 | 0.8977 | 0.03 | 1.0 | 186 | 217 | 6.2 | 171.6 |
| 4935 | 98 | 2 | 0.8983 | 0.06 | 4.3 | 186 | 219 | 9.8 | 168 |
| 4934 | 95 | 5 | 0.8992 | 0.06 | 8.7 | 188 | 221 | 12.2 | 162 |
| 4933 | 80 | 20 | 0.9041 | 0.25 | 40.8 | 192 | 225 | 35.5 | 149 |
| 4932 | 50 | 50 | 0.9119 | 0.64 | 96.5 | 195 | 229 | 64 | 136 |
| 4931 | 20 | 80 | 0.9221 | 1.00 | 158.2 | 215 | 243 | 82 | 132.2 |
| 4930 | 5 | 95 | 0.9262 | 1.22 | 189.1 | 249 | 310 | 91 | 132 |
| 4929 | 2 | 98 | 0.9281 | 1.28 | 191.8 | 264 | 326 | 92 | 132 |
| 4810 | 0 | 100 | 0.9286 | 1.30 | 195.7 | 294 | 334 | 101 | 132 |

Mineral Oil-Castor Oil.

| Lab. No. | Per cent. mineral. | Per cent. castor. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4921 | 100 | 0 | 0.8977 | 0.03 | 1.0 | 186 | 217 | 6.2 | 171.6 |
| 4920 | 98 | 2 | 0.8987 | 0.06 | 4.9 | 187 | 219 | 9.5 | 180 |
| 4919 | *95 | 5 | 0.9000 | 0.11 | 10.1 | 188 | 220 | 12 | 190 |
| 4918 | *80 | 20 | 0.9082 | 0.56 | 37.5 | 190 | 223 | 27 | 244 |
| 4917 | *50 | 50 | 0.9273 | 1.25 | 90.3 | 200 | 228 | 49.5 | 745 |
| 4916 | 20 | 80 | 0.9465 | 2.28 | 147.3 | 212 | 257 | 51.5 | 1240 |
| 4915 | 5 | 95 | 0.9569 | 2.66 | 176.8 | 245 | 303 | 58.5 | 1880 |
| 4914 | 2 | 98 | 0.9587 | 2.72 | 180.1 | 259 | 304 | 51 | 2000 |
| 4802 | 0 | 100 | 0.9599 | 2.86 | 183.5 | 271 | 304 | 58 | 2146 |

Mineral Oil-Rosin Oil.

| Lab No. | Per cent. mineral. | Per cent. rosin. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4921 | 100 | 0 | 0.8977 | 0.03 | 1.0 | 186 | 217 | 6.2 | 171.6 |
| 4928 | 98 | 2 | 0.8996 | .. | ... | 184 | 217 | 7.5 | 170 |
| 4927 | 95 | 5 | 0.9006 | .. | ... | 180 | 210 | 7.1 | 168 |
| 4926 | 80 | 20 | 0.9125 | .. | ... | 162 | 196 | 9.8 | 160 |
| 4925 | 50 | 50 | 0.9347 | .. | ... | 148 | 185 | 17 | 150 |
| 4924 | 20 | 80 | 0.9586 | .. | ... | 142 | 177 | 18 | 142 |
| 4923 | 5 | 95 | 0.9712 | .. | ... | 134 | 162 | 21 | 140.8 |
| 4922 | 2 | 98 | 0.9731 | .. | ... | 132 | 159 | 21.8 | 139.8 |
| 4818 | 0 | 100 | 0.9750 | 0.00 | 2.0 | 130 | 158 | 20 | 139.6 |

Cottonseed Oil-Linseed Oil.

| Lab. No. | Per cent cotton-seed. | Per cent. linseed. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4983 | 100 | 0 | 0.9184 | 0.08 | 196.1 | 299 | 340 | 71 | 175 |
| 4998 | 98 | 2 | 0.9188 | 0.08 | 196.0 | 299 | 340 | 69 | 165.6 |
| 4999 | 95 | 5 | 0.9201 | 0.11 | 195.0 | 299 | 340 | 74.5 | 162 |
| 5000 | 80 | 20 | 0.9209 | 0.31 | 197.2 | 298 | 340 | 79 | 158.4 |
| 5001 | 50 | 50 | 0.9232 | 0.64 | 194.4 | 297 | 340 | 77.5 | 146.4 |
| 5002 | 20 | 80 | 0.9268 | 0.98 | 193.9 | 294 | 336 | 97.5 | 140 |
| 5003 | 5 | 95 | 0.9280 | 1.12 | 194.7 | 294 | 337 | 102 | 132.6 |
| 5004 | 2 | 98 | 0.9284 | 1.15 | 196.2 | 294 | 336 | 105 | 132 |
| 4810 | 0 | 100 | 0.9286 | 1.30 | 195.7 | 294 | 334 | 101 | 132 |

Cottonseed Oil-Castor Oil.

| Lab. No. | Per cent. cotton-seed. | Per cent. castor oil. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4983 | 100 | 0 | 0.9184 | 0.08 | 196.1 | 299 | 340 | 17 | 175 |
| 4991 | 98 | 2 | 0.9193 | 0.08 | 197.4 | 298 | 340 | 76 | 176 |
| 4992 | 95 | 5 | 0.9206 | 0.17 | 195.3 | 297 | ... | 65 | 180 |
| 4993 | 80 | 20 | 0.9266 | 0.50 | 194.3 | 292 | 332 | 67.5 | 243 |
| 4994 | 50 | 50 | 0.9392 | 1.54 | 190.3 | 285 | 325 | 73 | 500 |
| 4995 | 20 | 80 | 0.9512 | 2.01 | 185.9 | 276 | 320 | 72 | 1204 |
| 4996 | 5 | 95 | 0.9577 | 2.50 | 181.9 | 273 | 317 | 64 | 1889 |
| 4997 | 2 | 98 | 0.9591 | 2.53 | 183.2 | 271 | 315 | 64 | 2070 |
| 4802 | 0 | 100 | 0.9599 | 2.86 | 183.5 | 271 | 304 | 58 | 2146 |

Cottonseed Oil-Rosin Oil.

| Lab. No. | Per cent. cotton-seed. | Per cent. rosin. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4983 | 100 | 0 | 0.9184 | 0.08 | 196.1 | 299 | 340 | 71 | 175 |
| 5005 | 98 | 2 | 0.9186 | 0.08 | 192.7 | 252 | 338 | 69.8 | 172 |
| 5006 | 95 | 5 | 0.9205 | 0.08 | 188.8 | 212 | 315 | 69.5 | 169 |
| 5007 | 80 | 20 | 0.9284 | 0.03 | 158.1 | 168 | 205 | 67.5 | 160 |
| 5008 | 50 | 50 | 0.9447 | 0.03 | 98.0 | 142 | 165 | 58.5 | 146 |
| 5009 | 20 | 80 | 0.9641 | 0.00 | 366 | 132 | 150 | 45.5 | 140.8 |
| 5010 | 5 | 95 | 0.9731 | 0.00 | 11.6 | 130 | 145 | 35.5 | 141 |
| 5011 | 2 | 98 | 0.9739 | 0.00 | 4.3 | 130 | 143 | 27.5 | 140 |
| 4818 | 0 | 100 | 0.9750 | 0.00 | 2.0 | 130 | 148 | 20 | 139.6 |

Linseed Oil-Castor Oil.

| Lab. No. | Per cent. linseed. | Per cent. castor. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4810 | 100 | 0 | 0.9286 | 1.30 | 195.68 | 294 | 334 | 101 | 132 |
| 4809 | 98 | 2 | 0.9290 | 1.30 | 194.90 | 293 | 334 | 98 | 134 |
| 4808 | 95 | 5 | 0.9294 | 1.30 | 194.40 | 293 | 334 | 100 | 136 |
| 4807 | 80 | 20 | 0.9344 | 1.58 | 192.18 | 290 | 329 | 92 | 178 |
| 4806 | 50 | 50 | 0.9432 | 1.86 | 189.72 | 283 | 320 | 91 | 393 |
| 4805 | 20 | 80 | 0.9534 | 2.36 | 187.20 | 277 | 316 | 73.5 | 1043 |
| 4804 | 5 | 95 | 0.9583 | 2.78 | 184.09 | 274 | 311 | 73.5 | 1677 |
| 4803 | 2 | 98 | 0.9597 | 2.78 | 185.50 | 273 | 306 | 47 | 1946 |
| 4802 | 0 | 100 | 0.9599 | 2.86 | 183.52 | 271 | 304 | 58 | 2146 |

Linseed Oil-Rosin Oil.

| Lab. No. | Per cent. linseed. | Per cent. rosin. | Gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4810 | 100 | 0 | 0.9286 | 1.30 | 195.7 | 294 | 334 | 101 | 132 |
| 4825 | 98 | 2 | 0.9290 | 1.14 | 190.8 | 246 | 334 | 102 | 130 |
| 4824 | 95 | 5 | 0.9301 | 1.14 | 184.7 | 220 | 322 | 93.5 | 124 |
| 4823 | 80 | 20 | 0.9370 | 0.92 | 151.7 | 172 | 215 | 84 | 116 |
| 4822 | 50 | 50 | 0.9510 | 0.58 | 96.0 | 146 | 172 | 86 | 112 |
| 4821 | 20 | 80 | 0.9644 | 0.19 | 40.8 | 139 | 160 | 52.5 | 112 |
| 4820 | 5 | 95 | 0.9720 | 0.03 | 13.6 | 132 | 162 | 31 | 120 |
| 4819 | 2 | 98 | 0.9741 | 0.00 | 7.7 | 131 | 159 | 26 | 124 |
| 4818 | 0 | 100 | 0.9750 | 0.00 | 2.0 | 130 | 158 | 20 | 139.6 |

Castor Oil-Rosin Oil.

| Lab. No. | Per cent. castor oil. | Per cent. rosin. | Specific gravity. | Acid No. | Sap. No. | Flash test. | Fire test. | Maumené No. | Vis. 70° F. |
|---|---|---|---|---|---|---|---|---|---|
| 4802 | 100 | 0 | 0.9599 | 2.86 | 183.52 | 271 | 304 | 58 | 2146 |
| 4811 | 98 | 2 | 0.9611 | 2.86 | 178.82 | 245 | 314 | 56 | 1977 |
| 4812 | 95 | 5 | 0.9613 | 2.69 | 175.26 | 216 | 285 | 54 | 1855 |
| 4813 | 80 | 20 | 0.9620 | 2.36 | 147.57 | 160 | 215 | 56 | 1320 |
| 4814 | 50 | 50 | 0.9658 | 1.64 | 96.37 | 137 | 180 | 57.5 | 647 |
| 4815 | 20 | 80 | 0.9736 | 0.61 | 37.53 | 132 | 165 | 39.5 | 259 |
| 4816 | 5 | 95 | 0.9744 | 0.14 | 10.37 | 130 | 162 | 27 | 142 |
| 4817 | 2 | 98 | 0.9748 | 0.08 | 5.23 | 130 | 162 | 21 | 140 |
| 4818 | 0 | 100 | 0.9750 | 0.00 | 2.0 | 130 | 158 | 20 | 139.6 |

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## A COMPARISON OF METHODS OF DETERMINING UNSAPONIFIABLE MATTER IN WOOL OILS.

By Augustus H. Gill and A. E. Shippee.

Received December 23, 1910.

There are two methods in common use for determining unsaponifiable matter in wool oils, the usual extraction method with gasoline, and the method by difference. In the latter method the free acid is determined, then the combined fatty acids, these latter calculated as olein, added to the free acid, and this sum subtracted from 100, giving the unsaponifiable matter. As this method is more rapid, and is quite extensively used, it seemed advisable to compare it with the other.

*Procedure: Extraction Method.*—The free fatty acids, unsaponifiable matter and saponification number were determined according to the procedure given in Gill's "Oil Analysis."

*Procedure: Differential Method.*—Ten grams of the oil are weighed into a 250 cc. Erlenmeyer flask, dissolved in neutral alcohol, heated to 65–70°, and titrated with *N*/6 alcoholic potash, using phenolphthalein as an indicator. This operation gives the free fatty acids. From this point two processes are available: (1) To the solution of soap and neutral fat is added 25 cc. of *N*/2 alcoholic potash, the solution boiled, 100 cc. of water added and the boiling continued. Finally the excess of alcoholic potash was titrated for with hydrochloric acid. The sum of these two figured as oleic acid and the triglyceride of oleic acid, respectively, gives the saponifiable matter. The unsaponifiable matter is the difference in weight between the sample taken and this amount. (2) After titrating for the free acids, an excess of alcoholic potash is added and the solution boiled. When saponification was complete, the alcohol was removed by adding 600 cc. of water and boiling, water being added as it evaporates. The fatty acids were then precipitated with dilute sulphuric acid. The boiling was continued till the fatty acids formed a clear liquid on top of the aqueous solution. They were then separated in a separatory funnel and washed till the washings were free from mineral acid. The fatty acids were then dissolved in neutral alcohol, heated to 65–70°, and titrated with *N*/2 alcoholic potash. The difference between this result and the free acid figured as the triglyceride of oleic acid and the free acid figured as oleic acid in the saponifiable matter; the difference between the sum of the free acid and saponifiable matter and the weight of oil taken is the unsaponifiable matter.

The extraction method suffers from the disadvantage of incomplete extraction by gasoline, of the solubility of soap therein, from the difficulty of complete removal of the solvent used in extracting the oil, and of losing any volatile constituents of the unsaponifiable matter.

The errors in the differential method come from assuming that all the acids and neutral fats consist of oleic acid and its triglyceride, and in the second modification from a loss of fatty acids in manipulation and their solubility in hot water.

From this it would seem that the method of finding the unsaponifiable matter by difference is sufficiently accurate for industrial purposes and is to be preferred to others on account of the greater rapidity and ease of manipulation.

The following table shows the results obtained by the two methods: the average difference between the two methods is less than the difference between two determinations by the same method, except with oil No. 3.

| Description of oil. | Sp. gr. 15 5° C. | Unsapon. by ext. | Matter by diff. | Sap. value | Per cent. free acid as oleic. |
|---|---|---|---|---|---|
| Scotch wool.......... | 0.908 | 65.7 | 65.4 | 73 | 12.8 |
| Wool oil............. | 0.908 | 91.7 | 90.9 | 17 | 3.3 |
| Oleine, 42 per cent. sapon. | 0.911 | 58.5 | 56.6 | 88 | 41.3 |
| Eng. oleine, 42 per cent. sapon............... | 0.911 | 59.4 | 59.2 | 80 | 40.7 |
| Woololeine, 75 per cent. sapon.............. | 0.910 | 31.2 | 31.0 | 140 | 65.2 |
| Woololeine, 35 per cent. sapon.............. | 0.910 | 65.2 | 65.3 | 69 | 32.6 |

## ON THE LIABILITY OF WOOL OILS TO GUM ON OXIDATION.

By Augustus H. Gill and A. E. Shippee.

Received December 23, 1910.

Besides the determination of the amount of unsaponifiable matter, free acid, and the flash point of wool oils, it is desirable to know if they gum on exposure to the air. An excellent opportunity for this is offered by their exposure on the textile fibers in the course of manufacture.

Richardson and Hanson[1] have used an apparatus in which a current of air was drawn over the hot oil. Although primarily designed for cylinder oils it gives useful information with wool oils. The apparatus consists of a copper oven 10″ x 10″ x 7″, all joints brazed, which constitutes the oil or water jacket. This jacket surrounds a chamber 5″ x 7″ x 1″ in height. The tray measures 4″ x 6½″ x ½″ deep. The inner chamber is surrounded by half-inch copper tube in eight coils; the last coil enters the chamber at the back of one corner and the exit is at the opposite corner diagonally and is connected with a half-inch copper exit tube, which is connected with a suction pump. The air is measured by a meter joined to the first coil of copper pipe surrounding the chamber, so that the meter is at the room temperature. A tube leads from the center of the chamber to the outside, and is fitted with a thermometer. The chamber is closed by an asbestos board outside of which is a copper plate, held firmly over the mouth of the chamber by two thumb-screws. Procedure: ten cc. of the oil are placed in the chamber in a shallow pan 4″ x 6½″ x ½″. Air at 100° is drawn over the oil at the rate of from 3 to 5 cubic feet in four hours, which was the length of a run. The tendency of an oil to oxidize and gum is indicated by its increase in viscosity.

The pans first tried were made of tinned iron. These were unsatisfactory because the metal was so thin that a level surface could not be obtained and consequently the oil did not cover the bottom of them in an even film. By using a pan made of iron about 1/16″ thick which had a level, rigid bottom, this difficulty was removed. The machine was leveled by placing 10 cc. of oil in it and, after allowing it to stand for an hour, noting at what point the bottom was not covered by oil. After one or two trials the apparatus could be adjusted so that every part of the bottom was covered with a layer of oil. Since there are 168 sq. cm. area, 10 cc. would form a layer 0.06 cm. thick; therefore, the apparatus was considered level enough when this condition was reached. In order that the pan might be placed in the same position each time, a mark was made on one corner and it was placed against two sides of the chamber, always having the marked corner opposite to the one touching the sides.

In order to test the viscosity after oxidation a special form of apparatus was necessary, the amount of oil oxidized being far too small for the ordinary forms. The only method which seemed feasible was that of allowing the oil to flow through an orifice. A tube

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[1] *J. Soc. Chem. Ind.*, **24**, 315 (1905).

was tried, surrounded by water at 100°, having a capillary sufficiently large to allow a stream to flow. This was unsuccessful because, when the oil became more viscous after oxidation, the stream would change to a drip and this would spoil the determination. If the size of the orifice were increased sufficiently to allow a stream of the more viscous oil to flow, the less viscous oil would run out so fast that the time could not be taken with accuracy. It was necessary, therefore, to depend upon a drip entirely and use a lower temperature.

The apparatus, which was finally used for testing the viscosity and which gave very satisfactory results, consisted of a glass tube about 80 cm. long and 3 mm. in diameter placed in an ordinary condenser jacket. The lower end of this was reduced to a capillary by placing it in the flame of a Bunsen burner and slowly turning, allowing the edges to run in towards the center. It was found that in this way a very smooth, round capillary of any size desired could be made, the size used being approximately 0.3 mm. in diameter. Two marks 25 cm. apart were made on this tube by placing narrow strips of pressure tubing on it, the lower mark being placed 25 cm. from the capillary. A temperature of 25° C. was maintained by a water bath circulated through the condenser by means of a circulating pump. The tube was filled to a point 10 cm. above the upper mark by placing a piece of rubber tubing on the upper end of it which projects above the condenser jacket and drawing the oil up through the capillary by suction. The time required for the oil between the two marks to run out was taken by a stop-watch. For the first two or three trials this varies slightly but finally reaches a constant value which can be checked to two-fifths of a second. This apparatus could be standardized against water or olive oil, but, since only the increase in viscosity is desired, this is not necessary.

By lengthening the time or increasing the temperature, the difference in viscosity can be increased. It was found, however, that when the differences in viscosity were much greater than those obtained, the results were very unsatisfactory, for the reason that the change in the time required for the given volume to flow out through the capillary was out of all proportion to the increase in viscosity. In such a case, the oil would run out comparatively fast at the beginning but would suddenly slow down and in many cases stop entirely; the results would vary from one or two seconds to any value whatever.

The table shows that the increase in viscosity is greatest when the oil contains the greatest amount of saponifiable matter. It is not, however, proportional to the amount of saponifiable matter present. In oils No. 1 and No. 6 which contain approximately the same amount of saponifiable matter, the difference in the change of viscosity is 14.3 per cent. In oils No. 3 and No. 4, which also contain about the same amount of saponifiable matter, the difference in the change of viscosity is 7.8 per cent. In both these cases the oil which has the higher iodine number has the greater increase in viscosity, thus indicating that oils containing more of an unsaturated constituent would be more liable to oxidize, which is in accordance with the fact. It is possible that the conditions under which these experiments were carried out were such that only the unsaturated parts of the oils were oxidized, the unsaponifiable part remaining unchanged. If this were the case, it would be necessary to get a greater increase in viscosity by raising the temperature or lengthening the time, which would require a different method of measuring the viscosity.

The results obtained are shown in the table below, the oils used being the same as those in the preceding paper.

| Description of oil. | Viscosity in seconds before heating. | Viscosity in seconds after heating. | Per cent. increase of viscosity. | Iodine number. | Unsaponifiable matter. | Free acid. | Flash, °F. |
|---|---|---|---|---|---|---|---|
| Scotch wool | 12.0 | 16.2 | 35.0 | 38 | 65.5 | 12.8 | 306 |
| Wool oil | 14.4 | 15.0 | 4.2 | 27 | 91.0 | 3.3 | 340 |
| Oleine, 42 per cent. sap | 17.2 | 24.8 | 44.2 | 58 | 57.5 | 41.3 | 325 |
| Eng. oleine, 42 per cent. sap | 19.2 | 26.2 | 36.4 | 51 | 59.3 | 40.7 | 335 |
| Wool oleine, 75 per cent. sap | 13.4 | 24.6 | 83.5 | 140 | 31.1 | 65.2 | 346 |
| Wool oleine, 35 per cent. sap | 14.4 | 21.6 | 49.3 | 46 | 65.3 | 32.6 | 327 |

The first and last oils contain the same amount of saponifiable matter; this is 12.8 per cent. free acid in the first oil, and nearly all free oleic acid (31 per cent.) in the last oil; the change in viscosity is 35 per cent. in the first oil and 49 in the last. It would seem that the change is not wholly due to the free oleic acid and that the first oil is to be preferred. A similar condition prevails with oils Nos. 3 and 4, except the fatty acid contents are practically the same; No. 4 shows 7 per cent. less viscosity after heating, and is to be preferred on this account.

It is worthy of notice in this connection that the iodine number gives information of almost identically the same value, hence it would seem that it might be said, in selecting a wool oil, other things being equal, particularly the free acid and unsaponifiable matter, choose that one having the lowest iodine value.

The flash points were taken as an additional criterion.

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## THE EXACT ELECTROLYTIC ASSAY OF REFINED COPPER. 1. STANDARD METHOD. 2. RAPID ASSAY BY ROTATION OF THE ELECTROLYTE IN A SOLENOID.

By George L. Heath.

Received December 20, 1910.

Prof. F. C. Frary[1] has described an apparatus which assures a very rapid deposition of metals by surrounding the beaker with a coil of insulated copper magnet wire through which a current is passed, making about 500 turns, and thus producing a magnetic field within the solution.

The lines of force passing from anode to cathode are constantly diverted in one direction by the pull

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[1] *J. Am Chem. Soc.*, **17**, 395; *Z. Elektrochem.*, **23**, 358.

of the outside current, causing a rapid rotation of the solution itself.

This discovery was given to the writer by Mr. Zimmerschied, of Michigan University, and before the appearance of Prof. Frary's notable paper. We constructed rotary devices, and the data to be recorded show our standard slow method which has been adopted, since 1897,[1] in several large plants together with the development of the solenoid with the aid of the author's assistants and the experience of Mr. W. H. Bassett and assistants, of the American Brass Co., as communicated by him.

*Discussion of the Theory.*—The prior discovery was made by the latter that copper, containing as high as 0.1 per cent. of arsenic, would give a pure deposit in a very short time with the rotary device, in the special acid "stock" mixture devised by us for the standard assay of 5 grams of refined metal.

The principle has been extended, by the writer and assistants, to the deposition of pure copper in the presence of 0.5 per cent. of arsenic, and even to the assay of 3 grams of Whitneyite, containing 10 per cent. of arsenic.

We have, since that time, perfected the slow assay with stationary electrodes, so that copper containing as high as 0.5 per cent. arsenic can be properly deposited by the electric current in about 16 hours from a 3.5- to 5-gram sample, provided that no more than a trace of antimony is present and the acid stock solution is increased one-half, or more, to hold back the impurities.

In the case of such impure material, it is advisable, in order to be sure that the deposit is strictly pure, to dissolve the cathode copper by placing the plate in a tightly covered beaker in a fresh lot of diluted acid mixture, and to redeposit the copper on the same cathode, and reweigh it.

Recently, Mr. W. C. Ferguson,[2] of the Nichols Copper Co., has given an excellent method for the assay of blister and converter material, in which the operator is directed to take a large quantity (80 grams, or more) in order to eliminate errors of sampling such material, and to dissolve and divide this sample volumetrically, checking each set of assays against a blank assay of analyzed refined metal, run at the same time, instead of making a chemical test for the completion of the electrodeposition.

This paper is, however, written, primarily, on the analysis of refined metal, for which a more exact method of getting the weights and estimating the end-point is considered necessary.

The advantage of the solenoid over any mechanical device for the rotation of electrodes[3] is due to the prevention of loss by the spraying from the anode, as the beaker can be covered with a double pair of split watch-glasses. The arsenic is held back, the moderate heat of the coil assists deposition, and the temperature can be controlled by changing the size of wire, and by introducing a water circulation between the beaker and copper cylinder. Results obtained with the rotary device average from 0.003 per cent. to 0.01 per cent. higher than with the 16-hour assay of refined metal (averaging 0.007 per cent. on pure copper), and this is due to a trace of platinum which is carried over from the anode, under the influence of heat, *nascent nitrous acid*, and high current.

If the cathode is dissolved in very dilute acids, the Pt may be filtered out, weighed and deducted from the total deposit.

The explanation of the remarkable purity of the cathode deposit may be found in the fact that the solution becomes pretty warm and more oxidizing, and that the time is too short to permit the reduction of much nitric acid to ammonia, the solution after removal of copper having been found to be much more acid when the metal has been rapidly deposited with high current in the rotary solenoid and on gauze cathodes.

### SAMPLING.

This procedure varies with the conditions in different works, but it is easy to get a good sample of a casting of refined metal by drilling properly spaced holes half way through from top, side and bottom, having first started the holes with a little larger drill, just enough to remove the surface oxide.

If the metal is very pure it is not necessary to drill so deep, not over $^1/_2''$ to 1 inch.

The drillings are cleaned from any trace of dust, tested with a magnet, and tightly bottled.

From this, two samples of 5 grams can be taken with a spatula that will check within 0.01 per cent.

*1. Details of Standard Slow Method.*—A 5-gram sample has been adopted by ourselves and at several other plants, because it eliminates errors of sampling the bottled drillings in the case of refined metal, and is the largest amount of material which can be started at close of business and taken off and weighed the next day before dinner-time without oxidation from too large a current.

Assays must finish, under the conditions described, in 16 to 18 hours, and *without any* more than a trace of preliminary gassing at the cathode, or be rejected.

This theorem goes farther than the requirement of other laboratories, but has been proved that we can thus absolutely prevent an occasional oxidation, or absorption of hydrogen, which can not be detected by any marked change in color, but which may amount to 0.02 per cent. by weight.

The assays are started with a current whose normal density, counting both sides of the cathode, is 1 ampere per 100 sq. cm., and in the morning as soon as the liquid is colorless, the split watch-glasses, covering the beaker, are washed down with a fine jet, and the current reduced to 0.5 ampere. If assays have to go more than 18 hours and the cathode shows bubbles of gas, the current is cut to 0.25 ampere to avoid oxidation or hydrogen absorption.

The sample is weighed into a lipless beaker, about $4^7/_8$ inches high, and $2^1/_4$ inches in diameter outside, across the bottom, and of 300 cc. capacity, which can be obtained from Eimer & Amend, New York.

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[1] *Trans. A. I. M. E.*, **27**, 390 (1897). *J. Am. Chem. Soc.*, **26**, 1120 (1904).

[2] THIS JOURNAL, **2**, 187 (1910).

[3] *Eng. and Min. J.*, **89**, 89 (1910).

In the slow method, chemists use the foil, plain or corrugated. The cylinder is 2 inches (or 5 cm.) high and the closed cylinder has a total surface of 150 sq. cm. The cylinder, opened on one side, which the writer prefers for the ease and quickness with which it may be withdrawn from the solution and dropped into a beaker of water, is 100 sq. cm., counting both sides and the stem extends 12.5 cm. above the cylinder.

The sample of drillings is heated on a steam plate, just *below the* boiling point, with a mixture of exactly 7 cc. of C. P. nitric acid (sp. gr. 1.42), 10 cc. of sulphuric acid (sp. gr. 1.84), and 25 cc. of distilled water, with the beaker tightly covered until solution is complete, as can best be determined by holding the beaker over a white paper.

The solution is brought to a total volume of 120 cc. before electrolysis. When the deposition is thought to be complete, 1 cc. of liquid is withdrawn with a glass medicine dropper, placed in the cavity of a white porcelain tile, and treated with a few drops of freshly prepared hydrogen sulphide water.

Any copper over 0.000005 gram will show at once, and is easily distinguished from the yellow of arsenic which would show later.

After years of experiment, we have found that the proportion of acids given produces exactly the right equilibrium of the acid ions in the solution at the completion of the assay, preventing the deposition of the arsenic if the amount of total acid is increased with the arsenic.

In practice, some works, like ourselves, make up a dilute acid, mixed, "Stock Solution" and run it from a large burette.

For 5 grams metal, containing less than 0.03 per cent. arsenic, the "Stock Solution" required would be 40 cc.; 0.03 per cent. to 0.100 per cent. arsenic, 50 cc.; for 0.11 per cent. to 0.500 per cent. arsenic, 60 cc.

It is found to facilitate the instantaneous removal and washing of the cathode without loss, if the beakers are arranged in a row under a vulcanite plate $^{1}/_{4}$ inch thick and perforated with one small hole for each wire stem to make connection with the split, brass terminals (which rest in pairs about $^{15}/_{16}$ inch apart from center to center) and are perfectly protected by the plate from acid fumes.

The under side of this strip, or shelf, is 12$^{1}/_{2}$ inches from the table, and the beakers stand on double-headed, turned wooden spools, 6 inches high. When an assay is finished, the spool can be slipped aside, and with one motion the beaker can be lowered, and a beaker of distilled water raised to cover the electrode and remove acid before it is disconnected.

The cathode is then washed well with a jet, the water removed by pouring a lot of clear 94 per cent. alcohol over the plate, and the little that remains after draining a moment is then burned off and the plate carefully passed across the flame of the lamp to be sure that no trace of liquid remains between the stem and the cylinder.

The electrodes are cleaned, heated, and weighed before use, allowing the same length of time for cooling before weighing, and the weights should be compared very carefully, and regularly, with a standard set.

The foregoing claims for the deposition of pure copper, either with the slow method or the "rotary," do not strictly apply to copper containing more than a trace of antimony, selenium or tellurium, in which special methods of preliminary purification of electrolyte are employed,[1] or a "dope" may sometimes be used as recommended by the chemists of one of the Tennessee copper companies.[2]

To relieve any doubt as to the purity of the copper deposits, in the case of material carrying over 0.1 per cent. arsenic, the cathode can be redissolved without loss by placing the cathode copper in 40 cc. of acid "Stock Solution" diluted to 120 cc. with water, allowing it to stand on the steam plate just below boiling for about an hour.

The beaker must be carefully covered with a glass cover, perforated near one edge with a small drilled hole just large enough to pass the stem of the electrode. If an assay was allowed to boil, any steam which raised the cover would cause a certain loss of copper solution by spraying.

Check results should agree within 0.01 per cent.

It will be noted that, whereas Mr. Ferguson recommends the previous removal of silver from converter metal when aliquot portions of a large sample are volumetrically taken, we find it better with standard refined metal to deposit the silver with the copper, and determine silver by a special assay if required, since weighing, even with the elaborate precautions sometimes adopted, is more accurate than measuring.

In the case of refined copper, we must also have an absolute test of the completion of the deposition, which is obtained by taking out 1 cc. of the electrolyte, when the assay is thought to be finished, by means of a glass medicine dropper, and treating it on a white porcelain tile with a few drops of freshly prepared water solution of hydrogen sulphide.

If the estimation of the arsenic is desired, the electrolyte from a 5- or a 10-gram assay can be used for the purpose, with certain precautions to be described in a paper on the estimation of the arsenic group.

Some works find the 110-volt direct lighting current to be the most satisfactory source of electric power, which is reduced by small rheostats, in series with each group of 5 or 6 assays, or by a bank of incandescent lamp sockets, into which lamps of different candle-power can be inserted to vary the current.

Where the current is alternating, recourse is had to small "motor-generator" sets, rectifiers, for the purpose of charging large storage batteries, which give a much steadier current than very small machines.

2. *Rapid Assay by the Rotation of the Electrolyte.*—Rotation in a magnetic field offers great possibilities for special rapid work where results are desired at once on copper or slags containing arsenic and antimony.

The principle has been somewhat discussed and so

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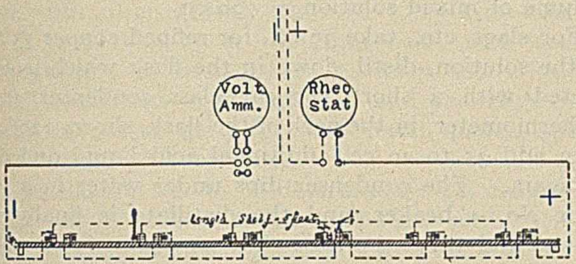
[1] *Trans. A. I. M. E.*, **27**, 390 (1897); *J. Am. Chem. Soc.*, **26**, 1120 (1904).

[2] *Eng. and Min. J.*, **89** (1910).

a description of the simple design we have adopted will be given.

There are two or three elaborate forms of these solenoids on the market already, one being made in Detroit, which have arrangements for raising and lowering both electrodes, and are mounted in pairs on a small marble slab. Some members of the Society may be using this type.

The pattern we use has been made in two sizes: the first to accommodate the battery assay beaker described, and a very large size, which will take a 500-cc. or even 750-cc. beaker, for the removal of larger quantities of copper, up to 50 grams, in a complete analysis of the metal. The best results have been obtained by winding 500 turns of No. 13 B. & S. gauge magnet wire upon a copper cylinder of a diameter a little larger than the top of the beaker, as specified in the sketch, and made of metal $^3/_{32}$ inch thick.



The cylinder is brazed to a water-tight joint, at the top and bottom, to thin plates of soft $^3/_{32}$-inch steel, which complete the spool, holding the coil of wire.

At first a thin shell was placed around the outside of coil after winding, to prevent magnetic leakage, but it was found that this confined the heat too much, and was not necessary.

A hole is bored in the upper steel plate of a size equal to the inner diameter of the cylinder and a 1-inch hole through the bottom plate for ventilation, or for the insertion of a stopper and glass tubes for water-cooling.

It is necessary to complete success with the rapid method to make use of a gauze cathode, weighing 16 to 17 grams, made of gauze, measuring about 17 meshes to the linear centimeter or 40 meshes to the linear inch, and wire bound for strength.

A closed cylinder to fit inside the beaker loosely would have an area, counting both sides of 150 sq. cm., but for the ease and quickness with which it may be withdrawn from the solution, the writer prefers the cheaper form open on one side, having a total surface of 100 sq. cm.

The copper is prepared for electrolysis exactly the same as in the standard method, but there is a limit as to the amount of acid "Stock Solution" which can be used.

If over 50 cc. are present in the 5-gram assay, the heat and strong current will finally cause the metal to redissolve from the cathode.

When the test is finished, as shown by the hydrogen sulphide test, the electrode is quickly withdrawn, or the liquid is siphoned out while a stream of fresh water is allowed to flow in.

The wire coil may be in series with the assay, or a set of wire coils in series with each other may have a current sent through them from an independent switch.

We find it advisable to use about the same amperage in the assay as in the coil, and a current N. density on 100 sq. cm. = 6 amperes will complete the deposition of 5 grams of metal in two hours, the amperage being cut, however, to 2 amperes, as soon as the solution becomes colorless and the cathode shows a little polarization, which requires about 70 minutes.

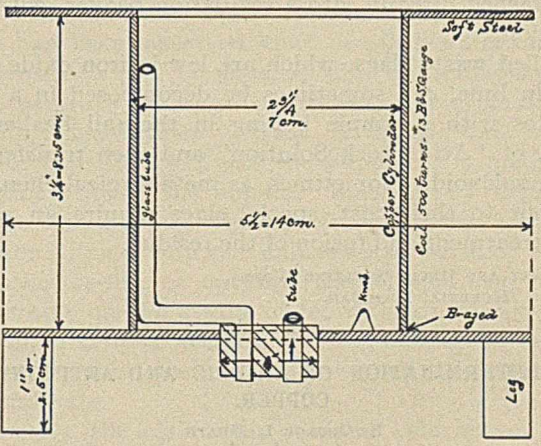
The writer prefers, nevertheless, to employ only $4^1/_2$ amperes, as there is not so much heating and oxidation effect, and the same current can be maintained throughout, completing the assay in $2^1/_2$ hours.

The double pair of split watch-glasses, used for a tight cover, are washed down as soon as the solution is colorless, and in about half an hour thereafter a test is made of the solution.

According to theory, $6^1/_2$ amperes would deposit the metal in about 39 minutes, but the removal of the last traces requires a long time.

The assay must be sharply watched, and the cathode removed as soon as the last trace of copper is out, or a difference of a few minutes may permit a slight oxidation of the deposit.

In very accurate work on extremely arsenical metal, the cathode can be redissolved with the precautions to avoid loss by spraying described in the first method and the deposition repeated in the fresh acid solution.



A trace of platinum will appear in the solution on dissolving the cathode in dilute mixture, and can be filtered out and deducted if desired.

This trace of platinum would interfere with the direct estimation of traces of arsenic in the copper-free electrolyte, unless removed.

*Rotary Apparatus Has Been Made in Two Patterns.*—Some prefer to make the frame 12.5 cm. (= 5 inches) high, and 12.5 cm. in diameter, but the dimensions in small sketch permit a better inspection of the liquid and concentrate the effect on the lower half of the beaker. A small glass overflow tube, as shown, will permit the regulation of the heat, but water circulation should not be employed in the regular battery assay with small apparatus as the heat, if not too near the boiling point, is one factor in holding the arsenic in solution.

*Rapid Assay of Copper in Furnace Slags.*—Thorn Smith[1] and others have improved the methods of assay of reverberatory and waste cupola slags containing such a large amount of iron that the old ammonia precipitation (Heine's blue test) will not yield all the copper.

The rapid electrolysis by rotating anode[2] or by the solenoid is far preferable, and the latter device is the best of the two, as we use it.

Two and five-tenths grams of waste slag, or 1 to 2 grams of richer slag or ore, are weighed and placed in a No. 4 porcelain casserole, moistened and treated with 15 cc. of strong nitric acid and boiled one minute to decompose it, but not long enough to burn on the bottom.

Most slags decompose well if the slag has been chilled by granulating in water at the furnace. Then add 10 cc. of concentrated sulphuric acid and boil to dryness over a gauze, but stop just before the sulphuric acid begins to fume. This allows a trace of nitric acid to remain, and in presence of excess of iron produces a good deposit in the rotating solution in 30 minutes, with a current whose strength is N. density 100 sq. cm. = $4^1/_2$ amperes, counting both sides of the cathode.

The assay must be watched and split electrode of foil removed promptly.

The gauze cathode will not be necessary except for rich slags, requiring over 30 minutes. The residue in the casserole is treated with water while still hot, and washed directly into a regulation beaker, without filtration.

Chilled waste slags, which are low in iron oxide and high in lime, can sometimes be decomposed in a few minutes with a simple boiling in the tall beaker in 60 cc. of "Acid Stock Solution" and then transferred to the solenoid. Sometimes, as metallurgical chemists find out to their cost, special slags require an aqua regia treatment and fusion of the residue.

CALUMET AND HECLA SMELTING WORKS,
HUBBELL, MICHIGAN.

## THE DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER.

By GEORGE L. HEATH.

Received December 20, 1910.

This paper will summarize the principal methods employed in American foundries and refineries, and include a new rapid method for arsenical metal by direct titration of the electrolyte from battery assays or by titration of a solution of precipitated sulphides of the arsenic group.

The principle of separation of arsenic and antimony from copper is either distillation or gravimetric separation.

*Distillation.*—Two of the largest laboratories in the United States use some form of this method.

If it is desired to estimate the antimony, as well, by evolution, a mixture made something like the following is used as a distilling solution for decomposition of the sulphides of the arsenic group, which are washed into the still with a little strong hydrochloric acid, completing the extraction from the paper with a few cc. of sodium sulphide solution, or the sulphides can be filtered on a felt which is transferred directly.

*A.*—Dissolve 150 grams of C. P. zinc in 140 cc. of hydrochloric acid (sp. gr. 1.2) and 440 cc. of distilled water, evaporate until the bulk is reduced to about 370 cc. Mix this solution with the solution of 100 grams of C. P. cupric chloride, dissolved in 330 cc. of concentrated hydrochloric acid. The total volume of mixed solution = 700 cc.

For slags, etc., take 30 cc., for refined copper 75 cc., of the solution, distil down in the flask which is connected with a short vertical glass condenser, until a thermometer, in the neck of the flask, shows 120° C., then add 35 to 40 cc. additional acid liquid and distil again. The condenser dips under water in a No. 3 or No. 4 beaker, and the distillate is finally removed and titrated with iodine as shown later under the "titration of arsenic."

A clean beaker of water is then placed below the condenser and the attempt is made, I understand, at two laboratories, to recover antimony by a further distillation at 122 to 160° C.

The antimony may be separated gravimetrically by separating its sulphide from the copper by extraction with dilute sodium sulphide solution (sp. gr. 1.08) and from the trace of tin, which is due to reagents and distilled water, by repeated precipitation and filtration in small volume (25 to 50 cc.) of concentrated oxalic acid.

*B.*—The iron precipitate, obtained as described under method *C*, is washed into the Allihn flask, by 100 cc. of strong hydrochloric acid, and then neatly reduced with about 5 cc. of 50 per cent. hypophosphorous acid, and distilled at a temperature below 120° C. The condenser dips under water in a No. 3 beaker, and the distillation is repeated with 50 cc. more of the acid. In the writer's opinion, a third distillation should then be made into a beaker of fresh water, which is separately titrated, and the process continued until the distillate shows no more traces of arsenic than one can always expect from the best acid.

Fifty cc. of concentrated zinc chloride solution are then added (W. H. Bassett's method) and the distillation continued at a temperature above 122° C. to evolve the antimony.

In the writer's experience, this distillation process is uncertain and requires repeated treatments to be sufficiently accurate for refined metal. The following gravimetric methods, accordingly, are to be preferred:

*C.*—Gravimetrically, by separation with large excess of iron salts and ammonia. Place the clean weighed copper drillings in a beaker, and dissolve on a steam plate in strong nitric acid (sp. gr. 1.42).

For refined copper, containing less than 0.03 per

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[1] *J. Am. Chem. Soc.*, **26**, 1647 (1904); also *Eng. and Min. J.*, **75**, 295.

[2] *Eng. and Min. J.*, **89**, 89 (1910).

cent. arsenic, we take 50 grams of copper, and treat with 210 cc. of acid, in a No. 7 beaker, but in the case of more impure material, it is sufficient to take 25 grams, or less, and treat in a No. 5 beaker (capacity 500 cc.) with 110 cc. of acid.

Dilute with water until the beaker is nearly half full, and add, to each assay, a solution of 2 grams of C. P. crystallized ferrous sulphate, which has been oxidized in a small beaker by heating with excess of nitric acid.

Heat nearly to boiling, and add strong ammonia until the iron is precipitated and the copper salts redissolved.

Fifty grams of metal will require about 300 cc. of ammonia. Heat to boiling, settle one-half hour on steam plate, and filter quickly through a 15 cm. washed filter, supported by a platinum cone with coarse perforations. It is necessary to keep the solutions warm to prevent crystallization, and the blue color is washed out of the filter with water made slightly alkaline ($1NH_4OH : 10H_2O$).

If the bismuth is to be determined with antimony, add 2 grams of ammonium carbonate and 5 cc. of saturated sodium phosphate solution to the solution as soon as the iron is precipitated as hydrate.

When the sample contains less than 0.100 per cent. arsenic + antimony, the filtrate is passed through a second filter, to recover any traces of iron mechanically lost in the first washing.

If the copper is more impure than the above limit, make the blue filtrate acid with nitric acid, add 0.500 gram of the oxidized ferrous sulphate, and precipitate and filter again to clear the solution.

Redissolve the large precipitate in dilute sulphuric acid, treat the filter paper with a little ammonia, precipitate again, and pass through the same filter. If a second iron precipitation was made, dissolve this small amount of iron, add it to the blue filtrate from the last treatment of the major precipitate and add excess of ammonia and filter on a small filter.

Combine the two precipitates, dissolving them in hot, dilute sulphuric acid, containing 5 per cent. by volume of hydrochloric acid, and throw down the arsenic, etc., with the last traces of copper, by 15 minutes' cold treament with a stream of hydrogen sulphide.

Allow to stand until granular, and well settled, then, before night, charge again with the gas and allow to settle over night.

In the morning, pass gas again until the solution smells strongly, and filter on a 7 cm. filter, then wash the beaker and tube by rubbing with bits of filter paper. Transfer paper and contents to a small, No. 0 beaker.

By the double gas treatment before filtering, the arsenic is generally brought down with the copper, instead of after it, but the filtrate should be charged with gas again and allowed to stand, until settled, and the operation repeated until precipitation is complete. We dissolve the sulphides of arsenic and antimony with traces of tin by hot digestion with sodium sulphide, using as little as possible, and washing, by stirring and pressure, with slightly alkaline hydrogen sulphide water. Heat and filter again if any copper goes through, add 0.2 gram solid sodium hydrate, or potassium hydrate, and evaporate to dryness on the steam plate, then treat the residue with about 20 cc. of the strongest fuming nitric acid, and digest until the sulphur is dissolved.

The method of oxidation of sulphides with hot hydrochloric acid and potassium chlorate sometimes involves a loss of arsenic.

Remove the cover from the beaker, if the arsenic is to be subsequently weighed, and evaporate to dryness again.

If the arsenic is to be separated from other elements, the following method used in Montana is found to be superior to distillation.

Dissolve the dry residue in 25 to 50 cc. of hydrochloric acid (2 parts of acid (sp. gr. 1.2) and 1 of water), adding a small crystal of tartaric acid. Precipitate the arsenic from a cold solution with hydrogen sulphide, allow to settle for a short time, and filter on an asbestos felt, and wash with acid of the same strength.

As soon as the filtrate is washed out and sulphide wiped from the beaker with a little asbestos, the filtrate can be removed and the acid removed from the felt with some $H_2S$ water.

Test the acid solution again and if no more arsenic appears throw down the antimony and traces of tin and copper with $H_2S$ gas.

Selenium or tellurium, if present in sufficient quantity to interfere, may be removed by reducing the HCl solution with sodium sulphite or $SO_2$ gas before the $H_2S$ treatment.

It has been observed that distilled water, unless condensed in iron or glass, as also the ammonia and HCl, generally shows a trace of tin, and a blank test of the acids reveals a trace of arsenic but, rarely, antimony. The felt, with the sulphides, is placed in a small beaker, the sulphur dissolved by digestion on the steam plate, with red fuming nitric acid, the solution diluted with one and one-half parts of water, the asbestos filtered out, and the solution evaporated to dryness on the steam plate, with 0.1 to 0.5 gram of sodium nitrate, according to the amount of arsenic present, if the latter is to be weighed as magnesium pyroarsenate.

Dissolve the residue in 5 cc. of cold water, with the addition of 10 drops of HCl, and 0.1 gram of tartaric acid.

Flter through a $2^1/_2$-cm. filter into a 25-cc. beaker, unless the arsenic is known to be over 0.05 gram, and wash with as little water as possible from a fine jet. Make slightly alkaline with ammonia, when the liquid should be clear and not have a volume of more than 11 cc.

Add 3 cc. of magnesia mixture, make up to 20 cc. with strong ammonia and stir 5 minutes. If the arsenic is excessive, increase the precipitant and dilute with ammonia so that the total volume shall be 25 to 30 cc., of which one-third is free ammonia water.

Allow to stand over night in a cool place, filter on a $2\frac{1}{2}$ or 3 cm. filter, aiding the transfer of the arsenic by the filtrate.

Wash with a fine jet of ammonia (1 to 3 of water) until free from chlorine, dry in an oven, remove the salt to a glazed paper, and place the filter in a porcelain crucible.

Add a few drops of acid ammonium nitrate solution, (saturated), char carefully, and repeat treatment until the paper is consumed without a perceptible odor of arsenic.

Transfer the remainder of the precipitate and ignite at a full red heat over the Bunsen burner to a constant weight. The Mg mixture, Fresenius' formula, is as follows: 1 part of magnesium sulphate crystals, 4 parts of ammonium chloride, 8 parts of water, and 4 parts of concentrated ammonia (sp. gr. 0.90). The Mg should be free from lime and the mixture should not be used after it has attacked the bottle and dissolved glass from its interior.

### COPPER FREE FROM ANTIMONY.

*D.*—Dr. Hampe, the German pioneer in accurate copper analysis, invented the method involving the reduction of the solution of copper by sulphurous acid gas with the removal of selenium and tellurium, and the subsequent precipitation of the copper as the white sulphocyanate. Dr. H. F. Keller has given a good account of this familiar but somewhat tedious method, and the reader is referred to his paper for details.[1]

Lake Superior metal, not electrolyzed, rarely contains antimony, hence it is not necessary to make the separation in (2:1) HCl if water free from tin is used or the arsenic is to be titrated instead of weighed.

### NEW VOLUMETRIC AND ELECTROLYTIC METHOD.

*E.*—This scheme of direct titration of an electrolyte is believed to be a new one, and will be found to permit much more rapid work with all classes of material, containing little antimony, and can also be used with any copper by preparing the solution for electrolysis,[2] separating the antimony and tin, if present, by methods previously published.

Such a method is adapted to routine control of impure material and was developed for the assay of a large tonnage of Lake copper, now produced, which runs high in arsenic, but has almost no antimony.

*First. Modification for Copper with Less than 0.01 Per Cent. of Arsenic; without Antimony.*—Dissolve the metal and separate the arsenic group as in method *C*, or perhaps *D*, but omit the final precipitation with hydrogen sulphide gas in (2:1) hydrochloric acid, as a trace of tin does not affect iodine in titration. In the rare case in which a trace of gold or platinum is present, the copper can be originally dissolved according to the method just devised by the writer, and which will be made the subject of a paper, at once, on a "New Method for the Determination of Gold in Copper Bullion."

Weigh 1 assay ton of very fine drillings (taken with a $\frac{1}{4}''$ drill) into a No. 4 casserole, add 25 to the 30 grams of C. P. solid potassium bisulphate and 100 cc. of concentrated C. P. sulphuric acid, cover, and boil carefully on a gauze, or plate, for 10 minutes, when metal should be practically dissolved.

Decant acid, without diluting much if possible, and boil any little residue with a little more acid mix., then dilute, settle, and filter out gold and platinum. If selenium or tellurium is present, it can be reduced from the hydrochloric acid solution of the residue, obtained by evaporation of the first sodium sulphide solution of the arsenic group with fuming nitric acid. Treatment with sodium sulphite will effect reduction, or hydroxylamine as recommended by Dr. H. F. Keller.

The titration of an electrolyte gives a little too high results on arsenic, when the arsenic is less than 0.01 per cent. because of the presence of a minute trace of platinum which may be found in the electrolyte, and in much of the cathode copper, produced in the laboratory by the regular 5-gram battery assay of refined copper.

Whether it has been found necessary to purify the arsenic sulphide from traces of antimony, Pt and Se, or not, the residue from evaporation of the sulphide with fuming nitric acid and excess of soda is taken up with sulphuric acid, or better, 25 cc. of strong sulphuric acid are added to the nitric acid solution of the arsenic as soon as the sulphur has disappeared. Instead of a little sodium nitrate which was recommended in the gravimetric method to hold the arsenic, we add 3 grams of solid potassium bisulphate, free from chlorides. This is adapted from Low's method for ores.[1] Heat rapidly on a hot plate until the sulphuric acid fumes for 5 minutes.

Cool, wash into a 300 cc., long-necked Kjeldahl flask of Jena glass, place in an inclined position on a lamp stand over a small flame, boil off the water, fume 5 minutes again, and when the time is nearly up, flash the neck of the flask with a lamp flame, long enough to drive out any condensed liquid from the neck.

This double fuming process, and removal thereby of the last trace of nitric acid, is the *secret of success* with the process, as in the iodide method for titration of copper.

After the flask has cooled a little, add from a paper 0.5 gram of solid tartaric acid and, giving the flask a whirling motion occasionally, digest until the solution is colorless.

Allow to cool, wash into a No. 3 beaker, in which a little water has been placed, and fill the beaker about half full.

One advantage of this scheme is that a dozen digestions can be carried through as easily as one. Drop a small piece of litmus paper into the beaker, add ammonia until the liquid is just alkaline and bring back to the acid condition with dilute sulphuric acid, adding only one drop in excess.

Place the beakers in a large pan of water to cool, when they will be ready for titration with iodine.

This titration will be taken up after the description of the second electrolytic process.

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[1] *J. Am. Chem. Soc.*, **16**, 784 (1894).

[2] *Ibid.*, **26**, 1120 (1904).

[1] "Technical Methods of Ore Analysis." q. v.

*E—2d part. Electrolysis followed by direct reduction and titration.* This is the quickest of all methods for control work, and is accurate for any copper containing more than 0.01 per cent. of arsenic, and no more than a trace of antimony, but the latter if present would have to be removed unless it was permissible to neglect its influence.

If the metal contains less than 0.1 per cent. of arsenic, we take two portions of 10 grams of drillings and place them in the beakers used for the usual battery assay of copper, as described in the first paper.

Dissolve in a slight excess of strong nitric acid (sp. gr. 1.42), add 17 cc. of strong sulphuric acid and evaporate to dryness.

A whole set may, of course, be started at once, and when dry, and the residue smells sweet, add 12 cc. of nitric acid, and water sufficient to cover the electrode, which has the usual dimensions for copper assaying, about 100 sq. cm., counting both sides of the plate.

Pass a current of N. density = 1 ampere until colorless, then reduce to one-half an ampere; in short, perform the regular electrolytic assay for refined copper, just as described in the writer's first paper.

The small portion of liquid, removed for test, is washed into a little beaker, treated with a small crystal of potassium bisulphate, or sodium nitrate, and a few drops of sulphuric acid and evaporated until the sulphur is gone when it is transferred to the main solution now free from copper, which is treated with 3 grams of the solid potassium bisulphate, and evaporated until the nitric acid is all driven off and the sulphuric acid has fumed strongly for 5 minutes.

The solution is then washed into a Kjeldahl flask and digested as already described. In very accurate analyses, the first copper cathode is redissolved in 40 cc. of "Stock Solution" as described in the paper on the electrolytic assay, and the copper again deposited and the second electrolyte boiled down with the first.

The "Stock Solution" mixture of dilute acids is not employed for the original solution of the drillings because it is necessary to oxidize all the arsenic to the condition of arsenic acid, or there appears to be some loss—due to the electric current.

If the metal has more than 0.1 per cent. of arsenic, two 5-gram assays are taken, using 15 cc. of sulphuric acid and a final addition of 10 cc. of nitric acid for each. If 0.2 per cent. of arsenic is known to be present, each of the assays is boiled down, reduced and titrated separately, or if the arsenic is less, they may be combined as one and boiled together.

If the arsenic is between 0.01 per cent. and 0.05 per cent., two 10-gram assays are combined. The remarks on replating apply here.

A blank should be made with each new lot of acids, and digested. If selenium or tellurium is present, we dilute the dry residue of copper sulphate with water and reduce this element with excess of sodium sulphite free from chlorine, or with a rapid current of sulphurous acid gas at a temperature of 40° C., filter and allow to settle, before adding the nitric acid.

Notes on the titration of arsenious acid by iodine will follow.

If very rapid work is necessary, the solution can be electrolyzed for removal of copper in the rotary device, if water-cooled, but more traces of platinum are introduced into the electrolyte, and affect the iodine in titration.

In presence of antimony, the electrolyte can be boiled down until the nitric acid is off, then diluted with one and one-half volumes of water, and strong hydrochloric acid added in amount equal to the total and the arsenic separated by treatment of the cold liquid with excess of hydrogen sulphide.

Even with this modification, this method is more rapid than the gravimetric or distillation, particularly as a number may be done at once, in conjunction with regular copper determinations.

A few words may be of interest in description of a large rotary device which is of great assistance in removing the copper from solutions of either 25 or 50 grams of metal, in order that the electrolyte may be evaporated down to small bulk for the estimation of iron, zinc, nickel, cobalt, lead, etc., and, with an extra precaution to separate a trace of platinum, may be used to determine arsenic.

Dimensions: Size of beaker, No. 4 and 5 low form, capacities 500 to 750 cc., permits the passage of 6–8 amperes, or more, of current through the coil and solution by water-cooling the space between beaker and cylinder.

The anode is a straight doubled wire, and the cathode is a large, closed cylinder of foil, 7.5 cm. in diameter, 11 cm. high, and perforated with holes 3 mm. in diameter and spaced 1 cm. apart.

In the iron determination, 25 grams of drillings are dissolved in 25 cc. nitric acid, 40 cc. sulphuric acid and 100 cc. of water; 50 grams would require 55 cc. of nitric acid, 80 cc. of sulphuric and 250 cc. of water. 20 grams of copper for sulphur determination would be dissolved in 120 cc. of pure nitric acid and free acid removed before diluting with water. For arsenic test, 25 or 50 grams of metal are dissolved in nitric acid, either 40 cc. or 80 cc. of sulphuric acid and the nitric acid evaporated, until the residue smells sweet, after which 25 or 50 cc. of nitric acid are added and residue dissolved, and electrolyte dissolved and electrolyzed it has a chance to crystallize.

The use of the large rotary device is a success for the rapid separation of copper from most of the elements mentioned, but does not give as good results for arsenic as the electrolysis of 5 or 10 grams by the slow method. It requires that a precipitation of the arsenic be made in (2 : 1) HCl to remove not only antimony but also a trace of platinum which is dissolved continuously from the anode by the nitrous acid and heavy current.

*Notes on the Accurate Titration of Arsenious Acid by Iodine.*—We have made many experiments to ascertain the proper conditions for the accurate titration of arsenious acid in either very small, or large amount, and to eliminate slight errors which some chemical authorities have declared to be inherent in the titration.

In the first place we have found that sulphuric acid is a better medium than hydrochloric acid for final solution and neutralization.

The blank tests for arsenic in the former acid or for the nitric acid used in the process are very small, but hydrochloric acid contains a variable trace of arsenic or element which distils and affects iodine.

The following are tests on two lots of C. P. HCl, from two makers.

| No. | Cc. acid taken. | Cc. of iodine. | Blank for end-point. | Cc. of iodine. | Arsenic found. Grams. |
|---|---|---|---|---|---|
| 1.............. | 100 | 0.22 | 0.08 | 0.14 | 0.00015 |
| 2.............. | 100 | 0.32 | 0.08 | 0.24 | 0.00027 |

The HCl was neutralized with ammonia, using a piece of litmus paper as indicator, cooled, made acid with one drop excess and treated with 12 grams of sodium bicarbonate; total volume, 300 cc.

The soda should be free from iron.

We also find that the titration of traces of arsenic is rendered exact if three drops of a 10 per cent. solution of potassium iodide are added. This supplies the conditions for a clear end-point with 2 cc. of a starch solution made up according to directions recently published.[1] That authority directs that the starch shall be soaked 24 hours in very dilute HCl, then washed, dried, and heated 3 hours in a hot oven at 100° C. The end-point thus obtained is a remarkably delicate blue, free from the muddy reddish tint given by ordinary starch indicator, and the blank for the amount to produce an end-point is only 0.04 cc. of iodine, of which 1 cc. = 0.001 gram of arsenic.

Most of the printed methods direct that 2 to 4 grams of sodium bicarbonate should be added to the slightly acidified solution before titration. In the titration of large quantities, or any unknown assay, we find it is an advantage to add a very much larger excess of pure soda, free from iron, as it insures a sufficient quantity of the ions present, which recent investigators have said to be necessary for the uniform action of the iodine, and production of the iodide of starch. The use of the precautions mentioned, with cooling of the solution before the final addition of the bicarbonate of sodium, enables an operator to titrate a milligram of arsenic or 100 mg. as closely as one can precipitate it by magnesia and weigh it, and with more certainty for small amounts.

The iodine solution is made by dissolving 3.5 grams of pure resublimed iodine and 7 grams potassium iodide in water, diluting to one liter, and allowing to stand in a brown bottle for at least 24 hours before use.

A 10 per cent. solution of potassium iodide is also made and 3 or 4 drops are added to every titration, after the bicarbonate of soda.

Standardize with pure arsenious acid, of which 0.06-gram portions are dissolved cold in a little water containing 1 gram, or less, of potassium hydrate, washed into a No. 3 beaker, diluted to nearly 300 cc., made slightly acid with sulphuric acid, using litmus paper as an indicator.

Make slightly alkaline with ammonia, then faintly acid with one drop in excess of the acid, add the carbonate, and titrate rapidly until the end-point is nearly reached, employing 3 cc. of starch solution as the indicator and 3 drops of the 10 per cent. solution of KI.

The beaker is allowed to stand on a white surface, and a fainter end-point is noted and taken with less than 5 mg. arsenic, than when the quantity is large.

A table shows the agreement in the titration of varying amounts of arsenic with ordinary untreated starch indicator, which causes a higher blank test as shown. Results with the new starch are better, so much so that we now prefer to titrate arsenic in accurate analysis, rather than to weigh it.

| As. taken. | Iodine, total cc. | Blank test. | Net cc. of iodine. | Arsenic found, gram. |
|---|---|---|---|---|
| 0.0010 | 0.99 | 0.09 | 0.90 | 0.0010 |
| 0.0020 | 2.02 | 0.09 | 1.93 | 0.00214 |
| 0.00206 | 1.86 | 0.09 | 1.77 | 0.00196 |
| 0.0024 | 2.27 | 0.09 | 2.16 | 0.0024 |
| 0.0020 | 1.91 | 0.09 | 1.82 | 0.00202 |
| 0.00998 | 9.12 | 0.09 | 9.03 | 0.01002 |

A thermometer is attached to the burette, when standardizing and during the regular work, and a correction is made to the burette readings for changes in the volume of the solution from that prevailing at the time of the standardization.

Calumet & Hecla Smelting Works,
Hubbell, Michigan.

## THE ESTIMATION OF VERY SMALL AMOUNTS OF CALCIUM BY MEANS OF POTASSIUM PERMANGANATE.

By L. T. Bowser.

Received October 11, 1910.

The well-marked difficulties attending the use of both the potassium oleate and the turbidity method for the determination of small amounts of calcium suggested the advisability of working out some procedure as simple as either of these but more accurate, as well as less subject to defects. At the time this matter claimed attention the writer had just completed a method for the estimation of potassium in very small amounts as the cobalti-nitrite, titrating the precipitate with very dilute potassium permanganate, and the idea occurred that a similar procedure might serve for the estimation of calcium. Preliminary trials showed that it was entirely feasible to do this, and a careful investigation was made to determine the best conditions for accurate work. The results obtained and conclusions drawn may be of interest to others, hence will be briefly presented.

The method is essentially an extension of the well-known permanganate titration, so carried out as to be applicable in cases where calcium is reckoned only in parts per million. To the solution to be tested, of a volume of from 5 to 10 cc., a few drops of ammonium hydroxide are added, then about 0.4 gram of powdered ammonium chloride. It is then heated to boiling and 0.2 gram powdered ammonium oxalate added, the boiling being continued for a moment in order to make the precipitate as granular as possible.

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[1] *Chem. Abs.*, **4**, 2617 (1910).

This boiling is best accomplished by setting the beaker, not over 50 cc. in capacity, on a wire gauze with Bunsen burner below. For the comfort of the analyst's hands it is well to use a circle of asbestos paper to cover the entire gauze save for a circle in the center just large enough to admit the bottom of the beaker. After the completion of this boiling the solution in the beaker is diluted with approximately its own volume of 3 per cent. ammonia to prevent crystallization of ammonium oxalate, then allowed to stand for some time, preferably two or three hours if the best results are sought.

Filtration is carried out under suction, using a filter of the Shimer form with an asbestos pad about one-fourth of an inch in thickness. For such small amounts of precipitate as are involved a tube much smaller than that used in ordinary work is advisable. The one in use here is of one-half inch internal diameter and two inches length, fitted with a small perforated aluminium plate. After the precipitate has been collected on the asbestos pad it is thoroughly washed with 3 per cent. ammonia to free it from excess of ammonium oxalate. The wash liquid should preferably be hot, although practically as good results may be attained if it is cold. The pad is pushed out and placed in the precipitating beaker, then water enough added to thoroughly moisten the asbestos and give a few cc. in excess.

The precipitate is decomposed by 1 cc. of 1/1 sulphuric acid and titrated with *N*/200 $KMnO_4$, the excess of $KMnO_4$ being titrated back by means of *N*/200 oxalic acid. All titrations are carried out with the titrated solution kept at nearly the boiling point. With a little practice the end-point of this reaction may be noted easily and with precision. From the results of the titration a blank, to be determined by a separate titration, must be deducted as an allowance for permanganate consumed by the asbestos, water and sulphuric acid used. The first blank titration of a pad of asbestos oxidizes out practically all the impurities, and a second one should be made for the real blank to be deducted. Practically all of the permanganate consumed is due to the 1 cc. of sulphuric acid, as ascertained by a number of trials, hence there is necessity for care that exactly the same amount be used every time. Almost every blank made by the writer has been 0.23 cc., although this figure would no doubt vary with the conditions. The same asbestos is used over and over again so long as it will make a good pad, and one blank serves for all. As many as 12 determinations have been made, using one portion of asbestos.

For some purposes sufficient accuracy may be attained by using for the titration an ordinary 50 cc. burette graduated to tenths of a cc., but for the most accurate work a small one graduated in fiftieths or hundredths is to be preferred, and this may, if desired, be read to two hundredths of a cc. There is in use here a 2 cc. size graduated in fiftieths for permanganate, and a 1 cc. graduated in hundredths for oxalic acid. Both are fitted with tips drawn out so fine that the drops are very small, a size such that ten drops of solution which equals 0.15 cc. is very satisfactory. A short rubber tube between the burette and small tip, with a glass bead in the tube to take the place of the more usual stopcock, gives a very delicate and satisfactory control of the rate of flow. The burettes are filled by inserting the tip in the desired solution and drawing it up by suction, taking care to avoid contamination in any way. When these small burettes are used in titrating it is well to add the greater part of the permanganate by means of a 5- or 10-cc. pipette, then to complete the titration with the burette.

Permanganate in such a dilute state does not oxidize as much as it should by theory, and it is necessary to standardize it against a calcium solution of known strength, under conditions similar as regards concentration and manipulation to those met in actual practice. Thus a *N*/200 solution such as used here should by theory oxidize 0.1002 mg. Ca per cc., whereas it is actually equal to only about 0.0793 mg. No satisfactory explanation of this behavior can be made at this time, but the matter is being made the subject of a study from which interesting results seem probable. That the best possible results may be secured it is important that an amount of solution be taken, such that not less than 4 cc. of *N*/200 permanganate shall be required to oxidize the calcium present, preferably a somewhat larger volume, and the same precaution must be observed when standardizing the permanganate. In case smaller amounts are used than those specified, there seems to be a tendency toward high results. It will be readily seen that this is a matter involving the total amount of calcium present rather than its initial concentration, and very good results may be obtained on exceedingly dilute solutions by taking a large volume and evaporating to the desired concentration. It is necessary to work with a final volume of 5–10 cc. of solution in order to overcome, to as great an extent as possible, the solvent effect of the water present.

By the use of this method extremely accurate and concordant results may be obtained in nearly every case, provided due care is exercised. The following results, taken at random from a large number secured in trying out the method, are typical of what may be expected. Table I gives a series on which was based the standardization of the permanganate solution.

TABLE I.

| No. | Cc. sol. used. | Cc. $KMnO_4$ consumed. | Mgm. Ca used. | Mgm. Ca found. | Parts per million used. | Parts per million found. |
|---|---|---|---|---|---|---|
| 1 | 10 | 4.300 | 0.3429 | 0.3410 | 34.29 | 34.10 |
| 2 | 10 | 4.335 | 0.3429 | 0.3438 | 34.29 | 34.38 |
| 3 | 10 | 4.315 | 0.3429 | 0.3422 | 34.29 | 34.22 |
| 4 | 10 | 4.340 | 0.3429 | 0.3442 | 34.29 | 34.42 |
| 5 | 10 | 4.345 | 0.3429 | 0.3446 | 34.29 | 34.46 |
| 6 | 10 | 4.310 | 0.3429 | 0.3418 | 34.29 | 34.18 |
| Aver. | | 4.324 | | | | |

From the average amount of $KMnO_4$ used, 4.324 cc., we find that 1 cc. oxidizes 0.0793 mg. Ca., and from this the recorded amounts are calculated. It will be noted that the agreement here is very close for a method involving such minute amounts. In

Table II is shown the result of a series where the initial concentration was less and the total amount of lime greater.

TABLE II.

| No. | Cc. sol. used. | Cc. $KMnO_4$ consumed. | Mgm. Ca used. | Mgm. Ca found. | Parts per million used. | Parts per million found. |
|---|---|---|---|---|---|---|
| 1....... | 50 | 5.75 | 0.4285 | 0.4560 | 8.57 | 9.12 |
| 2....... | 50 | 5.53 | 0.4285 | 0.4385 | 8.57 | 8.77 |
| 3....... | 50 | 5.82 | 0.4285 | 0.4615 | 8.57 | 9.23 |
| 4....... | 50 | 5.81 | 0.4285 | 0.4610 | 8.57 | 9.22 |
| 5....... | 50 | 5.71 | 0.4285 | 0.4530 | 8.57 | 9.06 |
| 6....... | 50 | 5.74 | 0.4285 | 0.4550 | 8.57 | 9.10 |
| 7....... | 50 | 5.59 | 0.4285 | 0.4430 | 8.57 | 8.86 |
| 8....... | 50 | 5.445 | 0.4285 | 0.4320 | 8.57 | 8.64 |
| 9....... | 50 | 5.425 | 0.4285 | 0.4300 | 8.57 | 8.60 |
| 10....... | 50 | 5.45 | 0.4285 | 0.4320 | 8.57 | 8.64 |
| Aver. | | | | | | 8.924 |

The agreement is not so close here, although toward the last of the set, as experience was gained, there was a considerable improvement. However, as a whole this series is quite satisfactory. What happens when too small a total amount of calcium is taken may be seen in Table III, the first five portions containing half the amount of the last six, and falling below the limit of 4 cc. of permanganate needed, equivalent to about 0.3 mg.

TABLE III.

| No. | Cc. sol. used. | Cc. $KMnO_4$ consumed. | Mgm. Ca used. | Mgm. Ca found. | Parts per million used. | Parts per million found. |
|---|---|---|---|---|---|---|
| 1....... | 50 | 3.34 | 0.2142 | 0.2650 | 4.29 | 5.30 |
| 2....... | 50 | 3.28 | 0.2142 | 0.2600 | 4.29 | 5.20 |
| 3....... | 50 | 3.40 | 0.2142 | 0.2695 | 4.29 | 5.39 |
| 4....... | 50 | 3.31 | 0.2142 | 0.2625 | 4.29 | 5.25 |
| 5....... | 50 | 3.27 | 0.2142 | 0.2595 | 4.29 | 5.19 |
| Aver. | | | | | | 5.27 |
| 6....... | 100 | 5.31 | 0.4285 | 0.4210 | 4.29 | 4.21 |
| 7....... | 100 | 5.49 | 0.4285 | 0.4360 | 4.29 | 4.36 |
| 8....... | 100 | 5.46 | 0.4285 | 0.4330 | 4.29 | 4.33 |
| 9....... | 100 | 5.44 | 0.4285 | 0.4320 | 4.29 | 4.32 |
| 10....... | 100 | 5.45 | 0.4285 | 0.4330 | 4.29 | 4.33 |
| 11....... | 100 | 5.44 | 0.4285 | 0.4320 | 4.29 | 4.32 |
| Aver. | | | | | | 4.32 |

This series is sufficient to satisfactorily illustrate the point that not less than 0.3 mg. of Ca should be present. This is the minimum limit, while there is apparently no maximum one. The last six results must be conceded to be exceedingly satisfactory, and constitute, along with those previously given, a very fair test of the capabilities of the method. It possesses a number of decided advantages over the other two, such as accuracy, speed, easy manipulation, and the absence of any necessity for preliminary decolorizing of a solution to be operated upon. The procedure outlined is in a measure adapted from the turbidity method used by the Bureau of Soils,[1] and prevents the danger of interference of magnesium. Uniformly good results have been secured by the method, and it is believed that its evident merits will commend it to those having occasion to estimate unusually small quantities of calcium for any purpose.

OHIO AGRICULTURAL EXPERIMENT STATION,
WOOSTER, OHIO.

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[1] *Bull.* **31**, 53.

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## LINSEED OIL.

By A. H. SABIN.

Received December 27, 1910.

It was observed some ten or twelve years ago by Weger and Lippert that a considerable proportion of their tests of drying linseed oil showed an increase of weight to a maximum and then a small decrease; but, with the exception of L. E. Andés, no notice seems to have been taken of this by recent writers, and it was in fact unknown to the present writer until this investigation had long been under way. It is generally assumed that this oil, when exposed to the air, absorbs oxygen, and that this is substantially all the action which takes place, although Toch has called attention to the fact that a small amount of $CO_2$ is evolved. Brooks has recently noted the presence of traces of formaldehyde and appreciable amounts of formic acid as oxidation products from this oil; although never published, these facts were known to the writer and to at least one other technical chemist many years ago.

Oil has long been oxidized by blowing air through it, usually with heat; if this operation is carried far enough, an insoluble product is formed, but this is different from the film of dried oil obtained when oil is dried in a thin film on glass or other support, being less perfectly oxidized. As the chief use of oil is in paint, it is best to conduct these experiments with films.

Glass plates, 4 x 5 or 5 x 7 inches, were used, as these can be weighed on a sufficiently delicate balance; these were coated with oil, both raw and boiled, and paints, the latter prepared by first ascertaining how many pounds of each pigment will make up, in paint, the volume of one gallon; for example, it is found that 55 lbs. of dry white lead, added to any quantity of oil or turpentine, increases the volume one gallon, whence it is inferred that 55 lbs. of white lead contain enough solid matter to measure 231 cu. in. Having determined these figures, paints were prepared by adding one-fourth of a gallon of pigment to three-fourths of a gallon of oil, or in that proportion, but in constructing the curves of drying, only the oil is taken into account, and the curves show the percentage gain or loss of the oil, as if no pigment were present; that is, the pigment is assumed to be inactive in all cases. These experiments were started about eight months ago, and in most cases four or six plates were coated with each preparation; very little variation was found between duplicates.

The boiled oil was ordinary raw oil cooked in a kettle with PbO and $MnO_2$, and contained the equivalent of 0.19 per cent. PbO and 0.023 per cent. MnO. The paints were made with raw oil, without driers.

It will be observed that raw oil rapidly increases in weight, gaining 16 to 18 per cent. in less than a week; the greatest part of this gain takes place before the oil begins to set or harden appreciably; then it loses weight rapidly but not as rapidly as it had gained, and in ten days or two weeks has lost about one-eighth its increment of added weight; then it loses more and more slowly, until in four months it has lost three-fourths of the original increase, and in eight months about nine-tenths, and the curve is still approaching the base-line.

Boiled oil, singularly enough, gains much less than raw, reaches its maximum about the same time, then loses, showing a curve similar but less accentuated.

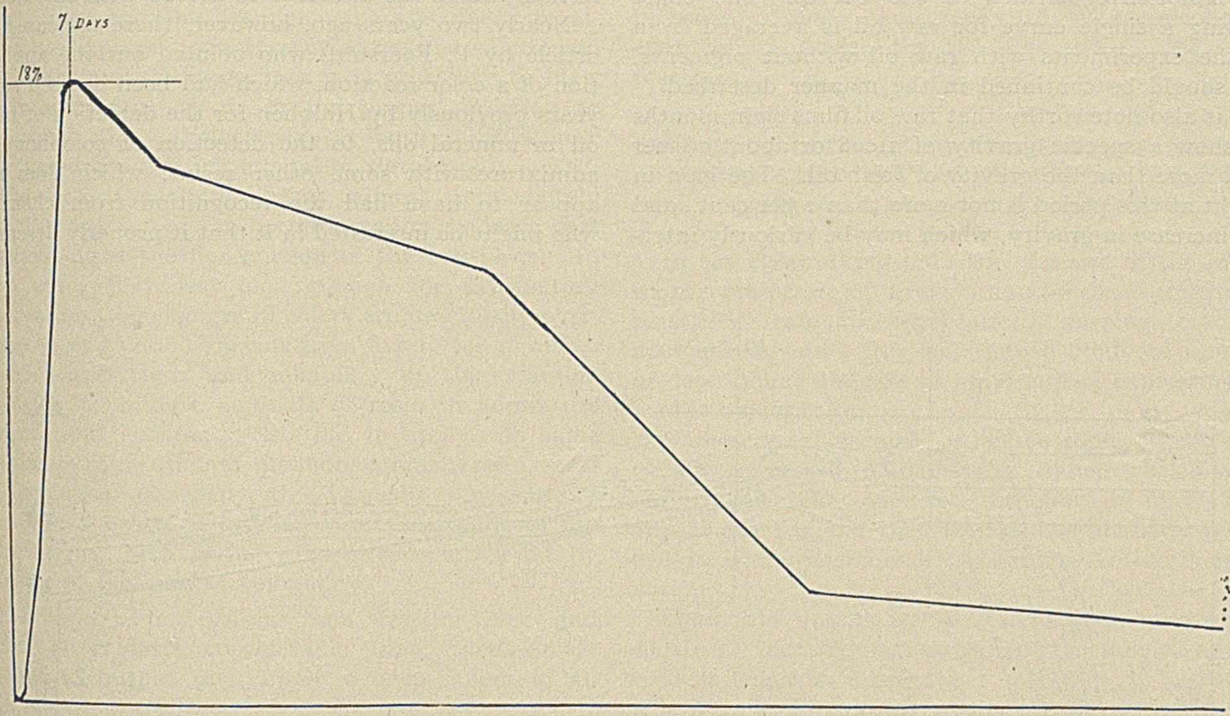

Fig. 1.—Linseed oil.

The raw oil paints follow, as might be expected, the raw oil curve, but have some remarkable eccentricities, which future investigation will probably show to have significance.

During the entire period, decomposition products are given off, most noticeably during the period of

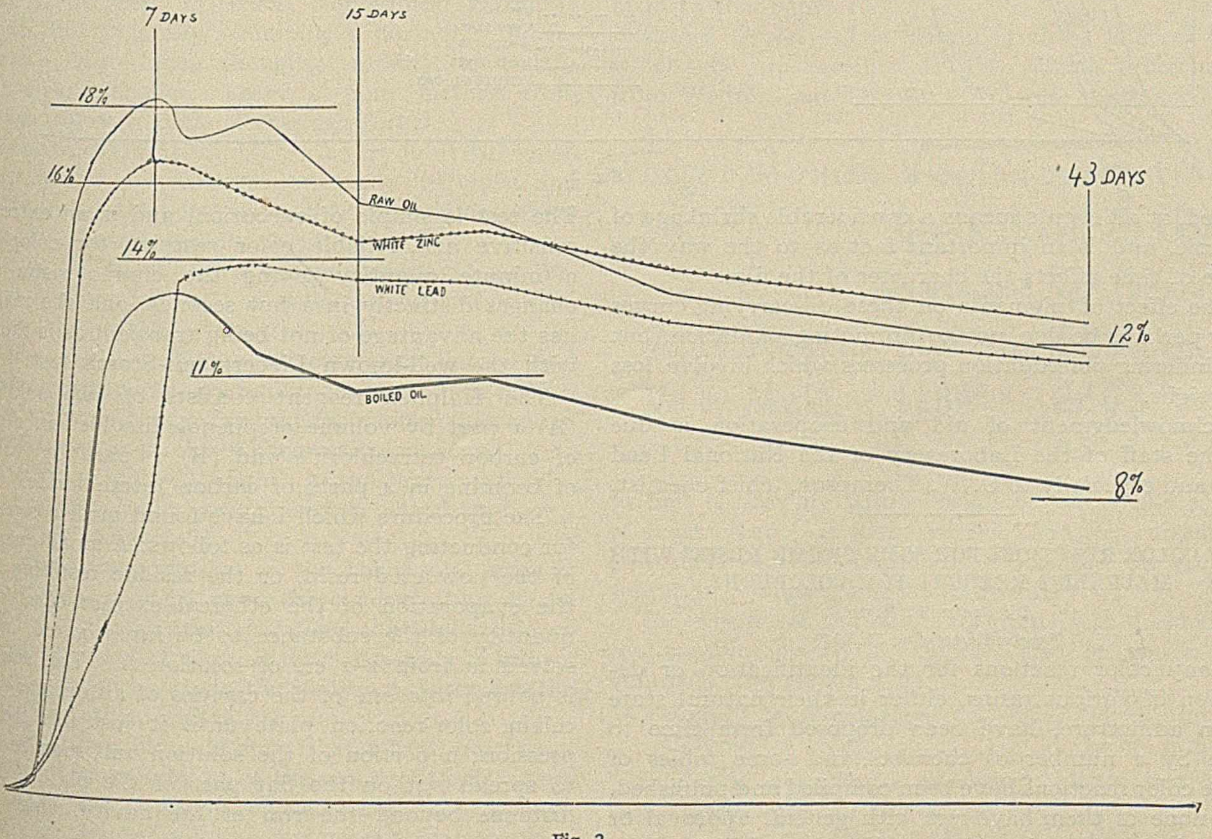

Fig. 2.

increase of weight, and the location of any point in the curve is possibly a result of partially balancing gains and losses. These are probably affected differently by atmospheric conditions, which accounts for the minor irregularities of the curves. The chart showing a single curve for raw oil is averaged from all the experiments with raw oil without pigments, and should be continued in the manner described.

It is also noteworthy that raw oil films eight months old show a specific gravity of 1.098 or about 18 per cent. more than the gravity of fresh oil. The gain in weight at this period is not more than 2 per cent., and this increase in gravity, which may be variously interpreted, at all events means a considerable shrinkage of volume, and is an important fact as to the way the lapse of time affects the character of the film.

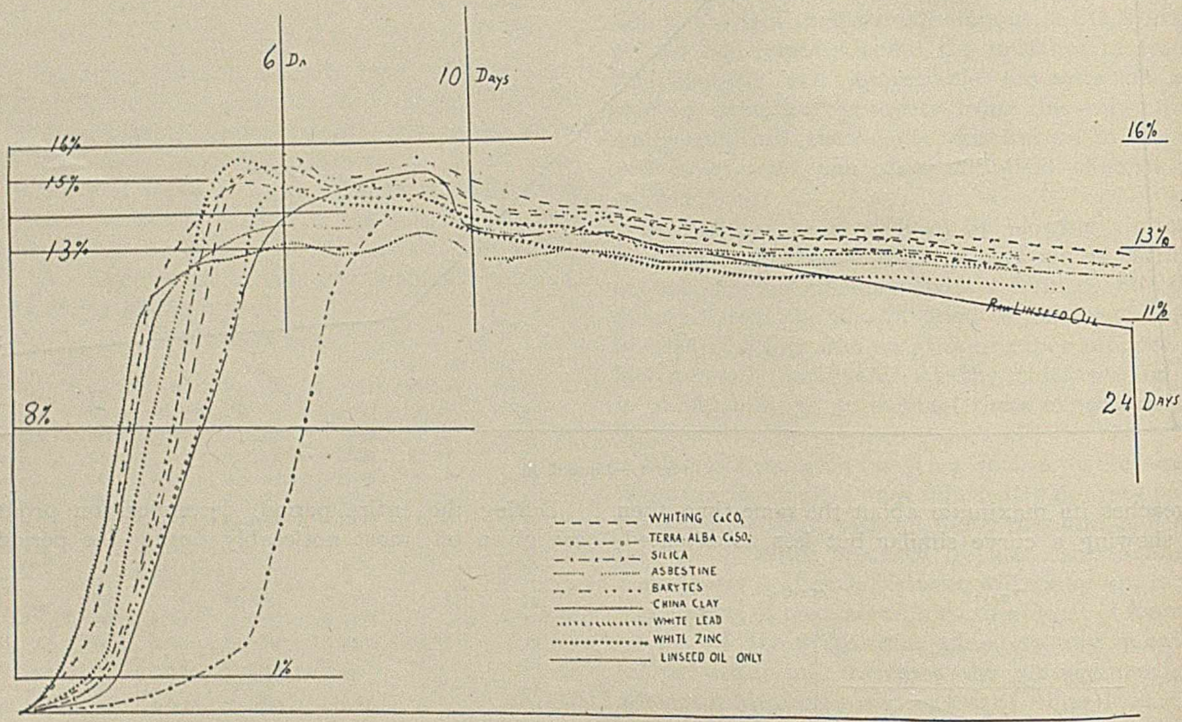

Fig. 3.

The effect of pigments on these oil-carrying curves may perhaps be due, not to promoting oxidation, but to hindering peroxidation processes which involve loss of weight.

Acknowledgment of aid and cooperation is due to the staff of the Laboratory of the National Lead Co., and especially to G. W. Thompson, chief chemist.

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## NEW COLOR REACTIONS FOR SOME OF THE RESINS WITH HALPHEN'S REAGENT FOR COLOPHONY.

By Edwin F. Hicks.

Received December 31, 1910.

Many color reactions for the identification or detection of various resins, either in their natural state or in admixture, have been proposed from time to time by a number of chemists, and some tables of these color reactions have been compiled and published, but none of them have met with general approval or extensive application, other than the Liebermann-Storch reaction for colophony, the general consensus of opinion being that their indications are unreliable or of so little sensitiveness as to be practically valueless to the analyst for most purposes of identification; in many cases the author is in accord with this belief.

Nearly two years ago, however, there appeared an article by P. Foerster,[1] who pointed out the application of a color reaction, which had been devised some years previously by Halphen for the detection of rosin oil in mineral oils, to the detection of colophony in admixture with some other resins, which does not appear to have had the recognition from chemists who might be interested in it that it properly deserves. The test is simple of execution, and is an extremely sensitive and reliable color reaction for colophony, a minute quantity giving the characteristic color changes distinctly in a few seconds, and the reaction has the advantage of not being transient as is the case with the well-known Liebermann-Storch test.

The Halphen reagent consists of two solutions: (A) 1 part by volume of phenol dissolved in 2 parts of carbon tetrachloride and (B) 1 part by volume of bromine in 4 parts of carbon tetrachloride.

The procedure which I have found most convenient for conducting the test is as follows: A small quantity of the powdered resin, or the residue resulting from the evaporation of the ethereal extract of a larger quantity of the substance to be investigated, is dissolved in from 1–2 cc. of solution A. This solution is poured into one of the cavities of an ordinary porcelain color-reaction plate until it just fills the depression; a portion of the solution will soon be seen to spread out on the flat part of the plate a short distance beyond the rim of the cavity, unless too

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[1] *Ann. Chim. Anal.*, **14**, 14 (1909).

much of the carbon tetrachloride has been lost through evaporation during the process of solution, when a drop or two more should be added to produce the spreading effect above referred to. Then immediately in an adjacent cavity of the plate a cc. or so of solution B is placed and the bromine vapors evolved are allowed to impinge upon the surface of the solution in the other cavity. Sometimes it is necessary to blow a gentle current of air in the proper direction to accomplish this satisfactorily, or both cavities may be covered by a watch crystal of suitable size.

The color reactions begin almost immediately with the contact of the bromine vapors and are best observed upon the flat portion of the test-plate. In most cases they last long enough for satisfactory observation; the changes in colors are practically over, however, in a period varying from five to ten minutes.

The sensitiveness and reliability of this reaction for detecting minute amounts of rosin in admixture with various substances led me to apply the same reaction to some other of the more common resins used in commerce, especially the varnish gums, and I have stated below in tabular form the results of my observations, first giving that already observed by Foerster in the case of colophony.

*Colophony.*—First green, then rapidly blue and violet; latter lasts considerable time, then slowly changes to purple, and finally a deep indigo in all parts.

*Dammar.*—Brown to lilac-brown, forms rather slowly; gradually changes into a distinct reddish brown (maroon).

*Elemi.*—Indigo-blue, forms at once, quite permanent; gradually deepens in color, sometimes becoming purplish, but generally remaining a dark rich indigo.

*Kauri.*—Azure-blue, changing rapidly to purple through violet shades. Later, at point farthest from bromine vapors a dark olive-green forms.

*Manila Gum* (spirit-soluble).—A very faint brownish green forms slowly; changes gradually to violet and finally purple. At point farthest from bromine vapors a chocolate-brown usually is produced.

*Mastic.*—Reddish brown, becoming almost a carmine nearest bromine vapors. A coffee-brown tint is produced at the far side of the test.

*Sandarac.*—Lilac forms almost immediately and is quite permanent; gradually changes to a violet, becoming violet-brown farthest from bromine vapors.

*Shellac*, (when pure.)—Gives no colorations.

*Zanzibar Copal.*—A light brown forms slowly, later brownish violet and finally a chocolate-brown mixed with some violet.

Of course the intensity of the colors and tints is to a degree dependent upon the concentration of the resin in the solvent solution A, but a little experience in the application of the test with materials of known purity will soon give one the ability to interpret the indications without difficulty.

In conclusion, I should state that I have not tested thoroughly the reliability of the color-reactions where several of those giving characteristic colors have been in admixture, but in a few cases that were tried the results have given valuable indications, except that the reaction with common rosin is so intense that if present in the mixture in any considerable amount it is apt to mask the other color indications.

Perhaps it would be well to state also that the presence of more than traces of water, alcohol or ether interfere with the sensitiveness of the color-reactions.

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## ERRORS IN DETERMINING THE SIZES OF GRAIN OF MINERALS AND THE USE OF SURFACE FACTORS.[1]

By Harrison E. Ashley and Warren E. Emley.

Received December 27, 1910.

In the clayworking industry, the size of the microscopic grains is of great importance in regard to plasticity, rate of vitrification, warping, cracking, appearance, etc. This led us to a study of methods of determining the size of grain and of expressing the results numerically.

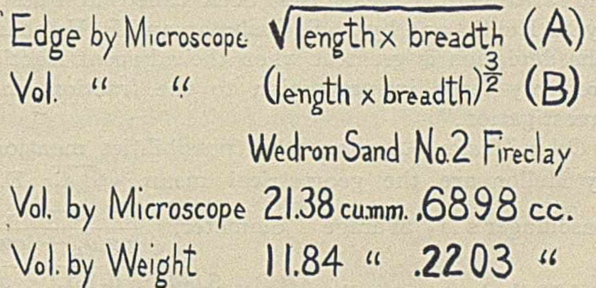
*Diameters.*—The size of microscopic particles is usually expressed in diameters. When we looked at our irregular clay particles, the effort to make them appear circular and then to read the diameter by the eye-piece micrometer exceeded the power of our imagination.

*Equivalent Rectangle.*—We were able, however, to construct mentally an equivalent rectangle, and to read its length and breadth.

Mr. A. V. Bleininger had previously done this and represented the size of particle as the square root of an area: $\sqrt{\text{length} \times \text{breadth}}$. A.

*Volume of Grain.*—The question remained, however, whether or not the depth of the grain bears a constant ratio to this figure.

*Round Grains.*—The round grained mineral with which we are familiar is the Illinois glass sand from Wedron and Ottawa. We were quite surprised to find it showing parallel rounded edges like a loaf of yeast bread. 28 grains of this sand were measured and their individual volumes calculated on the assumption Volume $(\text{length} \times \text{breadth})^{3/2}$. B.



Edge by Microscope $\sqrt{\text{length} \times \text{breadth}}$ (A)

Vol. " " $(\text{length} \times \text{breadth})^{\frac{3}{2}}$ (B)

| | Wedron Sand | No.2 Fireclay |
|---|---|---|
| Vol. by Microscope | 21.38 cu.mm. | .6898 cc. |
| Vol. by Weight | 11.84 " | .2203 " |

Fig. 1.

The weight of the same 28 grains was divided by the specific gravity of quartz, also to obtain the volume. The results were:

| | |
|---|---|
| Volume by microscope...... | 21.38 cu. mm. |
| Volume by weight.......... | 11.84 cu. mm. |

Evidently the depth averages a little less than half expression A for this sand.

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[1] By permission of the Director of the Bureau of Standards.

*Sharp Grains.*—A No. 2 fire-clay from Nelsonville, O., leaves sharp irregular fragments on a 20-mesh sieve. 50 of these grains showed:

| | |
|---|---|
| Volume by microscope.... | 0.6898 cc. |
| Volume by weight....... | 0.2203 cc. |

Here the depth is approximately one-third of expression A.

*Flat Grains.*—Evidently flat-grained minerals, like kaolin and mica, would give ratios far greater than these two cases.

This leads us to be very skeptical of most calculations based on the diameter of mineral grains as measured by the microscope.

*Correct Size Measurements.*—Zsigmondy[1] computed the size of gold particles from the concentration of the solution, the specific gravity of gold, and the observed number of particles in a measured volume, obtaining results free from objection. He made no conjecture as to shape of particle, avoided the use of the word "diameters," and assumed a cubical-shaped particle for computation purposes. This seems the most feasible procedure.

*Group Classification of Clays.*—Seger,[2] the founder of the scientific study of clayworking problems, found it convenient to classify the grains of natural clays in groups between definite size limits as follows:

| | | Average diameter. | Purdy surface factor. |
|---|---|---|---|
| Coarse sand............ | Over 0.333 mm. | ...... | ...... |
| Fine sand.............. | 0.333–0.040 mm. | 0.1865 | 5.36 |
| Silt................... | 0.040–0.025 mm. | 0.0325 | 30.77 |
| Rock dust.............. | 0.025–0.010 mm. | 0.0175 | 57.14 |
| Clay................... | 0.100–0.000 mm. | 0.0050 | 200.00 |

*Arithmetical Mean.*—Mellor[3] says: "A trial obtained by subdividing a given fraction shows that the arithmetical mean of the extreme diameters, namely, $^1/_2$ $(d_1 + d_2)$, may be less or greater than the true average diameter. The validity of the arithmetical mean has been called in question by A. Heath[4] and by A. S. Cushman and P. Hubbard.[5] The deviation is greatest when the adjacent fractions are very large in proportion to the fraction under investigation."

*Other Means.*—Among other possibilities mentioned by Mellor are the geometrical mean, $\sqrt{d_1 d_2}$; E. J Laschinger's "average diameter, $\frac{d_1 - d_2}{\log_e d_1 - \log_e d_2}$, and Mellor's average diameter," $\sqrt[3]{\frac{(d_1 + d_2)(d_1^2 + d_2^2)}{4}}$. Von Reytt,[6] using round-hole sieves, found the diameter of the mean particle passed by one sieve and retained by the next to be 0.87 times the diameter of the mean sieve hole.

As Von Reytt's results were obtained on so much larger particles, it is questionable whether we are justified in including them in the table below.

All of these formulas are equally as true for cubes as for spheres, save those involving length and breadth.

*Law of Variation in a Group.*—To investigate the reliability of duplicate measurements, we plot a sort of probability or variation curve, in which the measurements are plotted as ordinates, the lowest measurement having zero as abscissa, the next lowest 1, the

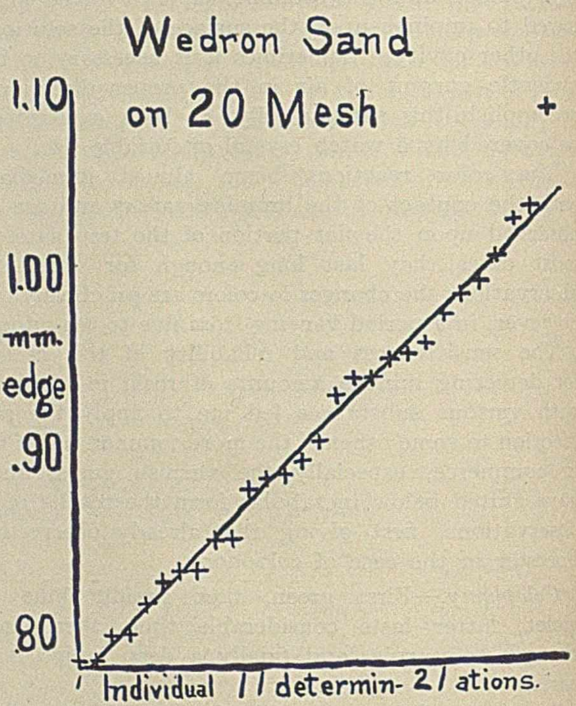

Fig. 2.

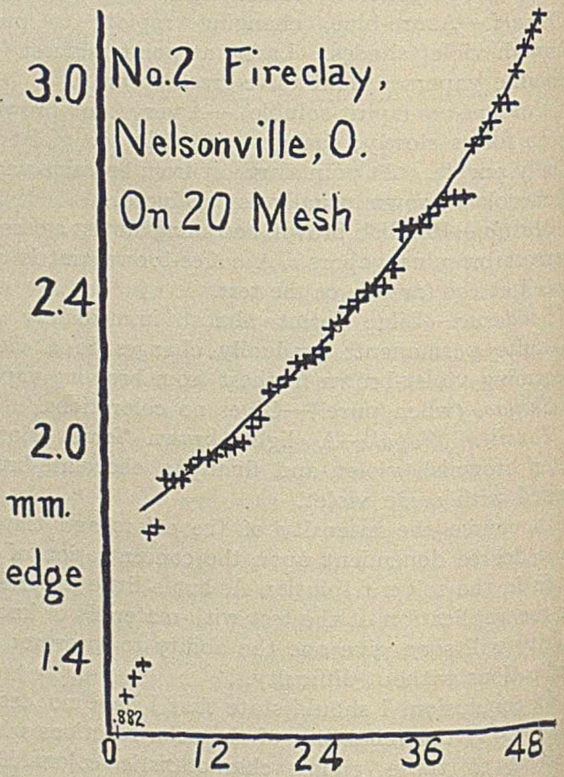

Fig. 3.

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[1] Zsigmondy-Alexander, "Colloids and the Ultramicroscope" (1909).

[2] "Collected Writings, American Ceramic Society translation," p. 43 (1902).

[3] *Pottery Gazette*, **35**, 789; *Trans. Eng. Cer. Soc.*, **9**, 94 (1910).

[4] *Trans. Eng. Cer. Soc.*, **3**, 23 (1904).

[5] *J. Am. Chem. Soc.*, **29**, 589 (1907).

[6] Richards, *Ore Dressing*, **1**, 305; *Oest. Zeit.*, **36**, 229, 246, 255, 268, 283 (1888).

next 2, etc. If perfect duplicates were obtained, this would give a horizontial line.

Fig. 2 shows such measurements on Wedron, Ill., sand retained on a 20-mesh sieve. Practically a uniform variation in size is shown. Fig. 3, No. 2 fire-clay retained on 20 mesh, deviates slightly from a straight line.

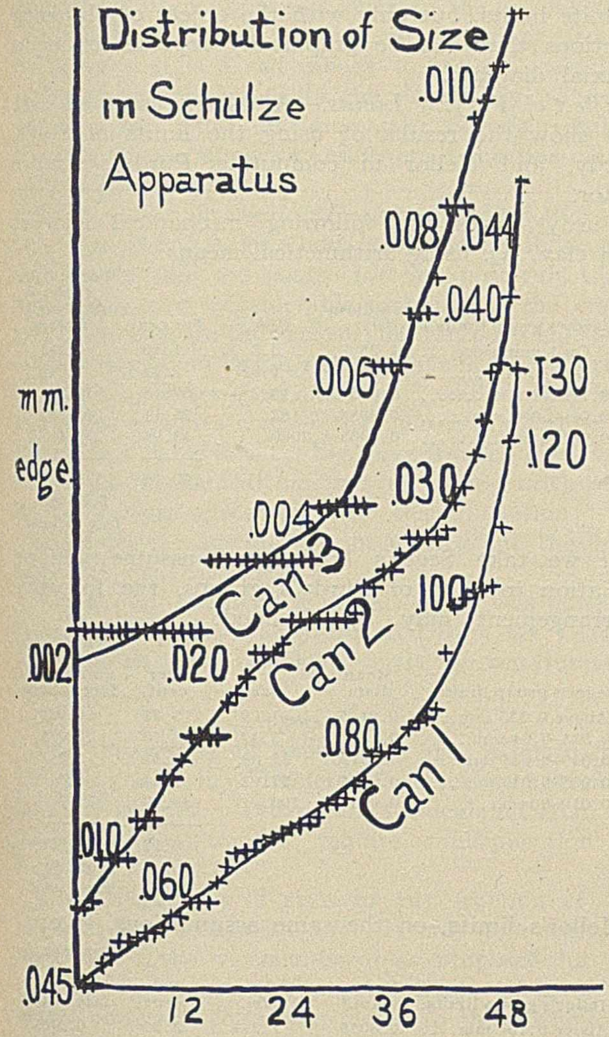

Fig. 4.

Calculated Meals for Typical Curves.

| | Can 1a. | Per cent. deviation. | Can 2a. | Per cent. deviation. | Wedron. | Per cent. deviation. | |
|---|---|---|---|---|---|---|---|
| Max. edge, mm. | 0.13127 | .. | 0.04682 | .. | 1.032 | ... | |
| Min. edge, mm. | 0.04498 | .. | 0.00643 | .. | 0.782 | ... | |
| Edge of av. cube | 0.07697 | 8 | 0.02462 | 16 | 0.905 | 0.6 | $\sqrt[3]{\frac{\Sigma(l \times b)^{3/2}}{n}}$ [4] |
| Average edge | 0.07143 | .. | 0.02126 | .. | 0.899 | ... | $\frac{\Sigma\sqrt{l \times b}}{n}$ |
| Arithmetical mean | 0.08813 | 23 | 0.02663 | 25 | 0.907 | 0.8 | $^1/_2(d_1+d_2)$ |
| Geometrical mean | 0.07684 | 8 | 0.01735 | —18 | 0.898 | —1.0 | $\sqrt{d_1 d_2}$ |
| Laschinger's mean | 0.0807 | 13 | 0.0204 | —4 | 0.900 | 0.1 | $\frac{d_1 - d_2}{\log_e d_1 - \log_e d_2}$ |
| Mellor's mean | 0.0946 | 32 | 0.0310 | 42 | 0.912 | 1.4 | $\sqrt[3]{\frac{(d_1 + d_2)(d_1^2 + d_2^2)}{4}}$ |
| Von Reytt's mean | 0.0767 | 7 | 0.02314 | 9 | 0.789 | —11 | $\frac{0.87}{2}(d_1 + d_2)$ |

Fig. 4 shows 3 curves representing the silicious residues of a Tenn. Wad clay left in the 3 cans of a Schulze elutriating apparatus. Only can 2*a* shows the theoretical form of the probability or variation curve, while the can 1*a* and 3*a* curves are very concave.

*Best Mean.*—On the 3 forms of curve so found, the average edge (assuming cubical particles) is given in the above table, calculated by each of the methods, and also from direct measurement.

All apply well to the straight line (Wedron) save Von Reytt's.

Mellor's mean is least satisfactory for the elutriation residues, and the arithmetical mean nearly as bad. The geometrical and Laschinger means have deviations of different sign for the two kinds of elutriation residues. Von Reytt's simple empirical device seems (perhaps by chance) to give best results, and would have given better had a smaller constant than 0.87 been employed.

By examining grains by the methods given above it should be possible to accumulate data showing what form of mean is most reliable.

*Surface Factors.*—For many chemical and ceramic purposes, the activity of a material is considered proportional to its area.

For computing the area, surface factors are employed:

*Rittinger's Law.*—Rittinger[1] proved that the work of crushing is very nearly proportional to the reciprocals of the diameters crushed to, hence to the total surface of the resultant particles.

Stadler[2] falls into error in assuming that for crushing Kick's law holds that "the energy required for producing analogous changes of configuration of geometrically similar bodies of equal technological state varies as the volume or weights of these bodies."

*Von Reytt's Factors.*—Von Reytt[3] confirmed Rittinger experimentally.

In computing the surface of a kilogram of material, for round-hole sieves, he used the factors 3.4 to $4.2 \times \frac{\pi}{4}\left(\frac{d_1 + d_2}{2}\right)^2$ and for square-hole sieves 4.0 to $4.2 \times \frac{\pi}{4}\left(\frac{d_1 + d_2}{2}\right)^2$.

This is the first use of a surface factor we have noted.

*Moisture Surface Factor.*—Von Reytt, following Rittinger's suggestion of measuring the adhering moisture, found that "while the adhering moisture is approximately proportional to the amount of surface on coarser

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[1] Richards, *Ore Dressing*, **1**, 304–10; Mellor, *Pottery Gazette*, **35**, 687; *Trans. Eng. Cer. Soc.*, **9**, 50 (1910).

[2] *J. Chem. Met. Soc. S. Africa*, **10**, 382–91; *Chem. Abs.*, **4**, 3059 (1910).

[3] Richards, *Ore Dressing*, **1**, 304-10; *Oest. Zeit.*, **36**, 229, 246, 255, 268, 283 (1888).

[4] When *n* is the number of particles measured.

particles, it does not hold on particles below 0.35 mm." A water surface factor was therefore impracticable.

*Other Discoverers.*—The idea of surface factors has also been worked out more or less independently by M. Whitney,[1] W. Jackson,[2] Arthur Yates,[3] R. H. Richards,[4] Algernon Del Mar,[4] Wo. Ostwald,[5] and doubtless numerous others.

*Jackson's, Mellor's and Purdy's Factors.*—Jackson's device was peculiarly lacking adaptation to different limiting sizes, and was simplified by R. C. Purdy. If $dm$ is the mean diameter (mm.) of any group, $Wm$ the weight of the group (expressed as a fraction of the total amount of material being tested), $s$ the specific gravity, then $6W/sd_m$ is the surface of the same fraction of 1 mg. of the material.

The total surface[7] of 1 mg. of the material is the sum of the surfaces of the several groups: $\frac{6}{s}\left(\frac{W_m}{d_m}+\frac{W_n}{d_n}+\frac{W_o}{d_o}+\right.$ $\left.\ldots\ldots\right)$ sq. mm. Owing to irregularities in the shapes of grains and to the errors discussed above in determining the mean diameter of a group the formula is only approximate, and Mellor employs it as an abstract number. As the materials used in clayworking (clays, kaolin, feldspar, quartz) have nearly the same specific gravity, Purdy threw away the factor $6/s$. The mining engineers, Yates, Richards, and Del Mar, follow Purdy's example exactly, though independently.

Whitney first calculated the approximate number of grains per gram by the formula $\frac{a}{A}\cdot\frac{6}{\pi d^3 s} = n$ and then the surface area by the formula $\pi d^2 n$. In these formulas

$n$ = the number of grains in one of the mechanical analysis residues;
$a$ = the weight of the group;
$A$ = the total weight of the sample;
$a/A$ = $W$ = the fractional portion of the whole in any one of the mechanical analysis groups;
$d$ = the mean diameter of the group;
$s$ = the specific gravity;

By substitution, the surface area $= \pi d^2 \cdot \frac{a}{A}\,\frac{6}{\pi d^3 s} = \frac{6}{s}\,\frac{W}{d}$.

Whitney's two formulas give identically the same result as the single formula now advocated by Mellor.

Whitney preceded all but Von Reytt, but used not a single factor but the product of two factors, giving the same result as Mellor's form.

*Limiting Sizes for Groups.*—In our present condition of inexact knowledge as to the laws governing the variation of size of particles, it is exceedingly important, for comparable results, that the same limiting size of group be used by all workers. Especially is this true of the smallest fraction, consisting of particles assumed to range in size down to zero. Mellor has indeed proposed and strongly insisted on certain definite limits, but only with the object of obtaining fractions that can be graphically represented on a triaxial diagram.

*Effect of Varying Limits.*—A partly assumed case will show the results of using the limits of Seger, Purdy, and Mellor in computing Purdy's surface factor.

Purdy[1] gives the following mechanical analysis of a clay, $K_3$, using arithmetical means:

| Purdy's group limits. | Mean diam ($dm$). | $1/dm$. | Per cent. | Per cent./100 × $1/dm$ = Purdy's surface factors. |
|---|---|---|---|---|
| On 1 mm. sieve.... | 1.25 | 0.8 | 1.50 | 0.012 |
| 1–0.1 mm......... | 0.55 | 1.82 | 2.41 | 0.044 |
| 0.1–0.01 mm........ | 0.055 | 18.2 | 57.15 | 10.34 |
| 0.01–0.001 mm...... | 0.0055 | 182. | 25.14 | 45.78 |
| 0.001–0 mm......... | 0.0005 | 2000. | 13.96 | 279.4 |
| | | | 100.16 | 325.6 Total surface factors. |

If we take Seger's limits, and assume uniform variation in each of Purdy's groups, the following rearrangement may be obtained:

| Seger's group limits. | Mean diam. | $1/dm$. | Per cent. | Per cent./100 × $1/dm$ = Purdy's surface factors. |
|---|---|---|---|---|
| Above 0.333 mm.... | 0.9165 | 1.091 | 3.29 | 0.036 |
| 0.333–0.04 mm...... | 0.1865 | 5.37 | 38.70 | 2.075 |
| 0.04 –0.025 mm..... | 0.03125 | 32.08 | 9.54 | 3.06 |
| 0.025–0.010 mm..... | 0.0175 | 57.02 | 9.54 | 5.44 |
| 0.010–0 mm......... | 0.005 | 200. | 39.10 | 78.2 |
| | | | 100.17 | 88.811 Total surface factor. |

Mellor's limits, on the same assumptions, give:

| Mellor's group limits. | Mean diam.[2] | $1/dm$. | Per cent. | Per cent./100 + $1/dm$ = Purdy's surface factors. |
|---|---|---|---|---|
| Above 0.107 mm.... | 0.8035 | 1.244 | 3.89 | 0.0484 |
| 0.107–0.063 mm..... | 0.085 | 11.76 | 23.49 | 2.77 |
| 0.063–0.010 mm..... | 0.0365 | 27.41 | 33.68 | 9.23 |
| 0.010–0 mm......... | 0.005 | 200. | 39.10 | 78.2 |
| | | | 100.16 | 90.25 Total surface factor. |

*Predominating Effect of Smallest Groups.*—When the mechanical separations end at 0.010 mm., as in Seger's and Mellor's work, the final fraction (0.010–0 mm.) will have equal and predominating weight (78.2) in both the total surface factors. Only 1.6 per cent. variation in total surface factor is caused in this case by changing from Seger's to Mellor's group limits. But if the group 0.010–0 mm. is subdivided at 0.001, as is done by Purdy and others, including our agricultural chemists, then the numerical value of the total surface factor is enormously increased.

*Seger's Limits Preferable.*—It is a difficult matter to say what limits should be chosen, but the senior writer having used Seger's limits for several hundred

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[1] U. S. Weather Bureau, *Bull.* **4,** 40; Wiley, "Agricultural Analysis," I, 251–254 (1894).

[2] *Pottery Gazette,* **25,** 1126 (1904); *Trans. Eng. Cer. Soc.,* **3,** 16 (1904); "A Text-book of Ceramic Calculations," London, 22 (1904).

[3] *J. Chem. Met. Soc. S. Africa,* **9,** 187–91; *Chem. Abs.,* **3,** 2672 (1909).

[4] *Mining and Sci. Press,* **101,** 614–15 (Nov. 5, 1910).

[5] "Grundriss der Kolloidchemie," pp. 80–81, 84–87 (1910).

[6] *Trans. Am. Cer. Soc.,* **7,** 441 (1905).

[7] J. W. Mellor, *Pottery Gazette,* **35,** 788; *Trans. Eng. Cer. Soc.,* **9,** 94 (1910).

[1] Illinois State Geological Survey, *Bull.* **9,** 152 (1908).

[2] This is not Mellor's mean, but the arithmetical mean.

mechanical separations[1] has been deeply impressed by their practical utility.

*Existence of Exceedingly Fine Mineral Crystals Doubtful.*—Certain writers are of the opinion that the minerals found in clays and soils do not retain the crystal condition, but pass over to the colloid state when slightly under 0.001 mm. in diameter. If such is the case, it is a sad fallacy to assume, calculate, and give preponderance to the size of crystal grains under 0.001 mm. in diameter. Seger's smallest fraction, 0.01–0, does not unduly exalt this fine matter in the surface factor.

*Effect of Size on Physical Properties of Clay Wares.*—Clays containing large amounts of residue above 0.04 mm. in size are too coarse for fine pottery. China clays containing considerable amounts of the 0.040–0.025 mm. size are the "safest" used in potting. Most of the commercial English china clays have practically no residues coarser than 0.025 mm., while if they have but slight residues coarser than 0.010 mm., they are exceedingly liable to cause big losses from cracked ware.

Purdy's mechanical analyses of paving brick clays show a general agreement with this conclusion. The coarsest clays made the toughest brick and the finest clays the weakest brick.

The experimental work of this paper was done before our laboratory was transferred from the Technologic Branch of the Geological Survey to the Bureau of Standards.

### SUMMARY.

It is inaccurate to express the size of microscopic mineral grains in "diameters," unless the term is carefully defined. The volumes calculated from microscopic measurement require multiplication by correction factors.

The distribution of sizes in any fraction of clay obtained by mechanical analysis may follow several laws; hence, the various formulas proposed for calculating the mean size are all liable to error. A simple empirical correction factor to the arithmetical mean is apparently as accurate as any more elaborate calculation.

Mellor's surface factor, $\frac{6}{s}\left(\frac{W_m}{d_m}+\frac{W_n}{d_n}+\frac{W_o}{d_o}+\ldots\right)$, or

Purdy's simpler form, $\left(\frac{W_m}{d_m}+\frac{W_n}{d_n}+\frac{W_o}{d_o}+\ldots\ldots\right)$,

best represent the results of a mechanical analysis. The surface factors become uncomparable if different size limits are used in calculations for the smallest sizes. It is advocated that Seger's limits—0.04, 0.025, 0.010 and 0 mm.—give results of most value to clay workers.

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## THE DECOMPOSITION OF CLAYS, AND THE UTILIZATION OF SMELTER AND OTHER SMOKE IN PREPARING SULPHATES FROM CLAYS.

By Harrison E. Ashley.[2]

Received December 27, 1910.

In Ost's "Technische Chemie," edition of 1890, p. 129, is the statement that at a Silesian smelter the fumes were made to extract alum from shale clay. I cannot find the statement in the 1898 edition of Ost, from which the inference is that the process has been abandoned. A post-mortem examination is not usually inspiring, but as we still have smelter and industrial smokes containing considerable percentages of sulphuric acid, and as clays are found everywhere, the subject is likely to be revived at any time. An uneconomic process of a past decade often develops into a profitable industry of the present through the more definite knowledge of the conditions to be met. During the past few years some notable physicochemical data on the properties of clays that are involved in such a utilization of clays have appeared in publications inaccessible to many of you, and, together with some original data, are summarized in this paper.

Considering their economic importance, the clays are very imperfectly known as to decomposition and other critical points, as indicated by loss of water, heat absorption and evolutions, specific gravity changes, and solubility in acids.

An incorrect notion that the combined water of kaolin is given off in two stages is very prevalent.

Hillebrand[1] described a sample of pure crystal kaolinite (sp. gr. 2.611) and said "None of the water escapes at a temperature of 330° C.; it is therefore probably all basic water...... Frenzel[2] has described a variety of kaolin (myelin) which loses none of its water until a very high temperature is reached." Purdy and Moore[3] said: "The majority of clays are dehydrated completely when subjected to heat at 500–600° C., others not."

The only experimental figures with which we are acquainted, that show the actual losses in weight on heating clays to different temperatures, are those of A. E. Barnes[4] and W. M. Kennedy,[5] a pupil of Orton's. The details of these two tests are given in Fig. 1. Purdy and Moore's statement was likely based upon these tests.[6]

Le Chatelier[7] made some determinations that appear to have been accepted by all French authorities. He heated tests of typical hydrous minerals in a 5-mm. platinum cone opening in a large crucible filled with calcined magnesia and heated by a Forquignon furnace, taking only 10 min. to reach 1000°. He states that variation of the speed had little effect. Our investigations show that whatever the cause, his results were 100 to 150° C. too high. His results on the decomposition of calcium carbonate have been shown in error by a similar amount.[8]

On the basis of the observed retardations and accelerations, Le Chatelier divided the clays into 5 types:

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[1] *Trans. Am. Cer. Soc.*, **11**, 543–547, 489–492 (1909); **12**, 277–293, 441–442, 445, 779–782, 795–799 (1910); U. S. Geol. Survey, *Bull.* **388**, 48–51 (1909).

[2] Published by permission of the Director of the Bureau of Standards.

[1] U. S. Geol. Survey, *Bull.* **20**, 98 (1885).

[2] Naumann-Zirkel, "Mineralogie," 11th Ed., p. 676.

[3] *Trans. Am. Cer. Soc.*, **9**, 213 (1907).

[4] *Clayworker*, **23**, 705 (June, 1895).

[5] *Trans. Am. Cer. Soc.*, **4**, 152 (1902).

[6] I have since learned that Ellis Lovejoy published in the *Clayworker*, 1886 or 1887, the loss of weight at the melting points of different metals, and found the decomposition near the melting point of antimony, 624°+.

[7] *Z. physik. Chemie*, **1**, 396 (1887). *Comptes rendus*, **104**, 1443, 1517.

[8] Zavriev, *J. chim. phys.*, **7**, 31–57; *Chem. Abs.*, **3**, 1112 (1909).

*Allophane*, $Al_2O_3.2SiO_2.Aq$. Retardation between 150 and 220°.[1] A sudden acceleration at 1000°.

*Halloysite*, $Al_2O_3.2SiO_2.2H_2O.Aq$.—Marked retardation ending at 700°. A sudden acceleration at 1000°.

*Crystal Kaolin*, $Al_2O_3.2SiO_2.2H_2O$.—Decided retardation, ending at 770°. A slight acceleration at 1050°, "due to colloidal clay always present in kaolin."

*Pyrophyllite*, $Al_2O_3.4SiO_2.H_2O$.—Retardation ending at 700°. A doubtful retardation at 850°.

*Montmorillonite*, $Al_2O_3.4SiO_2.H_2O.Aq$.—A considerable pause at 200°, one less sharp at 770°, a doubtful one at 950°.

He stated that the halloysite group is the most important, including all the sedimentary and most of the "chemical" clays.

We have made only what we consider preliminary tests, heating cylindrical test pieces (5 cm. long, 3.5 cm. in diam., 1 cm. hole half way through the center) in an electric furnace with sufficient current turned on from the start to bring the test-piece to about 1000° in 100 minutes. Usually the runs were carried to 800° only. This gives a very rapid rise for the first few hundred degrees. The results are most readily perceived when put on logarithmic plotting paper with temperature-time coordinates. The following is a summary:

| Clay. | End of retardation. | Remarks. |
|---|---|---|
| English china clay, No. 1.... | 573°, 582, 574 | |
| North Carolina kaolin ....... | 578 | Acceleration at 940°. |
| No. 1 fire-clay.............. | 592 | |
| No. 2 fire-clay .............. | 597 | |
| Paving brick shale........... | 583 | |
| English ball clay............ | 581 | |
| Tenn. No. 3 ball clay........ | 583 | Acceleration from 900 to 970°. |
| N. J. saggar clay............ | 612 | |
| Ohio surface clay............ | 595 | |
| Albany, N. Y., slip clay...... | 590 | |
| Illinois joint clay............ | 574 | |
| Another Illinois joint clay.... | 552, 567 | |
| Minn., highly colloidal....... | 574 | |
| N. Dakota, highly colloidal .. | 617, 614 | Indistinct. |

An individual test is shown in Fig. 2.

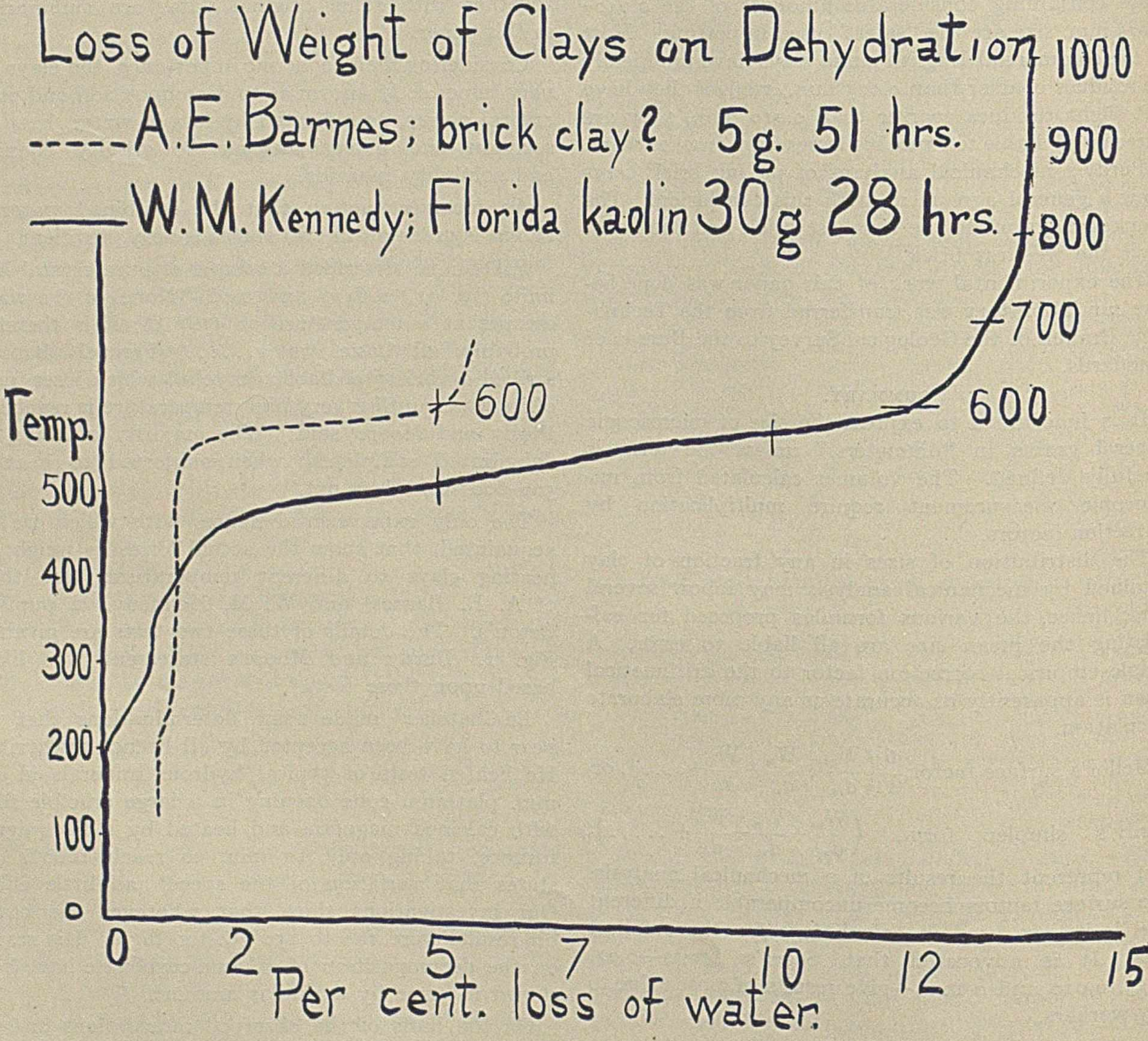

Fig. 1.

An initial slow rate of heating is due to the water held persistently by colloidal clay up to 200 or 300°.

A second retardation from about 500 to 575° is due to the expulsion of all the chemically combined water.

A third retardation from about 825 to 925° is of a wholly unproved nature, possibly the transformation of quartz to tridymite.

The same description, unproved, applies to the acceleration occurring at about 925°, which we suspect

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[1] Temperatures as given by Le Chatelier.

of being due to the formation of sillimanite, a mineral which crystallizes out in clay products at about 1350° C.

The specific gravity determinations of Knote[1] at the University of Illinois on the same sample of clay confirm our thermal results. Any attempt to determine from the specific gravities of sillimanite (3.2), quartz (2.65), tridymite (2.3), and corundum (4) what compounds exist at 1000° is futile, as the lightest possible mixture has a specific gravity of 2.95, as opposed to Knote's determination of 2.72.

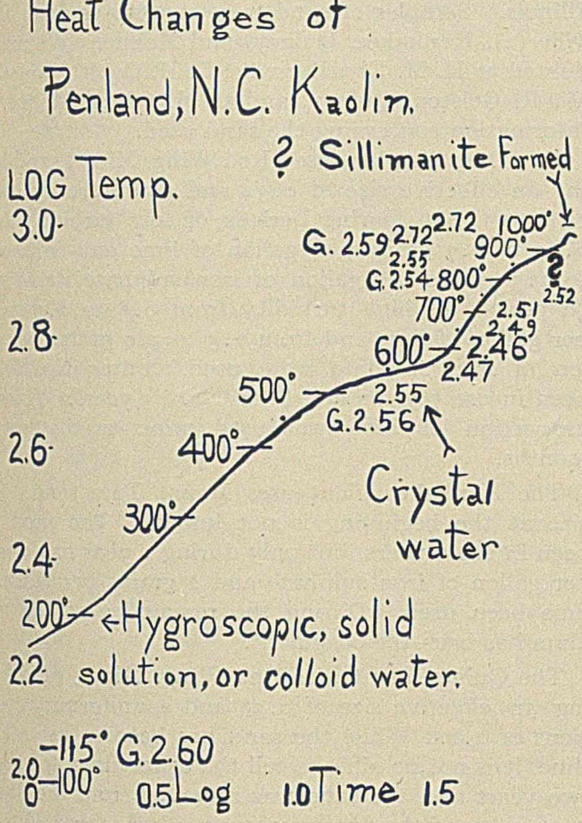

Fig. 2.

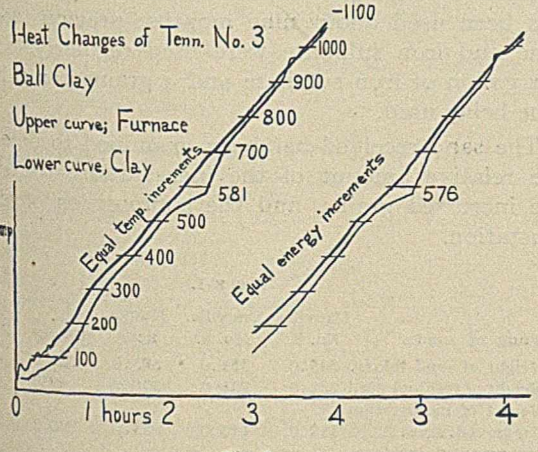

Fig. 3.

We have later tried heating the furnace at a regular rate, and also by equal electrical energy increments. All of the above-mentioned observations were repeated, except that the retardation at 825 to 925° did not appear with the clay tried (Fig. 3).

In Fig. 4 we have combined the results of Bleininger[1] and Knote[2] on the same clay. The apparent inconsistency of their results is due to the fact that Bleininger dried his sample at 100° and Knote at 115°. Such differences have a profound influence on colloid behavior, as has been noted by Hillebrand, Lord, and others. Knote made no determinations in the range from 115 to 450° that was studied by Bleininger.

With cold reagents the colloid matter of clay is very reactive with dilute reagents (below 0.1 formal), as described by the author,[3] but the crystal matter is quite insensitive.

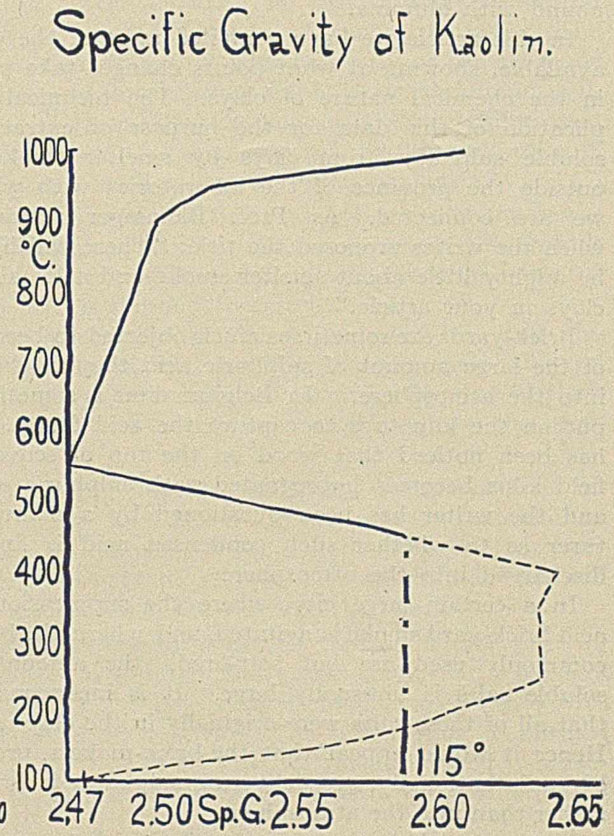

Fig. 4.

Below, say 300°, it is well known that the aluminum of clay is dissolved by hot concentrated sulphuric acid.

According to F. W. Clarke:[4] "After dehydration at low redness, kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution." The above data give a more precise temperature limit for the beginning of solubility.

Knote boiled Olive Hill, Ky., fire-clay with 1:3 hydrochloric acid, followed by treatment with 1 gram NaOH and 3 grams $Na_2CO_3$ per 50 cc. The results were:

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[1] *Trans. Am. Cer. Soc.*, **12**, 226 (1910).

[1] *Trans. Am. Cer. Soc.*, **12**, 504 (1910).

[2] *Ibid.*, **12**, 226 (1910).

[3] *Ibid.*, **12**, 768 (1910).

[4] U. S. Geol. Survey, *Bull.* **125**, 32.

| | Extraction. Per cent. |
|---|---|
| Raw clay | 6 |
| Ignited at 600° | 44 |
| Ignited at 1000° | 5 |

Edgar ball clay ignited at 600° gave 70 per cent. extraction, while raw clay and 1000° ignition also gave small extractions.

Le Chatelier stated that the heat evolution at 1000° accompanies the change by which $Al_2O_3$ becomes insoluble in acids.

Ries[1] found a few tenths of 1 per cent. soluble salts in unburned clay, 4.50 per cent. in soft-burned, and 1.03 per cent. in hard-burned. Evidently the soft-burned clay took up sulphuric acid from the fuel to some extent. At sufficiently high temperatures[2] silica will displace the sulphuric acid from its compound with alumina.

In this article we have compiled most of the data available, showing at what points changes take place in the chemical nature of clays. The technical application of this data for the purpose of extracting soluble sulphates from clays by smelter smoke is outside the province of the laboratories with which we are connected. As Prof. Bleininger remarked when the writer proposed the title: "There will likely be mighty little about smelter smoke and a lot about clays in your article."

Brick-yards are sometimes much objected to because of the large amount of sulphuric acid they discharge into the atmosphere. In Belgium lime is sometimes put on the kiln tops to capture the acid fumes. It has been noticed that wood on the top of scove or field kilns becomes impregnated with sulphuric acid, and the writer has been questioned by a manufacturer as to whether such condensed acid is finally discharged into the atmosphere.

In a certain large city, where the suppression of acid brick-yard smoke is agitated, and where the brick commonly used are but soft-fired, the amount of soluble salts is unusually large. It is inconceivable that all of these salts were originally in the clay used. Hence it would appear that the brick-makers, probably unintentionally, are delivering sulphates in bricks rather than into the atmosphere.

It appears, then, that any clay ignited between 600 and 900° C. will take up acids quite readily. The methods of utilizing this fact and the economy of processes are not discussed.

The retardation points given on p. 92 were determined under the direction of Prof. A. V. Bleininger by Messrs. R. K. Hursh and S. E. Young. The curves with equal temperature increments and equal energy increments were made by the writer.

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## EXTENT AND COMPOSITION OF THE INCRUSTATION ON SOME FILTER SANDS.

By E. Bartow and C. E. Millar.

Received January 7, 1911

When lime is used in connection with water purification there is a tendency to form an incrustation in the pipes or on the sand grains of the filters. In some cases the sand grains have become so large that it has been necessary to put in new sand. Cases have been reported where the sand near the bottom of the filters has caked into a solid mass.[1]

We have investigated the sand in some filters in Illinois. Samples of sand were sent to us from Danville (2), Kankakee, Quincy, and Moline. We are indebted to H. M. Ely, Danville, C. H. Cobb, Kankakee, W. R. Gelston, Quincy, and to M. Olson, Moline, for information concerning the sand used.

The Danville plant used Red Wing, Minn., sand having an effective size of 0.31 and a uniformity coefficient of 1.8. During periods of low turbidity from 0.27 to 0.7 grain per gallon of lime and from 0.58 to 1.5 grains per gallon of iron sulphate were used. In periods of high turbidity from 0.8 to 2.5 grains per gallon of lime and from 2.5 to 4.0 grains per gallon of iron sulphate were used. Filter No. 8 has been in use 7 years and filter No. 6 5 years. A larger proportion of lime was used prior to the last 15 months.

The Kankakee plant uses Mount Tom sand. The size at the beginning is not known. The sand has been in use 9 years, but only during 1 year has 1 grain per gallon of iron sulphate and 2 grains per gallon of lime been used. During the remainder of the time alum has been the coagulant.

The Quincy plant uses Red Wing, Minn., sand having an effective size of 0.38 and a uniformity coefficient of 2.1. While the sand has been in use a long time, it is not possible to tell the exact time, for about two years ago, the sand was removed from the filters, screened, and the finest replaced. It has undoubtedly been in use more than 7 years, for Quincy was the first plant in the country to use the lime and iron sulphate process. During the last 4 years an average of 2.05 grains per gallon of iron sulphate and 2.84 grains per gallon of lime were used.

The Moline plant has been in operation without removal or change of the sand for five years. Alum has been used about nine months; previous to that, lime and iron sulphate were used regularly, 1 grain per gallon of iron sulphate and 3 grains per gallon of lime being used.

The sand received has been examined to determine the relative amount of the incrustation, the size of the incrusted grains, and the composition of the incrustation.

Table I.

| Name of sand. | Danville, No. 8. | Danville, No. 6. | Kankakee. | Quincy. | Moline. |
|---|---|---|---|---|---|
| Weight of sand taken | 343.0 | 351.0 | 383.0 | 325.0 | 330.0 |
| Weight of residual sand | 232.0 | 238.0 | 330.0 | 49.0 | 94.0 |
| Weight of incrustation removed | 112.0 | 113.0 | 53.0 | 276.0 | 236.0 |
| Per cent. of incrustation | 32.4 | 32.2 | 13.7 | 84.7 | 71.4 |
| Per cent. increase by incrustation | 47.9 | 47.7 | 15.9 | 633.0 | 249.0 |

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[1] "Clays of Wisconsin," Wisconsin Survey, *Bull.* **15**, 22 (1906).

[2] H. A. Seger, "Collected Writings," American Ceramic Society Translation, **2**, 583, 646 (1902).

[1] *Eng. and Min. J.* May 6, 1908. Report of Ohio State Board of Health, 1908.

In determining the relative amount of the incrustation, we used approximately 250 cc. of each filter sand, which we carefully weighed and treated with hydrochloric acid until all the carbonate was dissolved. The residue was washed and weighed. The results are shown in Table I.

As the filter sands are of quartz and are unaffected by acids, this treatment gives quite an accurate means of determining the increase. It is hard to realize what an enormous increase these figures imply. An incrustation amounting to 71 per cent. means that there is an increase by weight of 249 per cent., and an incrustation amounting to 84.7 per cent. represents an increase of 633 per cent. With this increase in the size of the grains there has been an equivalent loss of sand, which has been carried into the sewers. The increase in the size of the grains is accompanied by loss of efficiency. As the grains increase in size, the interstices between the grains are larger and fine particles more readily pass through.

The size of the incrusted grains has been determined by the ordinary sieve method. The results are shown in Table II:

TABLE II.

| | Effective size. | Coefficient of uniformity. |
|---|---|---|
| Danville No. 6 | 0.52 | 1.30 |
| Danville No. 8 | 0.55 | 1.50 |
| Kankakee | 0.61 | 1.68 |
| Moline | 0.60 | 1.90 |
| Quincy | 0.77 | 1.67 |

A sand with an "effective size" above 40 would not be chosen for a filter sand. We can, from the table and by comparison with the original effective size, see that considerable deterioration has taken place. A calculation of the volume of the sand from Quincy before and after the incrustation formed shows a seven-fold increase. This corresponds to the 655 per cent. increase by weight shown by treatment with acid.

The composition of the incrustation was determined by evaporating to dryness a portion of the hydrochloric acid solution and analyzing the residue. The results obtained are shown in Table III:

TABLE III. COMPOSITION OF INCRUSTATION ON FILTER SANDS.

| Determinations made. | | Danville No. 6. | Danville No. 8. | Kankakee. | Quincy. | Moline. |
|---|---|---|---|---|---|---|
| Insoluble matter | | 5.89 | 7.58 | 1.83 | 0.32 | 1.20 |
| Oxides of iron and aluminium, | $Fe_2O_3 + Al_2O_3$ | 2.20 | 3.15 | 7.20 | 0.42 | 0.94 |
| Magnesium oxide, | $MgO$ | 1.16 | 1.00 | 1.09 | 0.83 | 0.12 |
| Calcium oxide, | $CaO$ | 49.58 | 47.70 | 47.75 | 54.03 | 53.10 |
| Sulphur trioxide, | $SO_3$ | 0.17 | 0.17 | 0.31 | 0.14 | 0.12 |
| *Hypothetical combinations.* | | | | | | |
| Magnesium sulphate, | $MgSO_4$ | 0.26 | 0.25 | 0.48 | 0.21 | 0.18 |
| Magnesium carbonate, | $MgCO_3$ | 2.23 | 1.90 | 2.00 | 1.63 | 1.37 |
| Calcium carbonate, | $CaCO_3$ | 88.53 | 85.17 | 85.26 | 96.48 | 94.83 |
| Ferrous carbonate, | $FeCO_3$ | 3.19 | 4.57 | 10.44 | 0.61 | 1.37 |
| Insoluble matter, | | 5.89 | 7.58 | 1.83 | 0.32 | 1.20 |
| Total | | 100.10 | 99.47 | 100.01 | 99.25 | 98.95 |

It will be noticed that calcium carbonate is the predominant substance. This corresponds to the composition of the incrustation found in the pipes at Quincy.[1] The incrustation at Kankakee contains the smallest proportion of calcium carbonate. This may be due to the composition of the mineral content of the water, or to the fact that lime had not been used for some time before the sample was taken. According to the analyses of the mineral content of the river waters,[1] the Kankakee river water contains the least carbonate and the greatest amount of sulphate.

The formation of incrustation on the sand grains is due to incomplete precipitation of calcium carbonate before the water reaches the filters. While the greater part of the calcium carbonate is precipitated quickly an appreciable quantity remains at the end of six hours. The precipitation will take place more rapidly if the water is agitated. The after-precipitation on the sand grains may be prevented by increased sedimentation, which often cannot be done because of the expense, by agitation of the treated water or by the addition of carbon dioxide. The carbon dioxide can be added directly or can be made by the addition of iron sulphate or aluminium sulphate. Carbon dioxide has been successfully used at Winnipeg. It was prepared by burning coke in the furnace used to run the filter machinery.

Sulphate of iron is being used in some of the newer installation as at New Orleans,[2] where the iron is added after the lime and where the water treated with lime is thoroughly agitated.

The reactions with the sulphates of iron and aluminium are double, for both calcium sulphate and calcium acid carbonate are formed. Neither of these substances will form an incrustation on the sand grains.

Laboratory experiments along the above lines indicate that the action of the iron and aluminium sulphates, following lime, is immediate, so that very little time need be allowed between its addition and the application of the water to the filters.

Experiments with carbon dioxide, either pure or as found in purified flue gases, show that there is a removal of the incrustation; blank experiments with air showed no removal. The substitution of purified flue gases for the air now so generally used in washing filters would probably prevent the formation of an incrustation.

ILLINOIS STATE WATER SURVEY,
URBANA, ILL.

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[1] *Proc. Am. W. W. Assn.*, **1908**, 172. Univ. of Ill., Water Survey Series, *Bull.* **7**, 35.

[1] U. S. G. S. Water Supply, Paper **239**, p. 89.

[2] *Eng. Rec.*, Apr. 23, 1910. *Eng. and Min. J.*, May 6, 1908.

# ADDRESSES.

## THE WORK OF THE CHEMICAL LABORATORIES OF THE BUREAU OF MINES.[1]

By J. K. Clement.

The organization of the chemical laboratories of the Bureau of Mines is perhaps unique, in that there is no chief chemist. The work is divided among a number of separate laboratories, each carrying on its own lines of work, under the direction of its own chief—the whole forming a group of more or less independent units. The relation of the work of the several chemical laboratories to that of the other departments of the Bureau varies with individual cases. In general, however, the problems of the chemists are closely connected with those of the mining and mechanical engineers.

*Fuel-Testing Laboratory.*—The oldest of the chemical laboratories of the Bureau is the Fuels Laboratory, which was established in connection with the fuel testing plant at the St. Louis Exposition in 1904. This laboratory, which is in charge of Mr. A. C. Fieldner, is occupied mainly with the analysis and calorimetric testing of fuels, including coal, coke, lignite and peat.

The samples submitted for analysis originate not only in the various sections of the fuel-testing and mine investigation divisions of the Bureau of Mines, but also in the various bureaus and departments of the Federal government. In addition to analyzing samples of all fuels used in the boiler and gas producer tests, ultimate analyses and calorific value determinations are made on mine samples of coal collected by the U. S. Geological Survey, as well as by certain state geological surveys. The data of these latter tests are of value in establishing the composition and heating value of the coals in connection with the classification of the coal fields of the United States.

A bulletin, now in course of preparation, gives the analyses and field data of all mine samples—about 5000—of coal tested since the establishment of the Government Fuel Testing Plant at St Louis.

In addition to the laboratory at Pittsburg, there is located in Washington, D. C., a laboratory in which are tested samples of coal delivered to the various buildings, arsenals, navy yards and military posts within the District of Columbia, and in various ports of the country and of the coal purchased by the Panama railroad.

*Fusibility and Clinkering of Coal Ash.*—In the use of coal under steam boilers, the property next in importance to its calorific value is perhaps the amount and fusibility of its ash. Indeed, some coals, which have a high heating value, are practically worthless for making steam on account of their tendency to clinker and adhere to the grate bars. The clinkering property of coal seems to be a function not only of the ultimate composition of the ash, but also of the character of the minerals from which the ash is formed.

Mr. F. M. Stanton is now engaged in an investigation of the relation between the fusibility and clinkering properties of coal ash and its chemical and mineralogical composition. Analyses already made indicate that the composition of clinkers obtained from different boiler tests with the same coal is constant, and that the composition of the clinker is more uniform than that of the ash itself.

It is interesting to note that $TiO_2$ was found in all the clinkers examined in amounts varying from 1 to 3 per cent. Determinations of the fusion point of various ashes give values ranging from 1150° to 1400° C.

*Chemistry of Petroleum Technology.*—Although the U. S. Geological Survey has issued a number of bulletins of a geological and statistical nature concerning the more important petroleum districts of the United States, until quite recently there has been practically no authentic or comprehensive information concerning the technical value of American petroleums available in scientific literature. Realizing the urgent need of such information, in 1907 the Technologic Branch of the Geological Survey began the systematic study of the commercial bodies contained in the crude petroleums of the United States, of the methods for their separation and purification and of their economic use. The California fields, because they gave at this time the greater promise of a large and continued production, and because of their proximity to naval stations, and the peculiar adaptability of the product as a maritime and locomotive fuel, have been selected for first study.

The following publications concerning this work are now in course of preparation by the Bureau of Mines:

A bulletin on the "Physical and Chemical Properties of the Petroleums of the San Joaquin Valley Oil Districts of California," including analyses of some 180 samples of petroleum from this valley, with a chapter on "Natural-Oil Gases" and with detailed descriptions of the methods of analysis employed in the Bureau of Mines laboratory.

A circular on "Methods of Sampling Petroleums and Oil Gases with Specifications for Fuel Oils."

A bulletin concerning "The Technology of Petroleums of the United States," showing the necessary steps and approximate costs of acquiring petroleum-bearing lands, their development and the technical handling of the oil and its disposal.

A "Chemico-geological Brochure of Petroleums," endeavoring to show the relations existing between the chemical-physical properties of the petroleums from the Coalinga and Midway-Sunset fields of California and its geological location.

Among the problems in which this laboratory is occupied are the following:

The determination of the specific gravity of petroleum, with special attention to variations of specific gravity with change in temperature.

The determination of the viscosity of crude petroleums and the factors governing its rate of flow through pipes.

The separation of water contained in the crude

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[1] Read before the Minneapolis meeting of the American Chemical Society. By permission of the Director of the U. S. Bureau of Mines.

petroleum by centrifuging, distillation, electrical treatment, and treatment with carbides.

The relation between the flash- and burning- points, and their significance.

The accurate determination of calorific value.

A study of the various processes of distillation, both on a laboratory and commercial scale.

An investigation of the methods of refining from an economic standpoint.

An investigation of the properties and uses of the various refined products of petroleum.

These and corollary problems are conducted primarily as a scientific study of the technology of the resources of the United States, and also to ascertain fixed properties and values, in order that the various government departments may be better able to make their purchases of petroleum products. These petroleum investigations are in charge of Mr. Irving C. Allen.

*Combustion Investigations.*—The work of the Fuel Testing Plant at St. Louis demonstrated the desirability of an investigation of the fundamental principles underlying the combustion of coal in boiler furnaces and in gas producers. Mr. J. C. W. Frazer, Mr. C. E. Augustine and the author are charged with an investigation of the processes of combustion and the conditions requisite for complete combustion, with coals varying in the content of volatile matter, with various rates of firing, various rates of heating of coal, and with variations in the amount of air supply, and in the rate of mixing of air with the volatile combustible. The work is being carried out in a furnace especially designed for the purpose, and having an unusually long combustion chamber. A single test involves the taking of about 35 gas samples simultaneously.

The author, with Mr. L. H. Adams, has completed an investigation of the rate of formation of carbon monoxide from carbon dioxide and carbon, and the rate of formation of water gas, at high temperatures. The results, which will appear in a forthcoming bulletin, No. 7, of the Bureau of Mines, show that the velocities of these reactions increase rapidly with rise in temperature, and that by operating gas producers at higher temperatures than is customary in present practice, a large increase in capacity should be obtained.

A special gas producer has been constructed for investigating the processes of producer gas formation, and an attempt will be made to apply the results of the laboratory tests on a commercial scale. The operations are in charge of Mr. C. D. Smith, mechanical engineer, Dr. Frazer and the author.

*The Composition of Coal.*—In connection with the chemical investigations undertaken by the Bureau of Mines, it was realized that the amount of information available relating to the chemical composition of coal was small in view of the importance of the subject. Our scientific knowledge of the chemical character of coal is limited almost entirely to its chemical analysis and its adaptation to certain industrial operations. It was considered by this bureau a matter of sufficient importance to justify the initiation of investigations having for their object the isolation and identification of some of the constituents of coal. So far the efforts in this work have been confined to such treatment of the coal as will not affect the composition of any of the constituents.

By the use of inert solvents, it is possible to extract as much as 35 per cent. of the original coal. By the subsequent use of neutral solvents and by fractional distillation in a vacuum, it has been possible to isolate a number of different substances. Some of these are oils, others solids varying in color from light yellow to dark brown. The analyses and molecular weights of some of these substances have been determined, and in a few cases it is believed the materials are practically pure substances.

This work is being continued on a larger scale than heretofore, in order to obtain greater amounts of the various fractions separated from the crude extract which is obtained from the coal, and it is hoped that results of a definite character will be forthcoming. Dr. E. J. Hoffman is associated with Dr. Frazer in the execution of this investigation.

*The Volatile Matter of Coal.*—Closely related to the boiler and gas producer tests of the Bureau of Mines, as well as to its investigation of the manufacture of coke, is the investigation of "The Volatile Matter of Coal," the results of which have been recently published in a Bureau of Mines bulletin, No. 1, by H. C. Porter and F. K. Ovitz. These authors have determined the quantity and composition of the gases evolved from various coals when heated to temperatures varying from 400° to 1000° C.

Further experiments along this line are now in progress, and particular attention will be given to the influence of the rate of heating on the character of the gases produced, to the initial composition of the gases at the instant of liberation, and to the thermal decomposition of these gases during passage over heated surfaces.

*Weathering and Deterioration of Coal.*—Under the direction of Dr. H. C. Porter, a series of tests is being carried on by the Bureau of Mines, in cooperation with the Navy Department, on the deterioration of coal in storage, with special reference to storage by submergence in sea water. The coal used in these tests is from the New River, W. Va., district. Analyses already made show that the coal stored in sea water and in fresh water has not deteriorated appreciably in the heat value of its fuel substance; and further, that the coal stored in the open air, under unusually adverse weathering conditions, has not lost in any case more than 1.0 per cent. of its heat value in one year. Similar tests, with Pocahontas coal, are in progress on the Isthmus of Panama, in cooperation with the Panama Railroad Company, the coal being stored in a 120-ton pile in the open air; and on Pittsburg coal, in cooperation with the University of Michigan, in which deterioration in gas-making qualities, as well as in heating value, is being investigated. Weathering tests on sub-bituminous coal have been made at Sheridan, Wyoming.

A forthcoming circular of the Bureau of Mines, entitled "The Accumulation of Gas from Coal," will present results which show the quantity and rate of formation of inflammable gas from freshly mined coal at ordinary temperature, and the rate of absorption of oxygen by the coal.

*The Burning of Coal in Mines under Diminished Supply of Oxygen.*—Another problem in which an appeal for aid has been made to the chemist is the combatting of mine fires. Dr. Porter has begun an investigation of some of the factors on which depends the propagation or extinguishing of fires in mines, especially the effect of variations in temperature and in the oxygen content of the surrounding atmosphere on the progress of combustion and on reignition.

*Examination of Mine Gases.*—One of the laboratories of the Bureau is devoted to the study of mine gases. An extensive investigation of the subject is being made on samples collected under all possible conditions—from normal mine air, from the afterdamp following mine explosions, from stagnant areas and from burning areas during mine fires, and from the gases produced by blasting explosives. These investigations are in charge of Mr. G. A. Burrell.

A new apparatus has been devised for the determination of small amounts of CO in gas mixtures by the iodic acid method.

Samples of gas, taken from burning areas, during the progress of mine fires, have been examined, with a view to gaining more complete knowledge of the chemical processes involved. By means of a specially devised portable apparatus, samples have been analyzed immediately after being taken, and valuable information furnished to those engaged in fighting the fire.

The effect of fluctuations in barometric pressure on the exudation of methane in mines is being investigated. The methods and apparatus used in the examination of mine air will be described in a forthcoming bulletin.

*Influence of $CO_2$ on the Explosibility of Mine Gases.*—The blanketing effect of carbon dioxide on the explosibility of gas mixtures is being investigated in one of the laboratories of the Bureau. The results show that the presence of this gas reduces considerably the range of explosibility of mine gas.

*The Chemistry of Explosives.*—The Explosives Laboratory, under Dr. W. O. Snelling, is occupied with (1) the analysis of all explosives submitted to the Bureau by manufacturers for test, and with such tests as are necessary to determine the stability of these explosives under different conditions of temperature, and the liability of the explosive to exudation; (2) the chemical analysis of the products of combustion of the above explosives obtained after explosion in the Bichel gauge; (3) the chemical analysis of electric detonators, blasting caps, fuses, etc., used in connection with the physical tests on explosives.

Among the research problems with which the laboratory is engaged are the following:

A study of a chemical method of determining the relative strength of electric detonators, blasting caps, etc., by means of the decomposition produced in a practically non-explosive body capable of undergoing decomposition under the influence of a strong detonating shock.

The development of a method of determining the relative strength of electric detonators, blasting caps, etc., depending upon the degree of pulverization of sand or other suitable material which is effected under fixed conditions by the force of the detonator or blasting cap.

Investigation of a method for determining the relative liability of nitroglycerine explosives to exudation, and of measuring the ability of different explosives to retain absorbed constituents.

An extensive investigation of methods of analysis of explosives. Considerable work has already been carried out toward the preparation of a bulletin on this subject.

In addition to the above work, this laboratory is engaged in the inspection of all explosives, including dynamite, blasting caps, electric detonators, fuses, etc., purchased by the Isthmian Canal Commission. This work includes the analysis of such explosives and tests to determine their safety during transportation. Daily analyses are made, at the works of the manufacturers, by one of the chemists of this laboratory, covering all dynamite purchases for the use of the Isthmian Canal Commission, and tests of other materials made at each inspection period. To illustrate the extent of this inspection work, it is noted that there were made during the fiscal year, ending July 1, 1910, 434 analyses of dynamite, 69 analyses of electric detonators, and 2279 physical tests of electric detonators.

*Coal Dust Explosions.*—Some of the most important and most difficult of the problems confronting the mining engineer relate to the safety precautions necessary to mitigate the dangers encountered in coal mining operations. The two greatest sources of danger to be combatted here are the explosive gases given off by the coal, and the finely divided coal dust which exists throughout most coal mines. The first danger can be overcome only by increasing the ventilation in the mines. Unfortunately, this increases the danger from the coal dust by the removal of its moisture. The coal dust problem has greatly interested mining engineers recently, and is now being investigated by nearly all coal mining countries, and a great deal of attention has been given to the subject by the Bureau of Mines.

The greatest danger from coal dust, in the absence of mine gases, is in connection with the use of explosives, as the ignition of coal dust from other sources is not so likely to occur. The first efforts of the Bureau of Mines, therefore, has been, by systematic tests, to determine those explosives which are least liable to cause the ignition of explosive gases and coal dust. This work has resulted in the preparation of a list of explosives known as "permissible explosives," which, when properly used, will minimize the danger from this source.

In this connection, efforts have been made to devise a laboratory method to test the inflammable character of samples of coal dust, and to classify them according to their inflammability. This method is based on determining the amount of combustion which takes place when clouds of dust of the same density are ignited under the same conditions, the amount of combustion being determined by the pressure developed within the explosion vessel. In this way it is possible to obtain results on any one sample of coal dust which agree to 3–5 per cent. of the total pressure developed. By varying the temperature of the platinum coil, used as the source of ignition, it is also possible to study the change in the amount of combustion taking place when the source of ignition varies. The result has been to show that when a highly inflammable dust is under investigation, the pressure developed soon reaches a maximum, and an increase of the temperature of the coil causes but little increase in the pressure developed, indicating that the combustion has propagated throughout practically the whole cloud of dust. With a slightly inflammable coal dust the pressure developed continues to increase with increasing temperature of the coil over the whole range of temperature at which it is practicable to operate.

One of the proposed means of lessening the inflammable character of coal dust is to add a non-inflammable dust. The laboratory method used to investigate the inflammability of coal dust has been extended to various percentages of coal dust and finely ground shale in order to determine to what extent the combustion is limited by the presence of the inert dust. The experiments indicate that a marked diminution of pressure is not obtained until about 25 per cent. of inert dust is added, the pressure then falling off rapidly with a further increase in the amount of shale dust added. This investigation is in charge of Dr. J. C. W. Frazer.

## DISPOSAL OF STARCH FACTORY WASTES.[1]

By T. B. Wagner.

When your esteemed President asked me, about two months ago, to read a paper before this meeting, I accepted his invitation with much hesitation, not only because of pressure of business, but particularly because I do not consider myself well qualified to speak on such subjects as come up before your Association. While I desire to make my remarks as brief as possible, I believe that I shall have to go back into the history of the industry of corn products, to give you a better understanding of the subject under discussion.

In the early stages of the corn products industry, that is, primarily the manufacture of corn starch, dating back fifty years or more, the manufacturers concerned themselves solely with the starch contained in the corn; the other constituents of the corn were to them of no concern. These constituents are, the outer hull of the corn—the so-called bran—the gluten located immediately underneath it, and finally, the germ of the kernel itself. When you consider that corn contains approximately 10 per cent. of nitrogenous matter, you will note that in a small factory consuming only about one thousand bushels of corn a day, this ingredient alone would amount to approximately 5600 pounds per day. The bran forms about the same percentage of the corn and there would be a like waste from this source. However, there are no starch factories operating on so small a scale to-day, the smallest consuming about five thousand bushels a day, whereas the larger factories, which usually produce not only starch but glucose and sugars as well, grind about twenty-five thousand bushels a day. Our Argo factory represents the latest achievement in the corn products industry and its grind, a year from now, will approximate fifty thousand bushels a day. I give you these figures so that you may fully appreciate the importance of the recovery of the by-products. If these by-products were not recovered, our industry could not exist, not only for financial reasons, but particularly because the waste of the by-products would lead to intolerable conditions from a sanitary point of view. Our industry has made remarkable progress. At the time the above conditions prevailed, that is, when starch factories did not recover any by-products, the total recovery of the corn did not amount to more than 50 per cent.; that is to say, all that a manufacturer produced from a bushel of corn weighing 56 pounds were about 28 pounds of commercial starch, part of the starch and all other ingredients of the corn going to waste.

With the introduction of the recovery of the by-products, this yield was, of course, greatly increased until it finally reached about 92 per cent. Only about ten years ago this was considered a good showing for any starch or glucose factory. With the construction of modern plants and the introduction of modern machinery, and through the closest attention of the operating men to the smallest details of the process, it was possible to increase this yield to 95 per cent., which as recently as four years ago, was considered a most excellent result. Since then, the yield has been further increased so that the new standard is 98 per cent., although we have had months where some of our factories recovered as much as 99$^1/_2$ per cent. You will note from this that the trade waste from a modern starch or glucose factory cannot be considerable, expressed in per cent., yet it reaches large proportions when applied to the corn consumed. Mr. Sjostrom will give you the exact figures as to the amount of this waste.

When we undertook to treat our trade waste at our Waukegan factory, it was not done for the purpose of recovering this waste, but our efforts were the result of an action taken by a number of residents of the town of Lake Forest, located on Lake Michigan, eight miles south of Waukegan. These parties claimed that our trade waste was carried in the waters of Lake Michigan and while in transit became putrefied and created obnoxious odors which made life very un-

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[1] An address delivered before the Lake Michigan Water Commission, Chicago, December 17, 1910.

pleasant for them. They brought an action in the Federal Courts, for the purpose of having the Warner Sugar Refining Company (the predecessor of the Corn Products Refining Company) either instal the necessary apparatus and process to remedy the trouble, or cease operating the factory. The principal factor in producing the trouble was the steep-water; that is, the water in which the corn is soaked and which contains by far the largest amount of the soluble ingredients of the corn. At the time the suit was brought this steep-water amounted to 200,000 gallons a day. While this suit was pending, the Corn Products Company succeeded the Warner Sugar Refining Company, and the first step it took was to instal the necessary evaporating apparatus to recover this water in the same fashion as is the practice in its other factories. This relieved the situation very much. Upon investigation, however, we found that the remaining waste was discharged into the lake immediately at the shore and that there was no means of diluting this trade waste, which was carried in concentrated form, so to speak, southward toward Lake Forest. We, therefore, laid a new sewer pipe, about thirty inches in diameter, and carried it into the lake a distance of two thousand feet; at this point the lake is about fourteen feet deep, and it stands to reason that with the current usually existing in Lake Michigan, we secured an enormous dilution of these waste waters. While a great improvement was made in this way, the conditions still remained unsatisfactory. This was because the waste waters contained a not inconsiderable amount of suspended matter which cannot be recovered or isolated by filter presses or other means usually employed for such purpose. Mechanical means being unsuccessful, our only hope lay in a chemical treatment, the governing thought being that if we employed a precipitant, such as lime, this finely suspended matter might be thrown down together with the precipitate formed by the action of the lime. The results obtained in experiments conducted on a small scale were so complete and surprising as to tempt one to consider this theory an inspired one. It is remarkable how completely this suspended matter is thrown down and how quickly the precipitate settles to the bottom.

Filter presses being out of the question, the success of this scheme depended upon the rapidity with which this precipitate would form and how clear the supernatant water was. The tests were carried out in a large tank with cone-shaped bottom, holding about 28,000 gallons of water. The results were highly satisfactory; immediately after the addition of the lime the precipitate settled to the bottom and the supernatant water was as clear as spring water. A series of tests were then made with the treated water, with the particular view of ascertaining how quickly the dissolved oxygen would oxidize the organic matter. The large amount of dissolved oxygen in Lake Michigan water and the enormous dilution secured by our method of discharge brought about this result in a very satisfactory manner. I shall not go any further into the details of this process, as Mr. Sjostrom will deal with that in his talk.

We do not claim that we have solved the problem of the proper treatment of trade waste from starch and glucose factories, but we believe that we have gone as far as we can go with the present knowledge of the subject. I think we are the first ones, so far as our industry is concerned, who have ever undertaken to treat waste waters on so large a scale as is being done at Waukegan. The undertaking was not a small one and involved a very large expenditure of money. I do not believe that a mechanical or chemical treatment will ever yield a trade waste free from objections. The ultimate solution must come from within the factories; that is to say, we shall keep on devising ways and means of recovering in the factory all the soluble matter still discharged in our waste waters, and while it may take years to accomplish this end, I believe that eventually we shall be successful.

CORN PRODUCTS CO., CHICAGO.

## TREATMENT OF WASTE WATER FROM A STARCH AND GLUCOSE FACTORY.[1]

By OTTO A. SJOSTROM.

The waste water from a starch and glucose plant is composed of effluents from different departments of the factory. In speaking of the components of the discharge through the main sewer we distinguish between condenser-water, gluten cones overflow-water, starch cones overflow-water, and feedpress-water.

Of these the condenser-water represents by far the largest amount but can be left out of consideration in this connection, as it does not contain any products from the manufacture. It happens occasionally, of course, that the vacuum pans entrain soluble solids so that some sugar is lost with the condenser-water. As this is a serious but avoidable loss, due to irregularity of the machinery, a close watch is always kept on this water and whenever tests indicate traces of sugar steps are immediately taken to remedy the trouble.

The different names of the other effluents do not indicate that the composition of the solid matter is different. A short outline of the method of manufacture will give a better understanding of the nature of the waste.

The corn is first steeped for some time with water, slightly acidulated with sulphurous acid. This softens the corn thoroughly and prepares it for grinding. The corn is first ground coarse and passed through machines for removing the germ. It is then ground very fine in stone mills. The so-called mill slop issuing from the mills is run over shakers and reels in order to separate the starch and gluten from the hulls. The hulls are washed to make this operation complete. The starch milk is run over the so-called tables, where the starch settles. The gluten is lighter and remains suspended in the water which tails over the end of the tables. This gluten milk is then run into settlers, which are built with a conical bottom. The operation of settling is continuous. The bulk of the

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[1] Corn Products Refining Co.'s Plant at Waukegan, Ill. An address read before Lake Michigan Water Commission, Chicago, December, 1910.

water overflows at the top and this is what we call the gluten cones overflow-water. The concentrated gluten milk which is drawn continuously from the bottom of the settlers is mixed with the hulls and this mixture is filter-pressed. The water from these presses, the feedpress-water, is evidently the same water as the overflow-water from the gluten cones. The starch milk, which results from the washing of the hulls, is not concentrated enough to be run over the tables. It is therefore run into settlers similar to the gluten settlers. The water overflowing from the top is the starch cones overflow-water.

These waste waters contain the soluble substances in the corn. The larger part of the solubles in the corn, however, is contained in the steep-water, which is obtained from the steeping of the corn, as mentioned above. As the steep-water is drawn from the corn it contains between 6 and 9 lbs. of solids per 100 lbs. of water. It is evaporated to what we call heavy steep-water, with a gravity of 16 to 20° Bé., and mixed with the cake from the presses mentioned above. This mixture is dried and forms a so-called commercial feed, an important by-product of the manufacture.

From these short hints about the manufacture it is easy to understand that the waste waters are practically nothing but extremely diluted steep-water. This dilution prevents, of course, all efforts to utilize the waste waters by concentrating them.

The amount of waste water varies considerably for the different plants, depending upon variations in the manufacturing process. In Waukegan, measurements have been made on several occasions. The first measurements, mentioned by Prof. Bartow, in his report No. 6 of the Illinois State Water Survey, were made by means of weirs and gave too low results, as we found later when we could use in making measurements the large tanks erected for treatment of the water. The discharge of overflow-water from the starch cones is about 1,000,000 gals.; the combined feed-press water and overflow-water from the gluten cones is about 650,000 gals., all in 24 hours. Including the condenser water, the total discharge from the plant is probably about 4,000,000 gals. daily.

The overflow-water from the starch cones contains about 180 grains per gallon dissolved matters. The gluten cones overflow- and the feedpress-water contain about 0.3 per cent., the gluten water about 0.4 per cent. dissolved matter. Obviously it is an impossibility to concentrate these waters economically.

The soluble matter contains about 50 per cent. nitrogenous matters, from 30 to 35 per cent. carbohydrates, and from 15 to 20 per cent. inorganic matters. A varying proportion of the nitrogen is present in the form of amides and amido acids. The inorganic content is mainly potassium magnesium phosphate.

In addition to the soluble matter the waste waters also carry a definite, though much smaller amount of insoluble matter, which consists of starch and gluten, suspended in the water. As the gluten does not settle as well as the starch the gluten overflow-water always contains more, say 25 grains per gallon. The starch overflow-water contains about 15 grains per gallon. The loss from this source represents about 0.35 per cent. of the corn, or about 2 tons of starch and gluten carried into the lake every day. Compared to the grind, 25,000 bushels per day, the amount of the loss is of course not considerable; but it is evident, that in case of irregularities in the run of the settlers, considerable quantities could occasionally escape to the sewer. A close control is therefore kept of the work of the settlers, and samples are taken and tested regularly many times during the day and night.

It is evident that waste waters like these, containing carbohydrates, proteins and other nitrogenous matters, furnish an excellent material for the fermenting action of organisms like yeast, moulds and bacteria. Microscopic examination of the waters discloses the abundance of these organisms. During the manufacturing process, however, their action is checked or retarded by the presence of sulphurous acid which, as is well known, even in small quantities, is a most efficient poison to microorganisms. The fermentation inside of the plant is in fact limited to the formation of a small amount of lactic acid. Upon emerging from the plant the waste waters contain on an average 0.03 per cent. of sulphurous acid, which amount is too small to prevent fermentation, if the discharged waste is left undiluted.

To our best knowledge, however, the trouble which we have tried to obviate by installing the purification plant is caused, not by the soluble matters, but by the presence of the comparatively small amount of suspended matters. As for the soluble solids, the effluents are carried away by the ever-present currents in the lake and become soon so diluted, and consequently the dissolved matters so widely distributed, that the effect of fermentation or chemical changes, which take place sooner or later, is lessened or not noticeable in the large body of water.

With the suspended solids conditions are different. If they drift shorewards under the influence of certain currents and are deposited along the shore, they may without doubt become offensive. They form an excellent medium for the growth of molds and bacteria and their decomposition is accompanied by the formation of foul-smelling compounds and gases.

More likely this decomposition along the shore is exceptional. As a rule it takes place too far out to become offensive. However, as complaints from residents on the North shore seemed to be supported by observations made by Prof. Bartow and his assistants—these observations are embodied in the State Water Supply Report referred to above—the company decided to act upon and follow the suggestion of Dr. T. B. Wagner in regard to a treatment of the waste water. Dr. Wagner had previously found from experiments on a small scale that the treatment with sulphate of iron and lime was the one best suited to conditions. Money was appropriated and experiments started on a fairly large scale. These experiments led to the erection, in 1907 and 1908, of a plant capable of treating 1,300,000 to 1,400,000 thousand gallons daily. It was not considered necessary to build the plant larger, because in the meantime the superintendent of the plant, Mr. Lenders, had found a way of utilizing part of the waste water over again in the manufacture.

The treating plant thus erected is simple in its arrangement but represents nevertheless an outlay of money of about $100,000. When it comes to handling such quantities of water within a limited space the apparatus required becomes very expensive, even if the operations are simple.

Before describing the arrangement of the plant I will first give some consideration to the chemical end and to manufacturing data.

It is well known that the iron hydrate formed by bringing together sulphate of iron and lime acts as a precipitant and, being flocculent, carries down with it all suspended matters including yeast, mold and—more or less completely—also the bacteria. In our case we happen to have in the soluble matter an amount of phosphates sufficient to furnish a precipitant in the form of lime phosphate upon addition of the lime. It is therefore not necessary to add any iron sulphate, although we have at times used this salt. The iron acts in the form of iron phosphate, which is of course a good precipitant.

Dr. Wagner found, from experiments on a small scale, that while a small amount of lime was sufficient to precipitate the suspended matters it was necessary to add a large surplus of lime in order to obtain a precipitation, which would be quick enough to allow the handling of the quantities in question without using apparatus of undue size and occuping space beyond what was available. He fixed the amount at 2 lbs. of lime per 1000 lbs. of water. We found later, when working on a large scale, that this amount could be cut down to about 1.4 lbs. per 1000 lbs., or 11.7 lbs. per 1000 gals. In case of less grind and consequent slower run of the settlers this amount can be cut down somewhat but not much, if we expect the water to run clear from the settlers.

This is a very large quantity compared to the amounts added in clarifying municipal water supplies. But as it was out of the question to use large settling tanks and this way of working allows the use of continuous settlers and consequent rapid removal of the sludge, there could be no hesitation as to the method to choose.

The chemical action of the lime is practically limited to the neutralization of the acids and the formation of lime phosphate. Only part of the phosphoric acid in solution reacts with the lime; the rest remains in solution as double salts and in organic combination. At the same time the reaction of the water becomes of course alkaline. A small amount of ammonia is set free from the easily decomposed amides, but otherwise the nitrogenous matters are not affected, or it is at any rate not possible to express the effect chemically. Upon the suggestion of Prof. Bartow we made a series of tests on the changes in dissolved oxygen and in oxygen-consuming power of untreated and treated water, undiluted and in varying dilutions. Prof. Bartow has discussed the results in the Report mentioned above. The figures indicate that the water is less putrescible after the treatment.

It is evident that if a removal of dissolved organic matters were required from the sanitary point of view, very little would be gained through this treatment. But, as said before, the trouble which has given rise to complaints lies with the suspended solids. These are completely carried down with the precipitate. In addition, the micro-organisms present are also, so to say, wrapped up in and carried down with the flocculent precipitate. The waste water is consequently practically sterile after treatment. This is a distinct point in favor of the treatment. Conditions may occasionally prevail in the lake, which minimize the action of the currents, so that the effluents are, so to say, held together in the lake and only slowly become diluted. In such a case fermentation would soon set in, started by the organisms abundant in the effluents. With these organisms removed through the treatment the danger of any troublesome consequences arising from such conditions is—to say the least—very considerably reduced.

Turning to manufacturing data, the proposition handled is the treatment of about 1,300,000 gals. of waste water in 24 hours. At a rate of 11.7 lbs. of lime to 1000 gals. there are required about 7.5 tons of lime daily. The amount of precipitate obtained is between 8 and 9 tons, figured as dry. Of this precipitate the organic matters—that is, starch and gluten—form about 25 per cent. The precipitate contains from 4 to 6 per cent. nitrogen figured as protein. There are from 5 to 8 per cent. of phosphoric acid in the precipitate. The fact that a large part of the lime acts only mechanically and is recovered as hydrate in the sludge naturally led to experiments in using the sludge over again for precipitating. But all efforts in this direction were futile. We could not get the required almost instantaneous settling with anything but pure lime.

The mechanical arrangement of the treating plant is very simple. The overflow-water is pumped up to the third floor of the plant, where the mixing tanks are located. In the first arrangement we had 5 tanks provided with agitators, each of about 3500 gals. capacity. On top of these tanks were small tanks for the lime, which is made up for use into a milk of about 12° Bé. gravity. The idea was to fill these tanks in succession, run in the proper amount of lime, agitate and draw off to the settlers. We soon found, however, that the thorough agitation was not only not necessary but in fact detrimental to a perfect settling, as the precipitate lost its flocculent character and did not leave a perfectly clear solution. It was further difficult to maintain the flow into the settlers at a constant rate—a condition, which is very essential when working continuous settlers. After some experimenting with baffle plates arranged horizontally above each other, which did not prove satisfactory on account of the enormous amount of foam created, we finally decided that the simple scheme of running the water and the lime together in a continuous stream into the same tank gave the best results. This tank has an overflow to the settlers about three feet from the bottom and is provided with an agitator which moves very slowly.

The regulation of the lime supply offers no difficulties. The man in attendance tests the treated water for alkalinity at fixed intervals. There is a certain relation between the alkalinity and the amount of lime added, and any variation in the amount of lime is indicated by a corresponding variation of the alkalinity. When using the normal quantity of lime the titer of the water is about one-fourth of the alkalinity of a completely saturated lime solution.

The lime is slaked with hot water in a trough-like iron tank. In the tank revolves a horizontal reel made of coarse 1/4-inch netting. The lime is charged into this reel through a funnel-shaped opening on the side of the tank. The lime milk is pumped to a diluting tank, in which it is made up to the desired gravity. From there it runs over a fine screen into a storage tank provided with an agitator. A centrifugal pump is connected to this tank. The lime milk is kept circulating through a pipe line, which runs up to the mixing tank and back to the storage tank, and the supply pipe to the mixing tank branches off from this line. In this way a constant supply of lime milk of uniform strength is insured.

The settlers are built like gluten settlers, with conical bottom. The diameter is 14 feet; the cylindrical part is 22 feet high. The capacity is about 28,000 gals. The treated water distributes itself into troughs running over the settlers. Each settler has in the center a vertical pipe, 15 inches square, connected with the bottom of the trough. This pipe ends about three feet from the bottom of the cone.

The supply to each settler is regulated by raising or lowering plugs, which fit holes in the bottom of the troughs over the vertical pipes. The water runs downward through the vertical pipe, rises slowly on the outside and overflows into troughs, which lead to a sewer discharging some distance out in the lake. The precipitate stays in the lower part of the settler and the sludge is drawn off continuously through the pipe at the bottom of the cone. There are 21 settlers, of which 16 are used for the first settling. The sludge from these settlers is pumped to the five so-called second settlers. From here it is pumped a considerable distance to the old Dry Starch House at the southern end of the plant. The sludge is filter-pressed here, the presscake is broken up, loaded upon trays and dried in kilns in the same manner as starch.

What to do with this presscake has been and is still a problem. Owing to the excess of lime, the only use which could be made of this product would be as fertilizer. As both the protein and the phosphoric acid are low it could command only a very modest price. Whether this would be profitable depends upon the proximity of a market. Part of the presscake is used for neutralizing the concentrated steep water, which contains a certain amount of acid phosphate and of organic acids. It is well adapted for this use, and by distributing the same among the other plants considerable quantities of this product have been disposed of. The bulk of the presscake, however, is bagged and stored away until some use is found for it.

These notes on the treatment of starch waste have, I hope, given an idea of the nature of the problem and of the manner in which the company has tried to solve the same in this particular case. Sanitary standards and requirements become higher gradually and the chemcal industry in particular is confronted more and more with the necessity of having to consider its various problems of waste, not only from the point of view of recovery and utilization but also in regard to their disposal to the satisfaction of the sanitary interests, which may call for strict and rigorous requirements without themselves being always able to offer any guide or suggestion as to the solution of the problems.

Corn Products Co., Chicago.

## PLANT AND MACHINERY.

### SAMPLING AND PREPARATION OF RAW MATERIALS FOR ANALYSIS AT SOUTH WORKS, ILLINOIS STEEL CO.

By Walter B. Wiley.

Chemical control in the manufacture of steel has at present not reached its ultimate importance, but, during the past decade, rapid steps have been made in that direction.

More and more is constantly demanded in this line, and at the South Works of the Illinois Steel Co. earnest and careful efforts are made to meet these requirements.

Here, the taking and preparation of large and representative samples of all raw materials, entering into the making of steel, is a matter of routine controlled by strict supervision and by intelligent methods, the result of many years of experience and much experiment.

There are two distinct theories as to the proper method for reduction of samples to laboratory requirements, crushing and grinding, and each has its advocates.

The champions of crushing, by means of rolls, insist that by this method there is less danger of contaminating the sample by the introduction of small particles of iron which may also carry with them phosphorus and other elements, thereby vitiating the value of chemical analysis.

On the other hand, grinding is probably much more rapid and the machinery required more compact.

The grinding method was chosen at South Works, but the chance of contamination of samples avoided, or at least greatly minimized, by the use of manganese steel for all grinding surfaces.

Sampling of raw materials must always be an integral part of modern steel-making, therefore its housing should be in permanent structures. The sampling house, preferably of concrete or brick construction, should have few exposed beams or ledges to furnish lodgment for the dust and dirt consequent to crushing, thereby making cleanliness possible and

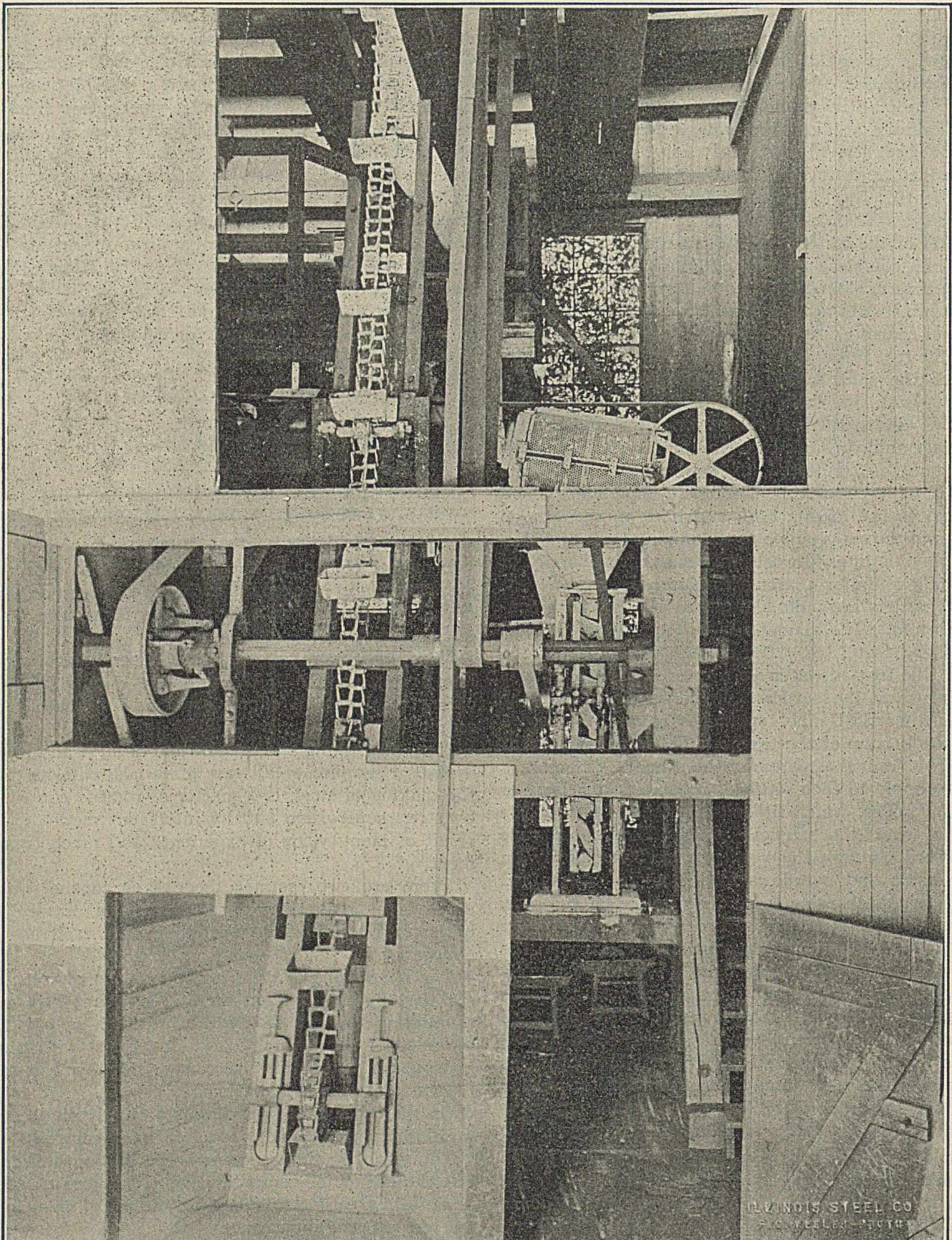

Fig. 1.—Machinery for primary ore crushing; O size, Gates crusher; revolving screen and Foster-Coolidge sampling machine (enclosing wall partially removed).

easy to maintain. Provision for an abundance of light and ventilation is an absolute necessity.

In 1907, when the present South Works sampling house was built, certain local conditions made necessary a frame construction, covered outside with corrugated iron and ceiled inside. At that time it embodied, probably, the best and most advanced ideas for the rapid and accurate mechanical preparation of large samples. Since then a few minor changes have been made to improve details and keep abreast with the times, so that at present the equipment is modern, in the best sense.

The house consists of a main structure 53′ by 38′ with a wing 30′ by 22′.

The wing, provided with dust-tight bins and boxes, to avoid contamination, is used for storing cumulative samples which are worked up at weekly, semimonthly and monthly intervals. Here, also, is installed the 10 h. p. constant speed induction motor which furnishes the power necessary for operation of all the machinery.

The main building is divided into a crushing room 40′ by 38′, a rubbing or finishing room 9′ by 13′, a still room 13′ by 20′ and an office 9′ by 13′.

In the still room is a Jewell still which furnishes all the distilled water used by the plant, for laboratory and other purposes. Here are kept shipping notices of all raw materials and by which our sampling is checked.

The rubbing room is provided with two open-hearth steel, properly tempered, bucking boards 24″ by 24″ with 45 pound mullers for the same, used for reducing samples to laboratory fineness. There is also an Iler disc pulverizer, speeded to 600 r. p. m., which aids in the final preparation of certain samples. Chilled steel mortars are used to finish samples like coke and scales for which, to date, no machine has been found capable, by us, of preparing properly.

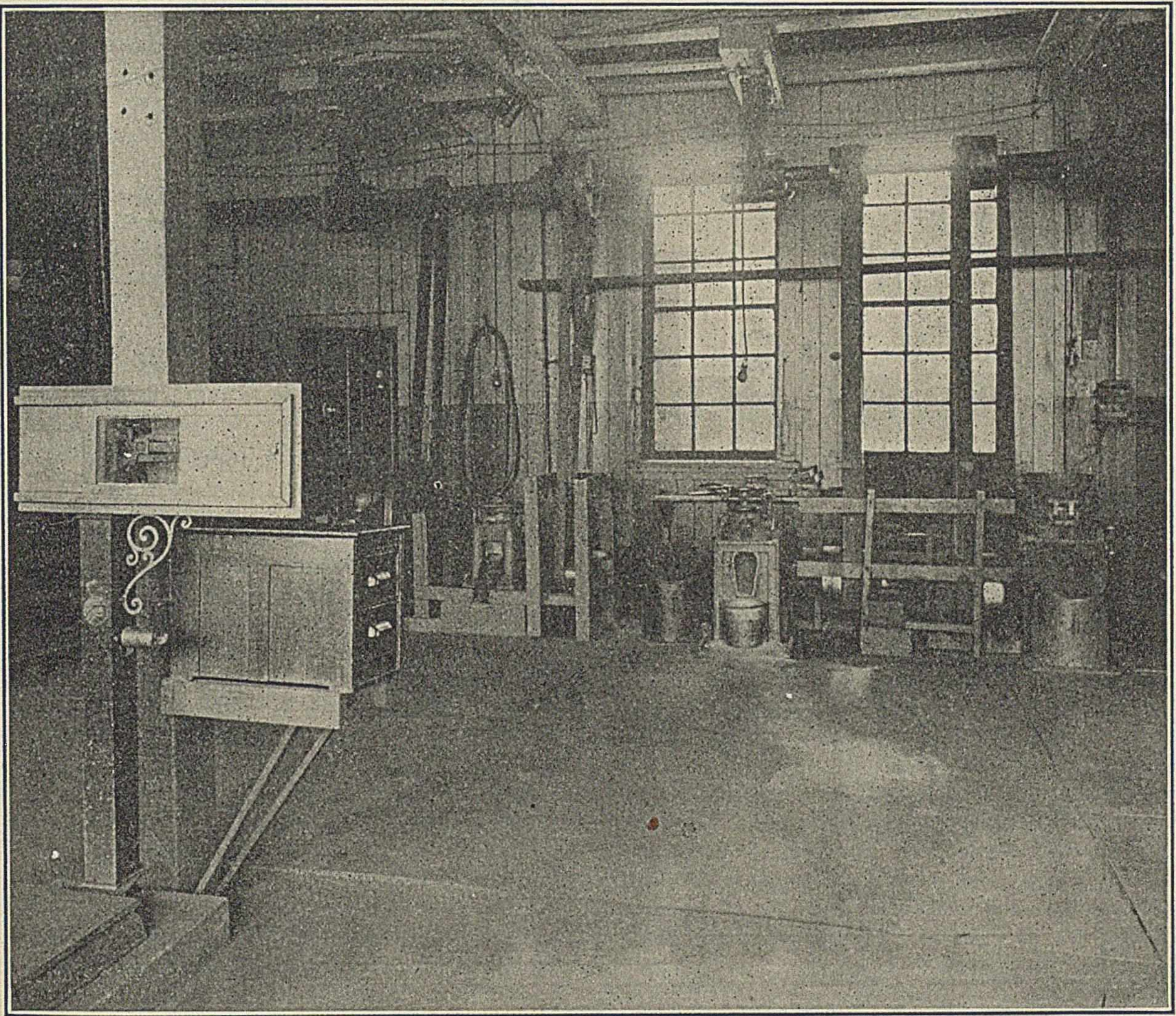

Fig. 2.—Machinery for intermediate grinding.

The crushing room is provided with a floor of smooth steel plates, to facilitate the mixing and quartering of samples. Six drying pans, 6′ by 6.5′ with double bottoms and heated by steam, are located here and used for drying ore samples before crushing. A group of machinery consisting of a "O" size, style "D" Gates gyratory crusher, a revolving screen with 1/2″ circular perforations, a Foster-Coolidge automatic sampling machine and all necessary shafting, conveyors and hoppers is installed in a space 17′

by 19′ in one corner of the crushing room, head room for the machinery being provided by a tower. This group is used solely for the primary crushing and reduction of ore samples and is enclosed to keep the consequent dust from the balance of the house.

In this room are also located one Blake jaw crusher; one Style "F" Gates gyratory breaker; two Gates sample grinders, one style "B," the other style "A;" and a steam-heated oven for determination of moisture in materials.

A scale, built to our specification by the Buffalo Scale Co., which frequent tests show to be sensitive to 1/100 of a pound with a load of 300 pounds, is placed perfectly level on a concrete pier and is used for weighing moisture and fineness samples. It is provided with three beams graduated to 5 pounds, 1/10 pound and 1/100 pound, respectively.

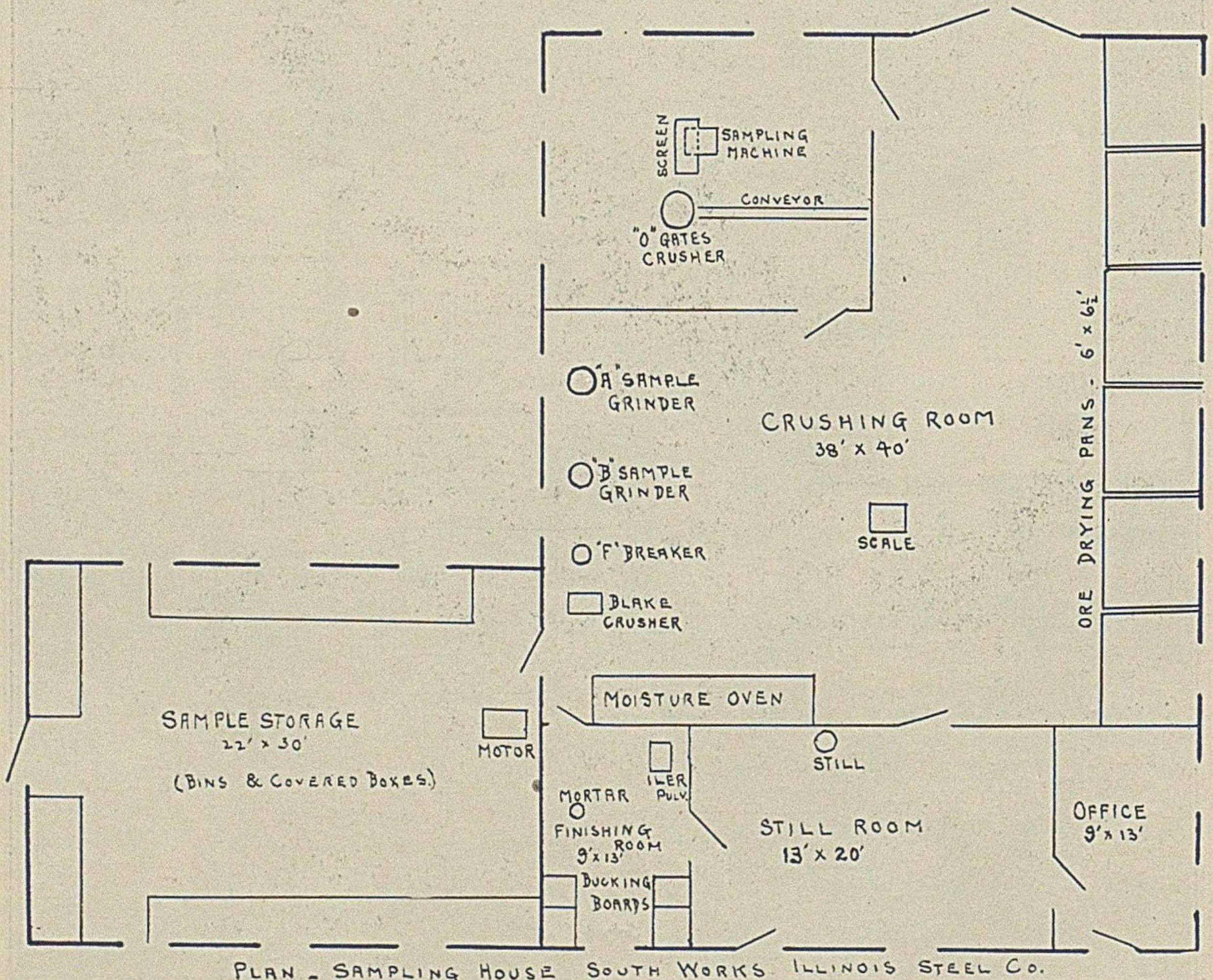

Fig. 3.

An electric air compressor with suitable tanks, piping and hose is provided for cleaning machinery, sieves, etc.

Each machine is fitted with tight and loose pulleys which permits the operation of any or all, as required.

Guard rails, belt shields and gear covers are placed at each point needed to insure absolute safety.

*Sampling.*—All samples of materials are taken during the unloading of either boats or cars in which they are received. By this means the portions or increments making up the sample are scattered throughout the mass and more nearly represent the material. This method assures an impartial and representative sample of cars which have been improperly loaded by the shipper or the surface improved by the material settling during transit. It is very seldom that surface samples are taken and then only when it is desired to quickly get a line on a material and these cars are resampled on unloading.

Ore is sampled by the methods described in a former issue of THIS JOURNAL (1, 107 to 115), but the preparation varies slightly from the method there described.

Material, such as coal, refractories, etc., received in cars and unloaded by shoveling, is sampled on the exposed faces, after the bottom of the car is reached, by taking equal portions from points touched at measured intervals.

Coke is generally received in side dump cars which quickly and completely empty themselves, so the only possible chance to obtain unloading samples is by holding a pail in the descending stream, thereby getting both fines and coarse in the samples. This method may be subject to some criticism, but more trustworthy results have been obtained than by any other we have employed to date.

*Preparation of Samples.*—Ore samples, whose average moisture content is about 10 per cent., are placed in the drying pans and dried sufficiently to prevent sticking in the machinery. They are then removed and placed in front of the conveyor, to which they are fed by means of a shovel, and elevated to the hopper above the crusher. This hopper is provided with a screen with 1/2-inch perforations, the fines are conveyed by a chute to the discharge spout of the crusher, the lumps over 1/2 inch size being ground by the crusher, and, joining the fines, all delivered to a revolving screen with 1/2-inch perforations. There is usually a small percentage of oversize which escapes through openings at the lower end of the screen, and is returned to the crusher for further reduction.

The half-inch material from the screen is delivered to a hopper above a Foster-Coolidge automatic sampling machine, which accurately reduces the original sample to 1/16, which is retained in a covered sheet iron box, rejecting 15/16, which is delivered to wheelbarrows outside the building, put in bins and afterward returned to the blast-furnace stock piles.

This sampling machine consists of a series of four hoppers and four split shovels which travel in opposite directions and horizontally, thus cutting very rapidly the vertically descending stream of ore. Before the installation of this machine all mixing and quartering was done by hand at considerable expense of time and money, and a long series of experiments has shown that the results from the sampling machine are obtained quickly, accurately and cheaply. Usually about 50 or 75 pounds of ore remain in the boot of the oversize conveyor; this is removed, ground in the "F" style Gates breaker, and put through the sampling machine to add its proportion to the sample. The 1/16 of the original sample is now ground by the style "B" Gates sample grinder, which grinds and automatically halves it, the discard going to one side of the machine and the sample to the other. By repeating this several times and gradually tightening the machine the sample is reduced to about 5 pounds that will all pass a 40-mesh sieve. This is intimately mixed, quartered and finished by means of the Iler disc pulverizer, having manganese steel discs, and bucking-board to pass a 100-mesh sieve. It is again mixed thoroughly, spread out very thin, and small portions selected from all parts of the sample and placed in a 6-oz. glass-stoppered bottle for the laboratory sample.

The cones and concaves of the sample grinder are made of manganese steel from patterns of our own design, and one set used for ore exclusively.

All machines are thoroughly cleaned by means of compressed air and brushes after working each sample.

For the past two years the experiment has been tried of giving the ore samplers and other employees, engaged in the preparation of these samples, free access to the results of ore analysis, both of our own samples and of those of the producing mines. It has proved of considerable benefit by giving the men a greater interest in their work, and, doubtless, an extension of the plan would be profitable.

*Coal.*—Samples are worked weekly, being crushed to 1/2-inch size with the Blake jaw crusher, thoroughly mixed by the cone and ring method, and reduced to about 60 or 70 pounds by Cornish quartering. The sample remaining is further ground and reduced by the style "A" Gates sample grinder to about 5 pounds, all passing 40 mesh, finished with the Iler pulverizer and bucking-board to pass 80 mesh and the sample taken out for analysis.

*Coke.*—Samples are worked daily and semi-monthly, the preparation being the same as for coal except that the final reduction to 80 mesh is done by pounding in a steel mortar, as, owing to the nature of coke, it is impossible to rub it fine.

*Refractories* and other material are prepared at the end of the month and if crushing to 1/2-inch size is necessary the Blake crusher is used, the medium grinding done with the "B" Gates and the finishing according to their character, made with the Iler pulverizer and bucking-board or by pounding in a mortar.

*Moistures.*—Moisture is determined in each cargo of ore unloaded, by taking an accurately weighed 100-pound sample out of the ore sample and drying for 12 to 18 hours, as found necessary by experience, in a steam-heated oven regulated to 100° C. The dried ore is carefully weighed and returned to the main sample. As the scale is accurate to 1/100 of a pound the loss of weight represents percentage direct, to the second decimal place, without further calculation.

Moisture in coal, coke, and other material is determined as above but on 25 pounds of the 112-inch crushed material, the loss multiplied by 4 gives percentage direct.

*Fineness.*—Each ore received, flue dust and flue dust sinter are shaken through a series of 18-inch sieves and the percentages remaining on 2-, 8-, 20-, 40-, 60-, 80- and 100-mesh sieves and through a 100-mesh reported monthly by the sampling house. Cumulative samples representing by tonnage the ore and other material are saved, dried, mixed thoroughly and reduced by quartering to 100 pounds and put through the sieves, the portions of different fineness accurately weighed, the weights representing percentage without further calculation. Frequently very small samples of material are received for fineness determination and a set of small brass sieves and a Troemner balance are provided and used for this purpose.

## CONCLUSION.

The sampling house is only operated on day turn, and, to date, its capacity for turning out finished samples has not been reached. Probably the amount of work could be more than doubled by running longer hours, but so far this has not been found necessary.

During the ore season of 1910, just completed, 3,825,963 gross tons of ore were unloaded and sampled at the two docks of South Works. From this ore, received in 522 boats, 863 samples (wt. 879,026 lbs.) were taken and prepared.

The complete data for the year 1910, just available, an average year, shows the following miscellaneous materials were sampled:

| Cars. | Material. | Samples. | Weight of samples. Pounds. |
|---|---|---|---|
| 30.265 | Coke | 3659 | 302,657 |
| 10,988 | Coal | 917 | 109,885 |
| 4,052 | Limestone | 2107 | 49,072 |
| 794 | Refractories | 378 | 19,840 |
| 105 | Ferro-alloys | 105 | 1,285 |
| 109 | Fire-brick | 113 | 2,739 |
| 696 | Scale and cinder | 264 | 26,190 |
| 58 | Slags—various | 3201 | 5,210 |
| 1,235 | Miscellaneous | 322 | 27,477 |
| 48,302 | | 11,066 | 544,355 |

Laboratory, South Works,
Illinois Steel Co.,
December 31, 1910.

## NOTES AND CORRESPONDENCE.

### EFFICIENCY IN ACID PHOSPHATE MANUFACTURE.

In even so simple a process as the manufacture of acid phosphate a high efficiency is not always attained. At the close of the spring season of 1908, at this plant, the average insoluble phosphoric acid on the acid phosphate produced was 2.50 per cent. and on the phosphate shipped was 1.74 per cent. About that time the writer was given charge of the acid phosphate manufacture, and since that time the same equipment has been producing acid phosphate with an insoluble of 0.75 to 1.00 per cent. and shipping this product out with about 0.30 per cent. insoluble. This one change means an increase in efficiency of nearly $20,000.00 annually.

A careful attention to details has brought about this result, but just what part of the change is due to each no one can tell. During the period mentioned, the change has been made from Tennessee to Florida rock, but the changes referred to and some of the results obtained were on Tennessee rock so that this change does not materially affect the points in this paper.

The more important details and the attention given them are as follows:

*Proportion of Acid and Rock.*—The amount of acid required for the most efficient manufacture of acid phosphate can be determined only by trial for each kind and grade of rock. That quantity of acid which will give an insoluble phosphoric acid of 0.75 to 1.00 per cent. at 48 to 72 hours old has proven best under our conditions.

*Strength of Acid.*—Acid is used which when calculated to 60° F. will show 52° Bé. Whether a formula calling for 51, 52 or 53 acid is used does not seem to be so vital as the necessity of having a constant strength of acid to use after the formula has been decided upon. We do not allow the strength to vary more than 0.3° Bé. either way from 52° when calculated to 60°.

*Temperature of Acid.*—In using the den system for acid phosphate manufacture the temperature of the acid does not seriously affect results, but in the single car open dump system the temperature must be above 100° F. and should be 130° for good work. If this is not the case the reaction does not start in the mixer promptly and a wet sloppy mixture is dumped on the pile which splatters so that it never properly reacts. For efficient work with the open dump system the phosphate when dumped from the car must "set up," that is, must remain where it is dropped, not being liquid enough to run. The temperature of the acid is the most important factor in attaining this end.

*Grade of Rock.*—Different kinds of rock and even different grades of the same rock require different quantities of acid. It is therefore evident that economy demands keeping the different kinds and grades separate or, if this is not possible, using a definite and constant mixture. Unless excess acid phosphate storage room is available a loss will be experienced in the open dump system through the mixing of various grades of phosphate. Plant operation can be made more efficient therefore if one grade and kind of rock only is used.

*Fineness of Rock.*—The results above cited have been obtained with rock ground until 95 to 97 per cent. pass a 60-mesh screen. 87 per cent. through the same screen will not give as good results and it seems doubtful if finer grinding would be more economical although some plants are operating on a finer rock dust.

*Time in the Mixer.*—The remarks above on condition of the acid phosphate when dumped on the pile are to the point here. The charge of acid and rock must be held in the mixer until it has reached a state that will give the required thick, pasty mass on the pile. The time required to do this will vary with the kind and fineness of the rock, the strength, quantity, and temperature of the acid but with these all properly regulated the time will be between 1 and 3 minutes.

*Time in the Pile.*—As far as the operating conditions of the plant will allow, the acid phosphate should be allowed to lie in the pile and cure as long as possible, the limit being when the interest charges on the money invested exceed the increase in value due to lower insoluble and better mechanical condition. The reduction in insoluble is, of course, slow after three months have passed.

When it is known that the acid phosphate must be used up in a few days or weeks after it is made, it is possible to use enough acid to reduce the insoluble to 0.40 per cent. by that time, but this may not be advisable because of the accompanying sacrifice of the mechanical condition. The proper course to pursue is a matter that must be left to the judgment of the man in charge.

In conclusion, the key-note to efficiency in acid phosphate manufacture by the open dump system is an untiring watchfulness and attention to details.

With the den system slightly less of this is demanded but the additional expense of one handling of the acid phosphate is required. F. B. Porter.

Swift Fertilizer Works,
Atlanta, Ga.

### LABORATORY DISTILLATIONS OF WATER GAS TAR.

The information regarding the composition and properties of water gas tar available in books and journals is scanty and not altogether reliable as applied to the modern American product. A large proportion of this tar is burned as fuel although some is used for road dressings and an unknown amount is distilled. If, as would seem probable from its resemblance to coal tar, the distillation of this tar will yield valuable products, a fuller knowledge of its composition than is to be found in the literature is desirable.

This paper gives the results of the fractional distillations of samples of water gas tar obtained at different points in the purifying system where gas was being manufactured by the Lowe system for making carburetted water gas. The gas oil is cracked in a stream of carbon monoxide and hydrogen, and at the plant where the samples were collected at a temperature of from 1400°–1420° F. By this procedure a large percentage—in the neighborhood of 25 per cent.—of the oil used is converted into substances which do not remain permanently in the gas but appear as tar removed by the purifying system. The petroleum oil used for carburetting is obtained from different fields, and varies somewhat in the nature of the constituent hydrocarbons. An Oklahoma oil was in use at the time the samples under analysis were obtained.

The gas after it leaves the superheater of the water gas set passes through a water seal and up the board scrubber which cools the gas to a considerable extent and removes about 60 per cent. of the tar. The tar taken out by the seal pot and the board scrubber is called the "*separator tar.*" From the board scrubber the gas passes to the water-cooled condensers where the "*condenser tar*" is removed. Between the condensers and the Pelouze and Audouin tar extractor is placed the exhauster, and at this point the gas shows a temperature varying but little from 140° F. The "P and A" tar is taken out by the Pelouze and Audouin extractor. The gas passes next through air-cooled condensers followed by a shavings scrubber; the tar separated in these two pieces of apparatus is known as the "*shaving scrubber tar.*" A small amount of tar is deposited in the connecting pipes between different parts of the purifying system, and in general drains forward. It will be noted that the different samples of tar are removed at progressively lower temperatures as the gas passes from the set to the last step of purification, and by the time it leaves the shaving scrubber it is down to about 105° F. and practically free from tar or fog.

In marked contrast to coal tar, water gas tar contains but little free carbon or soot. The samples worked with contained only traces of material insoluble in carbon bisulphide. The amount of nitrogen is small, an analysis showing but 0.08 per cent.

As might be expected, the specific gravities of the different tar samples were progressively less from separator to shaving scrubber. The following values were found: separator tar, 1.090; condenser tar, 1.081; P & A tar, 1.068; and shaving scrubber tar, 1,056—all at 15.5° C.

In carrying out the fractional distillations of the samples, advantage was taken of the better separation obtainable by the aid of a Hempel column and of the almost perfect temperature control afforded by electrical heating by means of a resistance coil immersed in the boiling tar as suggested by Richards and Matthews.[1] To effect this a special form of flask was devised as shown in the figure. By means of the tubulature, a pair of electrodes is introduced, and between them at the bottom of the flask is a resistance coil. During the distillations the flask is placed inside a glass jar, so that all drafts are avoided and radiation diminished, and yet the contents are in plain view. With this arrangement the current from a 110-volt lighting circuit controlled by a rheostat and an ammeter gives well-nigh perfect heating. The constriction in the neck of the flask provides support for a wire gauze upon which rest the glass beads of the Hempel column. It is a convenience to attach slender wires to this supporting gauze so that it and the beads may be lifted in and out without tipping the flask, the slender wires between the cork and the neck of the flask causing no inconvenience.

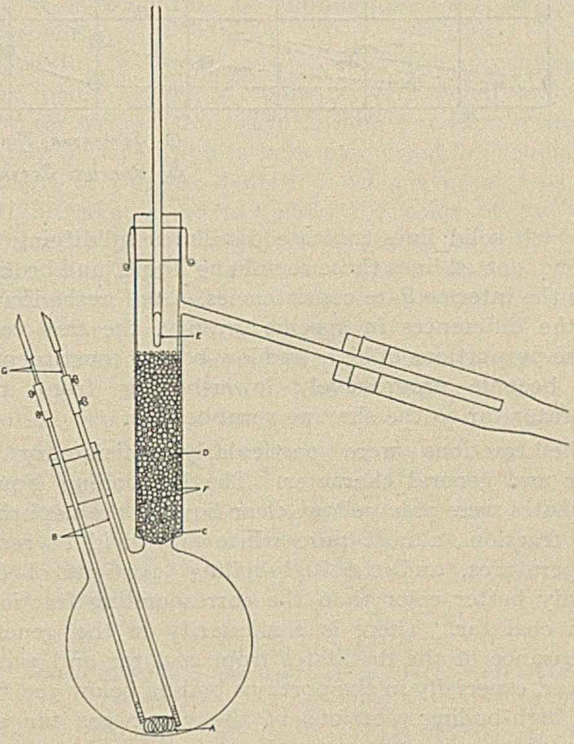

Fig. 1.—Apparatus for laboratory tar distillations.

(*A*) resistance coil; (*B*) electrodes; (*C*) gauze supporting beads; (*D*) glass beads of Hempel column; (*E*) Thermometer bulb; (*F*) wires holding the supporting gauze; (*G*) wires connecting through ammeter and rheostat to lighting circuit.

It was necessary in running the distillations to pause at 200° C. for a change from the water-cooled condenser to an air condenser, and to substitute a high range thermometer for the lower range instrument required for the early stage of the distillation.

A large number of fractions were taken in each distillation and the results are expressed as curves

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[1] *J. Am. Chem. Soc.*, **30**, 1282; **31**, 1200.

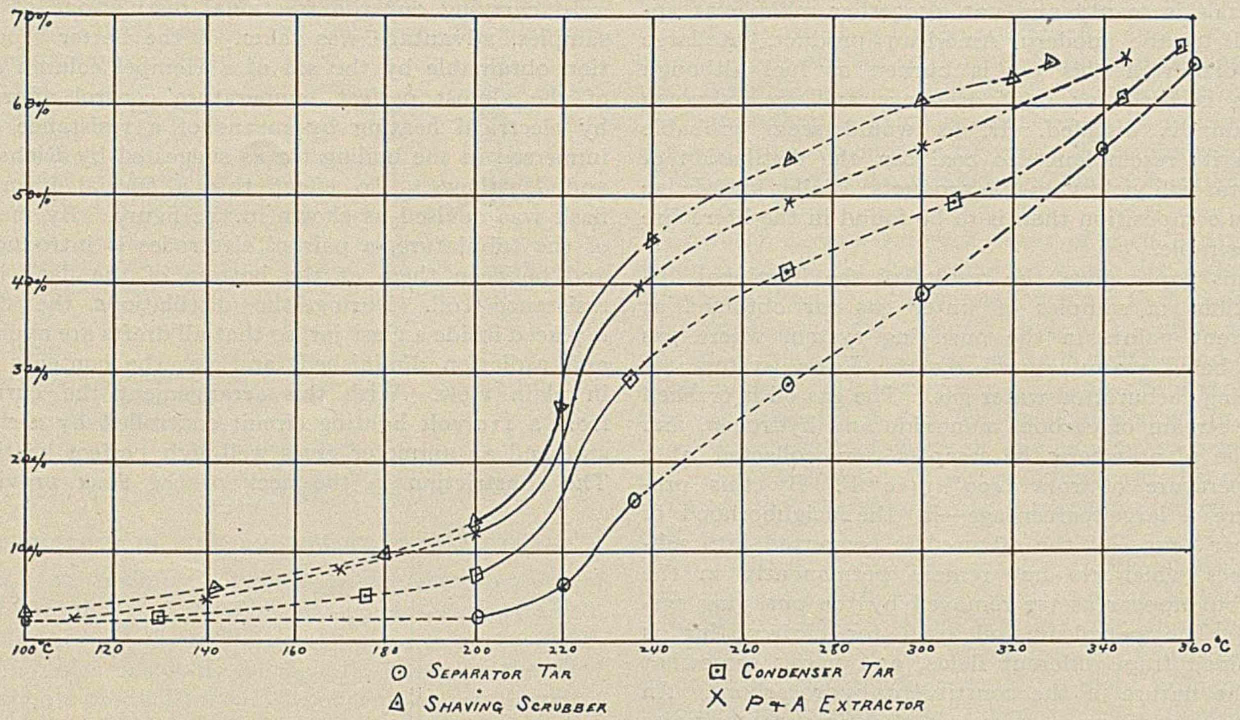

Fig. 2.

in which solid lines indicate distillates solidifying on cooling, dotted lines those remaining liquid, and broken lines the intermediate consistencies. As foreshadowed by the differences in specific gravity, the tars vary in the proportions of high- and low-boiling constituents, and become progressively lower-boiling from the separator tar to the shaving scrubber tar.

The fractions were particularly satisfactory in color and general character. The low-boiling liquid distillates were pale yellow, clear liquids, the naphthalene fractions almost pure white and solid at room temperatures, and the high-boiling portions of decidedly better color than the corresponding fractions from coal tar. There is a similarity in the general appearance of the distillates from coal tar and water gas tar, especially in the portions boiling below 300 °C. The high-boiling portions of the water gas tar are noticeably less solid than those from coal tar. In the case of the latter the distillate becomes decidedly hard as the temperature rises. Solid distillates are also obtained from the water gas tar above 300° C., but there is a range between 340° and 360° where with a good fractionating device a clear, heavy liquid distillate is obtained, which after standing shows some crystals but does not become solid, a marked contrast to the distillate from coal tar at this point.

The differences between the distillates from the different samples of water gas tar which had separated at different points in the purifying system were apparently quantitative rather than qualitative, the distillates coming off from the different ones at the same temperatures being indistinguishable.

A. L. Dean,
C. R. Downs.

Sheffield Chemical Laboratory,
Yale University.

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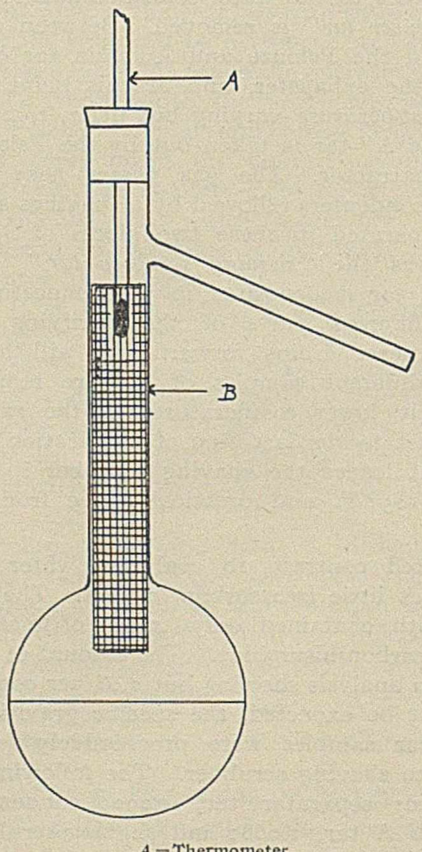
## NOTE ON THE DISTILLATION OF TARS CONTAINING WATER.

Great difficulty is met with at times when it is necessary to distil a mixture of tar and water. Some gas tars contain as high as 75 per cent. of water in the form of an emulsion that will not break on long



*A* = Thermometer.
*B* = Wire gauze.

standing. If this emulsion is distilled from a retort or ordinary distilling bulb it is almost sure to "bump over," the water condensing on the thermometer or sides of the neck and dropping back into the heated tar, causing it to bump. This is prevented by making two concentric cylinders of "30 mesh" brass gauze, which are slipped into the neck. This prevents any tar that does bump from going over at the beginning of the distillation. After the distillation has begun, the brass cylinders conduct heat upwards and any water collecting above is volatilized from the gauze instead of dropping back into the tar. There is plenty of room for the thermometer bulb inside the inner cylinder. Besides preventing bumping, the gauze cylinders act to some extent as a Hempel column and give a better service than the bare distilling bulb. The gauze is suspended by small wires that are held in place by the cork. C. R. Downs.

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Chemical Laboratory.

## PRECIPITATION OF SULPHUR FROM DILUTE LIME-SULPHUR SOLUTIONS.

A recent development in the use of the lime-sulphur solution for spraying purposes is as a summer fungicide, for which purpose it promises to supplant to a considerable extent the older Bordeaux mixture. The dilution is necessarily much greater than that used in the winter, since injury to the foliage would otherwise result, but as yet there is no unanimity of opinion among authorities as to the relative degree of this dilution, and sufficient data from practical results has not yet accumulated to permit of any positive conclusions.

The range of dilutions recommended in several publications is shown in Table 1. For the sake of comparison, the original data has been recalculated to the basis of a density of 1.30, assuming that the density of a solution varies inversely with the number of dilutions. This is not strictly true in the case of lime-sulphur solutions, but is accurate enough for the present purpose.

Table 1.

| Authority. | Solution used for: | Aver. sp. gr. considered. | Gals. water added to 1 gal. L.-S. sol. sp. gr. 1.30 |
|---|---|---|---|
| Niagara Sprayer Co. | General summer fungicide | 1.28 | 42 |
| The Rex Co. | Apple, pear, quince | 1.28 | 31–42 |
| | Peach, plum, cherry, grape | 1.28 | 53–79 |
| N. Y. (Geneva) Agricultural Expt. Station | Apple .................... | 1.294 | 36 |
| Penn. Agr. Exp. Sta. | Apple and pear (scab)..... | 1.30 | 19–29 |
| | Foliage tests............. | 1.30 | 14–59 |
| | Scab and brown rot, stone fruits................. | 1.30 | 37–59 |
| | Scab and brown rot, experimental............... | 1.30 | 99 |
| Va. Agr. Exp. Sta. | Apple, pear............... | 1.294 | 33 |
| | Peach, plum, cherry....... | 1.294 | 130 |

The minimum and maximum dilutions recommended are respectively 14 and 130 gallons of water to 1 gallon of 1.30 lime-sulphur solution. Practical results already secured would seem to indicate that in the case of apples a dilution of 30 gives a weak enough solution, but for more tender fruits a greater dilution will probably be necessary. There is, however, a factor entirely independent of spraying results which will be found to limit the dilution safely attainable, the precipitation of free sulphur by too great an excess of water.

While investigating the properties of concentrated lime-sulphur solutions, the writer noticed that a precipitate of sulphur quickly formed after running water into a beaker from which such a solution had just been poured. It appearing not improbable that this behavior might prove an important consideration in the dilution of solutions for spraying purposes, further attention was at once given it. The view is now quite generally held that the calcium-sulphur compounds, giving to the solution its principal value as an insecticide and fungicide, are the two higher sulphides $CaS_4$ and $CaS_5$. If by excessive dilution, these are broken up into free sulphur and various compounds, a direct loss of efficiency occurs, destroying, in a great measure, the value of the solution except insofar as a mixture of sulphur and water would be of benefit.

Qualitative tests showed that the precipitation took place slowly if comparatively small amounts of water were used for the dilution, but almost immediately if large volumes were introduced. The relative amount of sulphur deposited became greater as the dilution was increased, while the color of the precipitated sulphur ranged from orange to milk-white under the same conditions. There seemed to be no difference in results whether the solution was added to water or *vice versa*.

A short series of quantitative tests was then planned, in order to secure data for use in practical work. A solution was taken for dilution having a density of 1.03977, it having been already diluted up from a concentrated solution. Six 5-cc. portions were pipetted into beakers containing appropriate volumes of water, the time of addition was noted, and the beakers were allowed to stand until sulphur was precipitated. The results are shown in Table 2.

Table 2.

| No. | Cc. water added. | Added at: | Dil. from sol. taken. | Dil. from sp. gr. 1.30. | Time ppt'd. | Hours. |
|---|---|---|---|---|---|---|
| 1 | 15 | 7.56 A.M | 4 | 30.18 | — | — |
| 2 | 25 | 7.57 A.M. | 6 | 45.26 | — | — |
| 3 | 35 | 7.58 A.M. | 8 | 60.35 | — | — |
| 4 | 50 | 7.59 A.M. | 11 | 82.98 | 1.30 P.M. | $5^{1}/_{2}$ |
| 5 | 80 | 9.14 A.M. | 17 | 128.25 | 11.30 A.M. | $2^{1}/_{4}$ |
| 6 | 150 | 9.24 A.M. | 37 | 233.90 | 9.35 A.M. | $^{11}/_{60}$ |

Upon prolonged standing even the first three developed traces of a precipitate, but this was probably due to atmospheric action and would have been prevented had the solutions been protected by a layer of oil. As was the case with the qualitative tests, the more dilute the solution the greater the relative precipitation of sulphur and the more quickly it was thrown down.

In order to ascertain whether this precipitated sulphur could be redissolved a trial was made with precipitation No. 5, boiling the solution and sulphur together for some time. Apparently about half of the sulphur dissolved, but long before the solution was cool it was reprecipitated. A second boiling failed to give a similar effect, the sulphur having apparently settled in an insoluble form upon cooling.

This shows that when a precipitate is once formed in a solution, the latter is spoiled for spraying purposes.

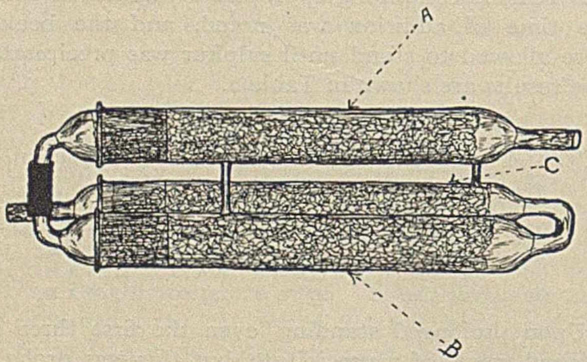
From the results in Table 2 it appears that a lime-sulphur solution of sp. gr. 1.30 may safely be diluted with 60 times its own volume of water without precipitating free sulphur, but that larger volumes will cause precipitation, the length of time before the beginning of which ranges from a few minutes to several hours. It seems probable that different solutions will give variations from the figures given here, as lime-sulphur has a great tendency to vary in behavior under parallel conditions, but the general results will be found in accord. As applied to actual work, the conclusion is that if a solution will be entirely sprayed out within two hours, after dilution it is safe to add as much as 125 gallons of water to 1 gallon of 1.30 solution, but if it may have to stand for several hours not over 60 to 70 gallons may be added without precipitating out free sulphur and spoiling the solution.

L. T. Bowser.
105 Grove St.,
Lynn, Mass.

## A NEW ABSORPTION APPARATUS.

This apparatus was designed primarily as weighing tubes replacing the U-tube in the determination of carbon dioxide by the soda-lime method. It may also be used to advantage in replacing the U-tube where the latter contains a solid absorbent used as a trap for gases.

The apparatus consists of three glass tubes 15 mm. in diameter and 100 mm. long. The tubes are lettered A, B, C, in the drawing. The right end of tube A is drawn out into a tube of 5 mm. in diameter and 15 mm. long. The left end of tube A is fitted with an open, hollow, ground glass stopper drawn out into a tube of 5 mm. diameter and bent at a right angle. The left end of tube B is fitted with a similar stopper and the two stoppers are connected by a piece of rubber tubing. The right end of tube B is drawn out into a tube of 5 mm. in diameter and with a U-bend is fused onto the drawn-out end of tube C. The left end of tube C is fitted with an open, hollow, ground glass, stopper drawn out into a tube 5 mm. in diameter and 15 mm. long. The tubes are attached to each other by short pieces of glass rods fused onto their sides.



To charge the apparatus, the stoppers are removed and a small plug of glass wool or cotton is placed in the opposite ends of the tubes. Tubes A, B, and two-thirds of tube C are filled with soda lime. The remainder of C is filled with anhydrous calcium chloride. The gas enters at the right end of tube A and circulates towards the left end of C until absorbed.

The calcium chloride and the soda lime should be crushed to pass a six-mesh sieve and caught on a twenty-mesh. The apparatus charged with lumps of this size weighs about 75 grams and will afford about eight determinations of $CO_2$, using $^1/_4$ gr. of a carbonate containing 40 per cent. $CO_2$, before recharging.

The advantages of this apparatus over the U-tube used for a similar purpose are:

1. This apparatus affords one-third more absorbing space than a U-tube of the same dimensions, thus affording a greater number of determinations before recharging.

2. The apparatus can be laid on the balance pan, whereas the U-tube must be suspended to the beam.

3. The apparatus will accommodate a larger amount and a greater variety of absorbing materials when used as a trap for gases than the U-tube.

The apparatus was made by Messrs. Eimer & Amend; cost $2.50, f. o. b. New York.

James S. McHargue.
Chem. Lab. of Ky. Geol. Survey,
Lexington, Ky.

## TENSILE STRENGTH OF HAIR CLOTH.

Following the recent edict of the Chinese emperor abolishing the wearing of queues, the European markets have been overstocked with human hair. The price of this article has fallen almost one-half, while the import has been doubled.

The usual use of human hair has been in making wigs, switches, etc. The increased production demanded an outlet for the surplus. According to a recent report made by U. S. Consul Ingram, Bradford, England, British weavers are furnishing the outlet by utilizing the material in weaving. Hair is used both alone and in combination with other fibers. Ingram says: "The hair (10 to 12 in. long) is first disinfected, then spun into yarn and woven into cloth. The finished fabric comes in 20-inch or 30-inch widths and up to 90-yard lengths. No dye is used, the color being the natural tint of the hair. The fabric is intended for interlining for men's wear and possesses the advantages of being absolutely *unbreakable, unshrinkable* and *uncreasable.*"

Several samples of these fabrics, the product of an enterprising Bradford weaver, have been examined for strength:

No. 1*a*. Weight per square yard, 8 oz.
Warp, wool, 40 lbs. tensile, per inch.
Filler, goats' hair, 28 lbs. tensile, per inch.
No. 1*b*. Weight per square yard, 9 oz.
Warp, wool, 57 lbs. tensile, per inch.
Filler, goats' hair, 42 lbs. tensile, per inch.
No. 2. Weight per square yard, 10 oz.
Warp, cotton, 89 lbs. tensile (one inch wide).
Filler, goats' hair, 69 lbs. tensile (one inch wide).
No. 3*a*. Weight per square yard, 9 oz.
Warp, wool, 49 lbs. tensile (one inch).
Filler, human hair, 47 lbs. tensile (one inch).
No. 3*b*. Weight per square yard, 6 oz.
Warp, wool, 44 lbs. tensile (one inch).
Filler, human hair, 30 lbs. tensile (one inch).
No. 4. Weight per square yard, 15 oz.
Warp, human hair, 67 lbs. tensile (one inch).
Filler, human hair, 84 lbs. tensile (one inch).

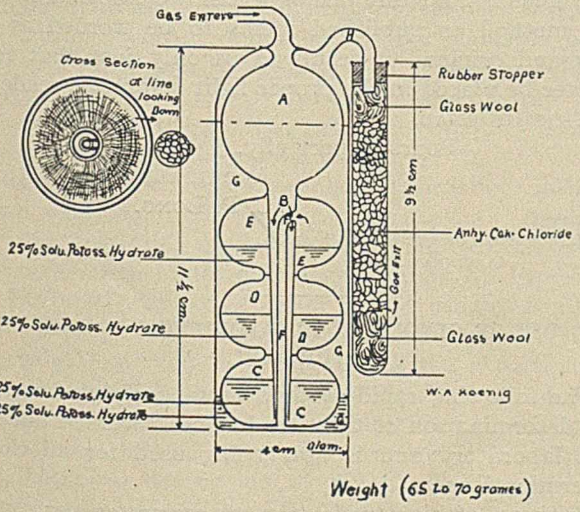
CHAS. P. FOX.

### KOENIG POTASH BULB.[1]

There are five advanages which this bulb has over the other bulbs thus far in use:

*First.*—Accuracy in cleaning at each weighing. All parts are easily accessible.

*Second.*—Accuracy in quick absorption. The bubbles bursting rapidly will not drive liquid over into the calcium chloride tube and as the gas is washed five times instead of three it allows of more rapid circulation.



*Third.*—Amount of condensation surface is much less in this bulb.

*Fourth.*—Center of gravity on balance pan at each weighing can be found quickly and correctly.

*Fifth.*—Saving of time can be seen from the above and better on trial. The simplicity of the exposed parts make it less easily broken.

*Description.*—The gas enters at tube marked "gas enters," passes into *A*, then into tube *B*, through it and out at bottom into bulb *C*, squeezing through contraction up into *B* again, up into *E*, then passing into tube *F* (which is fused open on outside of tube *B* and open on outside of bulb *C*), down through *F* and out into the bottle *G*,*G*,*G*, passing through solution, then up and out through tube *H* into the calcium chloride tube which it leaves at opening marked "gas exit."

The instrument holds nearly twice as much KOH solution as the Mohr bulb, therefore will act for twice as many combustions without refilling. It weighs not over twenty grams.

To fill the instrument a piece of rubber tube is attached at *H* and KOH solution sucked in at tube marked "gas enters." To empty, the liquid is forced out at tube marked "gas enters" by blowing at tube H.

W. A. KOENIG.

MIDVALE STEEL CO.,
PHILA.

### FILTERING RACK.

As any sugar-house chemist knows, the first few drops of a filtering solution shall be rejected. Letting these, generally turbid drops, first fall into the jars, often makes it very difficult to obtain a perfectly clear solution. With my rack I thought to simplify the operations by preventing these turbid drops from getting into the jars.

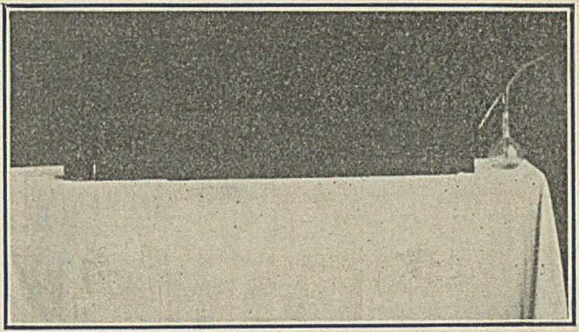


Fig 1.

Photo No. 1 shows the front of the rack, a stand for the filtering jars and a board for the funnels.

Photo No. 2 shows the back. Directly under the funnel board is seen an inclined gutter of a grade of about 2 per cent.; under the lower end of this is placed a receptacle.

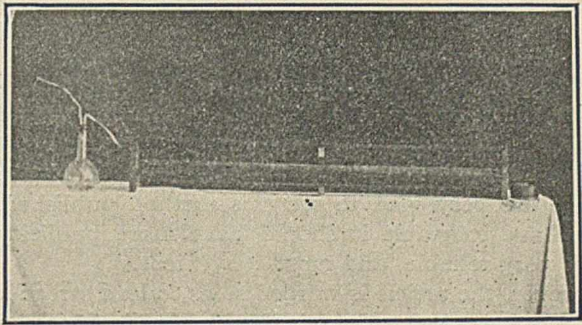


Fig. 2.

In operating, flasks, funnels and jars are put in their places; then the solutions are poured onto the filters, photo No. 3. The first parts of all the filtrates fall into the inclined gutter and flow into the receptacle.

If there be a series of samples, it will be found that by the time all the solutions are poured onto the filters, the first one is filtering perfectly clear and is ready to be transferred to its jar, as shown in photo No. 4.

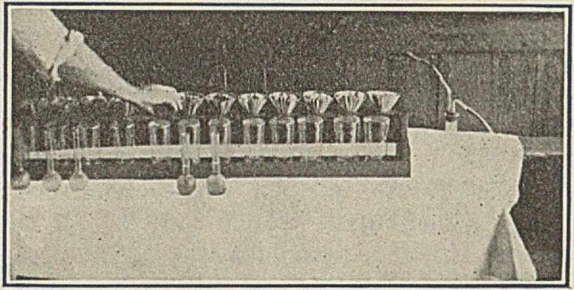


Fig 3.

The rack will be found convenient for another reason: When filling the polarization tubes, the funnels are put back into the corresponding holes in the funnel board, instead of being put on the jar previously used, as is generally done. In this way the solutions remain unaltered, and can be used again as a check, in case any doubt should arise about a reading on the polariscope.

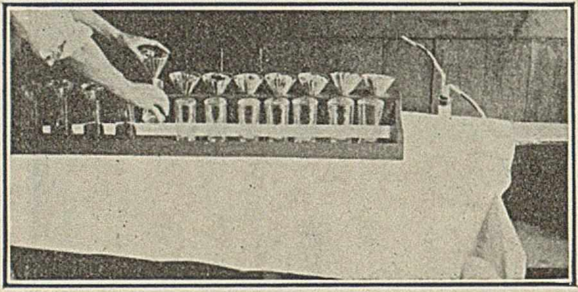


Fig 4.

The size of the rack can be increased or decreased at convenience. The one shown in the photographs has room for 12 samples. Alfred Krafft.

Chemical Laboratory
Waialua Agricultural Co., Ltd.
Waialua, Oahu, T. H.

## SAPONIFICATION OF FATS FOR TITER DETERMINATION.

*Editor of the Journal of Ind. and Eng. Chemistry:*

We notice the publication, in This Journal for November, of an article in the "Notes" entitled "Rapid Saponification of Fats for Titer Determination," by C. V. Zoul, of the Proctor & Gamble Co., Cincinnati, O. We are very glad to see this method published, as we have long felt it should have more publicity as it is very reliable, and most convenient.

However, the article is worded so as to lead a reader to believe it is new and original with Mr. Zoul, as can be inferred from the first paragraph of the article, also from his statement in the third paragraph: "Glycerine has been used for saponification but *never* for titers." If you will refer to a letter written to you by us, July 10, 1909, offering our cooperation to the Committee on Uniformity, you will find that we then enclosed you a copy of a method of glycerine saponification for titers which we suggested could be published in the "Notes" if you considered it of sufficient interest. The method was not published but in your letter of July 17, 1909, you stated that it and the soap-stock method accompanying it would be considered by the Committee on Uniformity.

Mr. Campbell, when chief chemist in 1900, first used the method for the titer test, adapting it from the Leffmann-Beam method of saponification for volatile fatty acid determination as given in Allen, 3rd edition, Vol. II, Pt. I, page 61. This method has been in daily use in our laboratory continuously and exclusively about ten years, and during that time we have handed it on to many others. Among these we may mention Mr. Oscar Wurster, chief chemist, The M. Werk Soap Co., Cincinnati, O., Mr. Robt. E. Divine, consulting and analytical chemist, Detroit, and Mr. Wm. E. Garrigues, chemical engineer of Detroit in 1907. We have noticed no mention was made of the method in the work on titer tests done by the Assoc. of Official Agricultural Chemists, Bureau of Chem., Bulletins 81 and 90, and from this assume that the method has not been in general use.

While we possibly may not claim to be originators of the application of glycerine saponification to titer tests, yet as we seem to have used the method more and longer than any one of whom we know, and as the method as published seems to be worded as if new and original, it seems to us only just that the matter be placed in the proper light before the readers of This Journal.

Yours respectfully,
Archibald Campbell,
C. P. Long.

Laboratory of the Globe Soap Co.,
Cincinnati, Ohio.

## THE USE OF GLYCERINE IN SAPONIFYING FATS IN THE TITER TEST.

The following rapid method of saponifying fats for the determination of the titer has been worked out in this laboratory and is now being used for all titer determinations.

Fifty cc. of high-grade c. p. glycerine (97 per cent. glycerine) and twenty cc. concentrated caustic potash solution (100 grams KOH dissolved in 100 cc. distilled water) are placed in a liter flask and warmed gently on an asbestos board over a low flame. When hot, fifty grams of the molten fat are poured in and the flask rotated gently. Saponification begins at once and is soon complete, although there is usually some foaming before the mixture becomes clear. Complete saponification is shown by the mixture becoming perfectly clear and homogeneous. When saponification is complete the flame is removed and five hundred cc. of hot water added, cautiously at first, to avoid excessive foaming. The flame is then replaced and sufficient dilute (1 : 3) sulphuric acid added to decompose the soap. A few minutes' boiling gives a clear layer of fatty acids. The acids are then washed and dried in the usual way. The process is quite rapid, clear acids being obtained in 20 to 25 minutes. The results show perfect agreement with standard methods.

The use of gycerine in the titer test was first suggested to the writer by Mr. R. R. Henley, Junior Laboratory Inspector in this Division.

The development of this method had been completed and its accuracy thoroughly tested when the paper entitled "Rapid Saponification of Fats for Titre Determination," by Charles V. Zoul, appeared in the November number of This Journal.

The present note is offered as an independent confirmation of the rapidity and reliability of Mr. Zoul's method. His priority in demonstrating the value of glycerine for this purpose is, of course, conceded.

R. H. Kerr.

From the Laboratories of the Biochemic Division,
Bureau of Animal Industry, U. S. Department of
Agriculture.

### CANDELILLA WAX.

Instituto Medico Nacional
7a De Balderas, No.94
*Mexico, D. F.*
Departamento de Quimica Industrial.

December 31st, 1910.

*The Editor, The Journal of Ind. and Eng. Chemistry.*

Dear Sir:

The attention of this Department has been directed to articles recently published in your valuable periodical, contributed by Messrs. G. S. Fraps and J. B. Rather, and relating to "Candelilla Wax," and also to previous contributions by Messrs. Hare and Bjerregaard referring to the same subject.

Since it appears that the above-mentioned authors have overlooked the publication in the "Anales" of this Institute, of articles referring to this wax, since the time of its discovery in 1905 by Professor J. McConnell Sanders, chief of the Division of Applied Chemistry in this Institute, until the present year, we would ask you to kindly direct the attention of the above-mentioned authors and of your readers to a treatise recently published by the Educational Department of this Government, in which is included the botanical description of the Candelilla plant as classified by Prof. Gabriel Alcocer, curator of the herbarium, and a resumen of the chemical data obtainend by Prof. McConnell Sanders.

In this resumen the chemical and physical constants of waxes from diverse territories in Mexico and from plants collected in different seasons of the year are compared, and the discovery of the hydrocarbon hentriacontane claimed by Messrs. Fraps and Rather is shown to have been anticipated by McConnell Sanders in the "Anales" for October, 1907.

As the exploitation of this wax has now become one of the National industries of this country, and since its properties have attracted some attention in the commercial world, an English edition of the treatise above mentioned is in course of preparation, and a copy will be sent you as soon as published.

In the meantime we would ask you to kindly give the necessary publicity to this letter, for which courtesy we beg to anticipate our best thanks.

Remaining yours very truly,
Jefe del Departamento de
Quimica Industrial.

*Editor, Journal Industrial and Engineering Chemistry:*

Through an oversight of the printer and ourselves in our article "Some Imperfect Paving Bricks," This Journal, Dec., 1910, we omitted to acknowledge the kind assistance of Dr. W. G. Brown, Professor of Technical Chemistry at the University of Missouri, in giving us the use of his apparatus and private laboratory, and for the many helpful suggestions and criticisms that he proffered during the course of the work. The work itself was suggested by him, and through his influence the authors obtained all the material necessary for the tests, and we wish to take this opportunity of expressing our appreciation.

Jas. C. Lawrence.
Chas. J. Boner.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS OF THE AMERICAN CHEMICAL SOCIETY.

Minneapolis Meeting, December 30–31, 1910.

The meetings of the Industrial Division held at Minneapolis, December 30 and 31, 1910, were presided over by Arthur D. Little, *Chairman* of the Division. John White was selected as temporary *Secretary*.

The election of officers to serve during the year 1911 resulted as follows:

*Chairman*, G. C. Stone, 55 Wall St., New York.

*Vice-Chairman*, William Brady, 7642 Marquette Ave., Chicago, Ill.

*Secretary*, F. E. Gallagher, 93 Broad St., Boston, Mass.

*Executive Committee*, The Officers, The Editor of the Industrial Journal, *Ex-Officio*, and H. S. Minor, J. O. Handy, W. H. Walker, Clifford Richardson, G. E. Barton.

The Secretary's report was read and approved. The following abstracts are taken from this report:

"The enrolment in the Industrial Division is now 1040. The special work carried on by the Secretary since the last meeting has been largely directed towards the accumulation of data from the Industrial members leading to the publication of a descriptive directory of the members of the Division. For this purpose blank cards were mailed to all the members, and the returns have been satisfactory. We may consider, therefore, that the data is at hand for the proposed directory, and that it can be published as soon as funds are available for this purpose."

Only two of the Divisional Committees submitted reports for this meeting:

#### REPORT OF THE COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS.

Your "Committee on the Definition of Industrial Terms" has the honor to report that it has continued its labors since the San Francisco meeting, with results which are not entirely encouraging.

*Definition of Bronze.*—Attempts to define bronze have met with great opposition on the part of producers. It would seem that a large proportion of the material which is put upon the market as bronze is merely brass and contains no tin, and great objection has been raised to any attempts to change the designation of such material. It will not be listened to by producers unless legislation, similar to the Pure Food Law, should be enacted which would compel them to do so. The American Chemical Society could define bronze and brass with little difficulty, but such definitions would not be adopted industrially, for reasons which are too apparent to need mention. It would require an authority greater than that of the Society to impose such definitions on the producers. The policy to be followed in this respect must be decided upon by the Division. It has been suggested that the authority of the United States Government must necessarily be invoked to accomplish anything in this direction.

*Definition of High-grade Inorganic Chemicals.*—This sub-committee has been giving consideration to the proper definitions of the term "pure," "chemically pure" and "technical" as applied to high-grade inorganic chemicals. No definite conclusions have been reached up to the present time, but it is hoped that something may be arrived at at the meeting to be held in Minneapolis as a basis for further work.

The sub-committee reports that there seems to be in the minds of different manufacturers a desire not to give information to the committee, and until it can satisfy them that the work is for their benefit, it will be unable to come to any definite conclusions. It has been suggested that the aid of the Bureau of Standards at Washington be enlisted.

*Definition of Heavy Chemicals.*—This sub-committee reports that it has been unable to accomplish anything for the same reasons that have been met by the previous committee.

*Definition of Pharmaceutical Products.*—The chairman reports that it will be impossible for this committee to do anything until the appearance of the new Pharmacopoeia.

*Definition of Iron and Steel.*—The chairman of this committee reports that he has had a conference with the chairman of a similar committee appointed by the International Society for Testing Materials, the result of which is that they have arrived at the conclusion that very little progress can be made along this line at the present time, and they suggest that an effort be made to bring up the subject in 1912 at the 8th International Congress of Applied Chemistry, and at the meeting of the International Society for Testing Materials, and possibly the Iron and Steel Institute. A full discussion of this subject before some section at the meeting on one of these organizations might result in overcoming some of the difficulties which, at the present time, stand directly in the way of progress towards the adoption of any standard definition or nomenclature, as applied to the iron and steel industry.

*Definition of Portland Cement.*—Awaiting the results of the research on the constitution of Portland cement now being conducted by the Geophysical Laboratory of the Carnegie Institution, it would seem inadvisable to attempt to define Portland cement at the present time.

*Definition of Petroleum Products.*—At the present time it seems possible to go beyond the classification of these products presented in our last report, in view of the fact that commercial distillates from various petroleums vary in gravity for the same class of material, thus making any general statement of their density impossible.

*Definition of Bitumen and Asphalt.*—A meeting of a sub-committee of the American Society for Testing Materials, consisting of the same gentlemen composing the Committee of the Division of Industrial Chemists, have not been able to arrive at anything satisfactory in this direction. Industrial influence, as in the case of bronze, has been the stumbling-block which has prevented agreement.

It appears that the attempt on the part of the Division to define "Industrial Terms" has met with such opposition that a satisfactory agreement upon anything, at the present time, will be impossible, but your committee hopes to pursue the subject in such a way that the resistance at present encountered may be overcome, but the prospect for immediate success does not seem promising.

An expression of individual opinion at the meeting at Minneapolis or to the committee would be of value, as well as suggestions as to any other industrial line in which an attempt may be made to define industrial products, in which there would be probability of success.

COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS,
(Signed) CLIFFORD RICHARDSON,
*Chairman.*

REPORT OF COMMITTEE ON STANDARD SPECIFICATIONS.

The Committee on Standard Specifications regrets its inability to present a more complete report at this time.

Nine sub-committees have been endeavoring for the past six months to formulate specifications for the following materials:

Soda Ash
Alum
Bleach
Caustic Soda
Sulphuric Acid
Muriatic Acid
Nitric Acid
Turpentine
Solder

Reports for the Minneapolis meeting were promised by four committees, but they have been obliged to disappoint us as it proved impossible to submit their data in proper form, and have requested an extension of time.

The Committee on Bleach completed its work and submitted a specification based upon the present trade custom of 35 per cent. of available chlorine. After carefully considering this, however, our committee felt that owing to the variable composition of bleaching-powder, provision should be made for purchasing bleach upon a unit basis, in much the same manner as caustic soda and other chemicals are bought. It has, for this reason, been deemed advisable to refer the matter back to the sub-committee.

The committee wishes to call to the attention of the Division the desirability of closer coöperation with other societies interested in these same lines in order to prevent duplication of effort and thus secure the greatest possible efficiency. This is especially advisable in the work of the committees on specifications and standard methods, since in many cases the drafting of a specification resolves itself into the selection of a standard method. Some plan of organization whereby the work on specifications and methods for this Society could be carried on jointly with that of other societies having committees engaged on similar subjects would in the opinion of the committee be decidedly beneficial. (Signed) HERVEY J. SKINNER,
*Chairman.*

Both of these reports were approved by the Division and it was also voted to continue all of the committees now at work.

After the reading of an important paper by P. H. Walker and F. W. Smither upon the subject of "Platinum," a committee was appointed, consisting of P. H. Walker, F. W. Hillebrand and a third to be selected by them, to consider the whole question of the Quality of Platinum Laboratory Utensils, and to report at the Indianapolis meeting. (E. T. Allen has since been selected as the third member of this committee.)

It is voted to make an assessment of $1.00 per member upon the membership of the Division for carrying on the divisional work. Up to the present time the expenses of the Division have been met entirely by the officers, the members never having been called upon to contribute to meet the expenses of the Division. An endeavor will be made during the next few months to publish the directory of members which has been compiled by the Secretary, and it is particularly for carrying on this work that the assistance of the members is required.

A vote of thanks was extended to the Bausch and Lomb Optical Company for the loan of a lantern during the meeting.

In the absence of the chairman, the temporary chairman, Mr. William Brady, upon motion appointed W. D. Richardson, S. W. Parr and John White to draft suitable resolutions expressive of the appreciation of the Division for the work which its first chairman, Arthur D. Little, has accomplished in organizing and building up the Division. This committee will report at the next general meeting of the Division and their resolutions will be embodied in the minutes of that meeting.

Subsequent to the business meeting the following papers were presented and discussed:

J. T. Donald. "An Improved Process for Finishing Beef Extract."

A. D. Smith. "Self-Recording Efficiency."

F. B. Porter. "Efficiency in Acid Phosphate Manufacture."

Walter P. Schuck. "Chemistry as a Factor in Foundry Efficiency."

Jas. C. Lawrence. "Note on the. Utilization of Lumber Waste."

W. S. Williams. "The Use of Peroxide for Silk Bleaching."

C. F. Wood. "Economical Steam Generation."

C. M. Bullard. "The Importance of Eliminating Air Leaks in the Manufacture of Sulfite Acid."

S. W. Parr and F. W. Kressman. "The Spontaneous Combustion of Coal." (Illustrated by lantern.)

George P. Dieckmann. "The Modern Manufacture of Portland Cement from the Chemical and Mechanical Standpoint." (Illustrated by lantern.)

Harrison E. Ashley and Warren R. Emly. "Errors in Determining the Sizes of Grain of Minerals and the Use of Surface Factors."

Harrison Everett Ashley. "The Utilization of Smelter Smoke in Preparing Sulfates from Clays.

G. A. Abbott. "The Determination of Water in Mixed Paints."

A. H. Sabin. "Linseed Oil."

Harry McCormack. "A Modified Process for Cane Sugar Manufacture."

G. W. Thompson. "The Importance of a Standard Temperature for Specific Gravity Determinations and for Standardizing Standard Measurings."

Percy H. Walker and F. W. Smither. "Platinum Laboratory Utensils."

J. K. Clement. "The Work of the Chemical Laboratories of the Bureau of Mines."

W. D. Richardson. "Experiments on the Corrosion of Iron."

John White. "The Determination of Moisture in Coal."

Charles P. Fox. "Tensile Strength of Hair Cloth."

The following papers were read by title:

H. W. Rohde. "Notes on the Production and Composition of Mexican Pulque and Mescal."

H. C. Hamilton. "Soaps from Different Glycerides. (Their Germicidal and Insecticidal Values in Themselves and When Mixed with Active Agents.)

Wm. M. Barr. "The Disintegration of Concrete in Septic Tanks."

Geo. C. Whipple and Melville C. Whipple. "The Solubility of Oxygen in Sea Water."

Geo. L. Heath. "The Exact Electrolytic Assay of Refined Copper. 1. Standard Method. 2. In Solenoid with Revolving Electrolyte."

Geo. L. Heath. "The Determination of Arsenic and Antimony in Copper, including a New Rapid Volumetric Method."

In addition to those on the regular program the following papers were presented:

Perry Barker. "Fuel Costs."

B. T. Babbitt Hyde. "Determination of a Basis for the Compensation Allowance to Employees."

H. E. Mills. "Methods of Rubber Analysis."

Mr. F. G. Heuchling, Efficiency Engineer for the Chicago Civil Service Commission, read by consent of the Division a paper on the work of the commission, especially in their efforts to bring about greater efficiency on the part of their employees.

A letter was read from Mr. H. A. Schwartz, Chairman of the local Publicity Committee, inviting all members to attend the Indianapolis meeting of the American Chemical Society in the summer of 1911.

F. E. Gallagher, *Secretary.*

## AMERICAN CHEMICAL SOCIETY. DIVISION OF FERTILIZER CHEMISTS.

Minutes of Minneapolis Meeting, December 30, 1910.

Meeting called to order by Chairman, F. B. Carpenter.

Minutes of last meeting read and approved.

On motion it was decided to have the papers read first.

The following papers were read:

1. Chairman's Address, F. B. Carpenter. "The Results of Soil Investigations as Affecting the Use of Fertilizers."
2. J. M. McCandless. "A Bacteriological Method for Determining Available Organic Nitrogen."
3. J. M. McCandless. "Uniform Rules and Regulations for the Admission of Ammoniates Throughout the Southern States."
4. J. E. Breckenridge. "Availability of Organic Nitrogen."
5. Charles S. Cathcart. "The Use of Nitrate of Soda in Commercial Fertilizer."

Reports of the following committees were made:

Phosphoric Acid by G. Farnham, *Chairman.* Report received and accepted.

Potash by J. E. Breckenridge, *Chairman.* Report received and accepted.

Nitrogen by P. Rudnick. Report received and accepted.

Legislation Committee by A. Lowenstein, *Chairman.* Report received and accepted.

Phos. Rock Com. by C. F. Hagedorn. Received and accepted.

On motion Nominating Committee for officers for 1911 was appointed by *Chairman:* P. Rudnick, G. Farnham, A. Lowenstein.

Committee reported the following:

P. Rudnick, *Chairman,*
J. P. Street, *Vice-Chairman,*
J. E. Breckenridge, *Secretary.*

*Executive Committee:*

F. B. Carpenter,
A. Lowenstein,
W. J. Jones, Jr.,
G. Farnham.

The above were elected.

Availability of Organic Nitrogen was referred to Nitrogen Committee.

Publishing of Proceedings of meeting was referred to Executive Committee.

Many important subjects were discussed.

On motion meeting adjourned.

J. E. Breckenridge, *Secretary.*

## CO-OPERATIVE WORK ON PHOSPHORIC ACID BY THE DIVISION OF FERTILIZER CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY, 1910.

Letter Accompanying Samples:

Two samples are being mailed you. No. 1 Acid Phosphate, No. 2 Acid Phosphate, blood, bone, tankage, peat and potash. There is also a sample of Standard Ammonium Citrate being sent by express. The sample of citrate which was prepared by Dr. W. J. Jones has been sterilized. It has been found that when sterilized the citrate does not undergo any changes.

You are requested to determine insoluble phosphoric acid only, using the standard citrate and also a citrate solution prepared as follows:

Place 300 grams of citrate acid in porcelain dish, add 600 cc. distilled water to partially dissolve the acid and then with constant stirring, one liter of 0.96 ammonia until acid is dissolved. Make solution alkaline to litmus paper with 0.96 ammonia and allow to stand 24 hours in open dish out of contact with laboratory fumes.

Next make neutral by the official alcoholic calcium chloride method. The filtrate from the alcoholic calcium chloride precipitate is made neutral to one drop of $N/10$ acid or alkali using cochineal as indicator. Place the filtrate diluted with an equal volume of water in a Hessler jar and use a second jar containing the alcoholic calcium chloride, also diluted with an equal volume of water, as a check. Bring solution to sp. gr. 1.09 by weight at 20° C.

Determine ammonia as follows: Measure 25 cc. of the citrate solution at 20° C., in duplicate, into 250 cc. graduated flasks and bring to volume at room temperature. Place 25 cc. of these solutions into 500 cc. Kjeldahl flasks, dilute to 350 cc. with distilled water, add NaOH or MgO and boil until the distillate measures 300 cc., the distillate being caught in $N/2$ acid, titrate excess acid and calculate ammonia to grams per liter.

A large number of solutions prepared in this way have been found to vary between 43.5 and 43.7 grams of $NH_3$ per liter. The analytical method is intended to solve as a check on the alcoholic method. Report number of grams of $NH_3$ per liter in the standard citrate solution, also in your solution.

In weighing portions for analysis pour entire sample on piece of glazed paper, mix thoroughly and draw sample from different parts, mix after each weighing.

*Moisture.*—Take 2 to 5 grams and heat until weight is constant at 100° C.

*Washing.*—Place 2 grams on 9 cm. filter paper and wash until neutral to litmus.

*Digestion.*—Place 100 cc. citrate in 200 or 250 cc. flasks, either Erlenmeyer or round bottom and have level of water in bath at least one inch higher than liquid of flask. Run a blank with a thermometer in flask, since it has been found that the

RESULTS OF THE CO-OPERATIVE WORK OF THE PHOSPHORIC ACID COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY.

| Analyst. | Moisture, Sample No. 1. | Moisture, Sample No. 2. | Standard citrate. Grams $NH_3$ per liter. | Standard citrate. Ins. $P_2O_5$. Sample No. 1. | Standard citrate. Ins. $P_2O_5$. Sample No 2. | Standard citrate. Filter paper. | Analyst's citrate. Grams $NH_3$ per liter. | Analyst's citrate. Ins. $P_2O_5$. Sample No. 1. | Analyst's citrate. Ins. $P_2O_5$. Sample No. 2. | Analyst's citrate. Filter paper. | Time for filtering and washing (min.). Sample No. 1. | Time for filtering and washing (min.). Sample No. 2. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| T. S. Gray, Jacksonville.... | ... | .. | 43.61 | .. | .. | ...... | 43.54 | .. | .... | .... | ... | .... |
| | 9.22 | 4.80 | 43.75 | 0.88 | 4.40 | 589 | 43.61 | 0.96 | 4.23 | 589 | 30 | 2 h. 45 min. |
| A. G. Stillwell, New York... | ... | .. | ... | 0.87 | 4.93 | ...... | ... | .. | 5.04 | .... | ... | .... |
| | ... | .. | 43.60 | 0.90 | 4.89 | ...... | 43.70 | 0.95 | 5.06 | .... | ... | .... |
| | ... | .. | ... | .. | .. | ...... | ... | 1.01 | 5.07 | .. . | ... | .... |
| F. B. Porter, Atlanta....... | 10.46 | 5.76 | 43.80 | 0.86 | 4.56 | ...... | 45.50 | 0.83 | 4.27 | .... | ... | .... |
| | 10.44 | 5.82 | 43.80 | 0.96 | 4.46 | ...... | 45.50 | 0.92 | 4.37 | .... | 3 | 4 |
| | ... | .. | 44.00 | .. | .. | ...... | 45.20 | 0.88 | 4.55 | .... | ... | .... |
| | ... | .. | ... | .. | .. | ...... | ... | 0.90[1] | 4.60 | .... | ... | .... |
| C. S. Warner, Cincinnati.... | 11.35 | 7.42 | 44.08 | 0.80 | 4.08 | ...... | 44.43 | 0.80 | 4.16 | .... | 15 | 30 |
| | ... | .. | ... | .. | .. | ...... | ... | 0.68 | 4.08 | Purp | 5 | 5 |
| J. Q. Burton, Atlanta...... | 9.90 | 5.01 | 43.66 | 1.01 | 4.86 | ...... | 43.57 | 0.94 | 4.83 | .... | 13 | 2½ hrs. |
| | 10.01 | 5.02 | 43.66 | 1.02 | 4.89 | ...... | 43.60 | 0.93 | 4.79 | .... | 10–15 | .... |
| | ... | .. | ... | 0.46[2] | .. | ...... | ... | .. | 0.59–0.59 | .... | ... | .... |
| | ... | .. | ... | .. | .. | ...... | ... | .. | 0.46–0.63[2] | .... | ... | .... |
| Stillwell & Cladding, N. Y.. | 9.67 | 4.95 | 43.67 | 0.77 | 4.40 | ...... | 43.78 | 0.74 | 4.59 | .... | 10 | 10 |
| W. D. Richardson by | 9.74 | 5.41 | 44.54 | 0.64 | 3.90 | ...... | 43.60 | 0.76 | 3.63 | .... | 20 | 20 |
| E. F. Scherubel, Chicago.. | 9.66 | 5.65 | | 0.50 | 3.70 | ...... | ... | 0.79 | 3.82 | .... | ... | .... |
| L. Watling, Cincinnati...... | 10.30 | 5.90 | 43.40 | 1.00 | 4.50 | ...... | 43.40 | 1.00 | 4.50 | .... | 25 | 2½ hrs. |
| J. E. Breckenridge, Carteret | ... | .. | ... | 0.62 | 4.85 | ...... | ... | 0.65 | 4.95 | .... | ... | .... |
| W. J. Jones, LaFayette..... | 9.43 | 4.65 | 43.52 | 0.92 | 4.53 | 597 | 43.50 | 1.03 | 4.55 | 597 | 2–3 | 8–10 |
| | 9.58 | 4.46 | 43.52 | 0.85 | 4.38 | 597 | 43.50 | .. | 4.44 | 597 | ... | .... |
| | 9.80 | .. | 43.52 | 0.83 | 4.50 | 590 | 43.50 | 0.82 | 4.45 | 590 | 3–5 | 10–30 |
| | ... | .. | 43.52 | 0.85 | 4.53 | 590 | 43.50 | 1.03 | 4.52 | 590 | ... | .... |
| | ... | .. | 43.52 | 1.03 | 4.57 | 589 | 43.50 | .. | .... | ... | 4 | 25 |
| | ... | .. | 43.52 | .. | 4.62 | 589 | ... | 0.79 | 462–467 | 575 | 30 | 46 |
| | ... | .. | 43.52 | .. | .. | ...... | 44.59 | 0.96 | 4.54 | 597 | 2 | 12[5] |
| | ... | .. | ... | .. | .. | ...... | ... | .. | 4.64 | ... | ... | 4[5] |
| | ... | .. | ... | .. | .. | ...... | 42.48 | 0.99 | 4.07 | 597 | 2½ | 12[5] |
| | ... | .. | ... | .. | .. | ...... | ... | .. | 4.29 | .... | ... | 9[5] |
| G. Farnham, Cincinnati..... | 9.6 | 4.72 | 43.80 | 0.88 | 4.65 | ...... | 44.08 | 0.85 | 4.84 | .... | ... | .... |
| | 9.9 | 4.53 | 43.80 | 0.83 | 4.65 | ...... | 44.10 | 0.82 | 4.73 | .... | 4 | 25 |
| F. B. Carpenter, by | 10.2 | 5.51 | ... | 0.83 | .. | 589+589[3] | ... | 0.81 | .... | 589+589 | 18 | .... |
| H. G. Lewis, Richmond.... | ... | .. | ... | 0.87 | .. | ...... | ... | .. | .... | .... | ... | .... |
| | ... | .. | ... | 0.85 | .. | ...... | ... | .. | .... | .... | ... | .... |
| | ... | .. | ... | 0.87 | .. | 589[4] | ... | 0.88 | .... | 589 | 50 | .... |
| | ... | .. | ... | .. | 4.60 | 597[4] | ... | .. | 4.47 | .... | ... | 5–6 hrs. |
| | ... | .. | ... | .. | 4.12 | 597+597[3] | ... | .. | 4.00 | 597+597 | ... | 35–50 |

[1] Citrate sol. prepared by method in THIS JOURNAL, 1, 618.

[2] 9 cm. funnel used which allowed some of the insoluble to pass through. Previous results by same analyst where 5.5 cm. funnel was used gave brilliantly clean filtrates.

[3] Glass funnel with platinum cone.

[4] Washed once on Hirsch funnel.

[5] Contents of flask were poured on filter. After liquid was drawn off the filter and contents were removed to another funnel, covered with an unused filter paper and washing continued.

water in bath will have to be kept at 66 to 67 degrees in order that citrate solution may be at 65°; shake blank same as regular flask and agitate water in bath each time flasks are shaken. Remove flasks from bath promptly at end of half hour.

*Filtration.*—Use a Hirsch or Buchner funnel having a perforated bottom of at least $2^1/_2''$ diameter, with suction. Use S. & S. 590 or similar grade of paper with sample No. 1 and S. & S. 597 with sample No. 2. (Paper should be exactly same diameter as perforated bottom.) Pour off the citrate solution first, before allowing the paper pulp to clog filter. Wash with small portions of water at 65° C., using about 30 cc. at each washing. Wash six times after entire contents of flask have been placed on filter. Report length of time required for filtering and washing.

*Solution.*—Make solution by any of the official methods.

*Precipitation.*—Determine p205 by the official gravimetric method. At this point run a blank on your reagents, using double the quantity of reagents and divide the result by two. Report individual determinations not averages, also blank.

You are respectfully asked to follow instructions closely, as the Committee thinks that the value of coöperative work in the past has been considerably lowered by the analyst not following instructions closely enough. Unless this is done results are not comparable.

If for any reason you find it impossible to follow instructions kindly mention any change of methods in your report.

Reports should be sent to G. Farnham, cr. The Jarecki Chemical Co., Cincinnati, Ohio, on or before the expiration of one month from the time samples are received.

Thanking you for your valued coöperation and with every assurance that same is greatly appreciated by

The Committee on Phosphoric Acid:
G. Farnham, *Chairman*,
J. Q. Burton,
W. J. Gascoyne,
W. J. Jones,
J. R. Powell.

## AMERICAN CHEMICAL SOCIETY, DIVISION OF FERTILIZER CHEMISTS. POTASH COMMITTEE WORK FOR DECEMBER MEETING, 1910.

Letter accompanying samples:

A sample of fertilizer has been sent you marked "Official Potash Sample, A. C. S. for December meeting 1910."

Will you test it by the following methods?

*Potash.*—Method 1: Official method for water-soluble potash as stated by the A. O. A. C., U. S. Dept. of Agr., Bureau of Chemistry, *Bulletin* 107, allowing solution having had the ammonia and ammonium oxalate to stand only long enough to cool before filtering, not over four hours, or stating in your report the time the solution stood before filtering.

Method 2: Weigh 2 grams on to a 11 cm. filter paper and wash with small portions of hot water (as near boiling as possible) into a 200 cc. flask, allowing each washing to run through before adding the next, until about 175 cc. are in the flask. Add to washings in the flask about 2 cc. HCl (conc.), heat to boiling, add ammonia and ammonium oxalate as usual, cool at once, make to mark and filter. Proceed as in official method, evaporating at least 50 cc.

*Moisture.*—Make moisture determinations in duplicate according to your usual method, specifying what weight was taken, how long drying and what kind of an oven was used and inside temperature of oven.

*General Remarks.*—Use Gooch filter for potash and wash the potassium platinic chlorid off the filter with hot water and reweigh the filter.

Kindly make report in full reporting all tests and not averages, and give any experience in potash work which you care to relate.

Send report to J. E. Breckenridge, Carteret, N. J., by June 1st.

Thanking you for whatever work you can do in this line.

Committee on Potash:
J. E. Breckenridge, *Chairman*,
F. B. Porter,
E. L. Baker.

Results of Co-operative Work in Potash, Div. Fertz. Chemists.

| | Meth. No. 1. | Av. | Meth. No. 2. | Av. | Dif. in favor. Meth. No. 2 plus. | Mois. av. |
|---|---|---|---|---|---|---|
| E. L. Baker, N. Y. Exp. | 9.99 | | 10.50 | | 0.50 | |
| Station, Geneva, N. Y. | 9.98 | 9.99 | 10.48 | 10.49 | | 17.69 |
| J. A. Bizzell, Cornell Univ., | 10.13 | | 10.24 | | 0.12 | |
| Ithaca, N. Y. | 10.15 | 10.14 | 10.28 | 10.26 | | 16.73 |
| E. O. Thomas, 812-814 | 10.30 | | 10.09 | | | |
| Paul - Gale - Greenwood | 10.23 | 10.27 | 10.04 | 10.07 | | 16.99 |
| Bldg., Norfolk, Va. | | | | | | |
| Carlton C. James, Pac. | 9.97 | | 10.20 | | 0.14 | |
| Guano & Fert. Co., | 10.01 | 9.99 | 10.06 | 10.13 | | 18.52 |
| Honolulu, Hawaii. | | | | | | |
| Filtered after 1/2 hr. cooling. | | | | | | |
| Stillwell & Gladding, 181 | 10.50 | 10.50 | 10.44 | 10.44 | | 17.26 |
| Front St., N. Y. City. | | | | | | |
| Filtered after 2 hrs. cooling | | | | | | |
| P. K. Nisbet, Am. Ag. | 9.95 | | 10.14 | | 0.17 | |
| Chem. Co., North Weymouth, Mass. | 9.98 | 9.97 | 10.14 | 10.14 | | 16.28 |
| H. D. Young, Univ. of | 9.86 | | 10.11 | | 0.10 | |
| Cal., Whittier, Cal. | 9.90 | 9.88 | 9.85 | 9.98 | | 17.29 |
| Method No. 1 filtered after 1 hr. cool. | | | | | | |
| H. B. Battle, 103 S. Court | 10.20 | 10.20 | 10.28 | 10.28 | 0.08 | 16.62 |
| St., Montgomery, Ala. | | | | | | |
| Three 1/2, 2 1/2 and 2 hrs. standing. No difference. | | | | | | |
| Geo. W. Miles, 29 Central | 10.16 | 10.16 | 10.31 | 10.31 | 0.15 | 16.81 |
| St., Boston, Mass. | | | | | | |
| E. W. Gaither, O. Ag. Exp. | 10.13 | | 10.54 | | 0.31 | |
| Station, Wooster, O. | 10.17 | | 10.40 | | | |
| | 10.13 | | 10.54 | | | |
| | 10.20 | 10.16 | 10.41 | 10.47 | | 17.16 |
| W. P. Colvin, Kansas City, | 10.32 | | 10.38 | | 0.10 | |
| Kas. | 10.33 | | 10.44 | | | |
| Three hrs. before filtering. | | 10.33 | 10.47 | 10.43 | | 17.25 |
| F. A. Nantz, Box 17, Little | 9.95 | 9.95 | 10.31 | 10.31 | 0.36 | 17.05 |
| Rock, Ark., | | | | | | |
| One hr. before filtering. | | | | | | |
| F. B. Carpenter, Mr. Henry, | 10.11 | | 10.20 | | 0.13 | |
| Vir. Car. Chem. Co., | 10.12 | 10.12 | 10.30 | 10.25 | | 17.08 |
| Richmond, Va. | | | | | | |
| F. L. Parker, 40 Broad | 10.14 | | 10.44 | | 0.15 | |
| St., Charleston, S. C. | 10.28 | | 10.44 | | | |
| | 10.22 | 10.21 | 10.20 | 10.36 | | 16.84 |
| W. H. Whithouse, Moosic, | 10.22 | | 10.34 | | 0.13 | |
| Pa. | 10.22 | | 10.36 | | | |
| | 10.22 | 10.22 | | 10.35 | | 17.08 |
| A. Lowenstein, Morris & | 10.13 | | 10.20 | | | 0.02 |
| Co., Chicago, Ill. | 10.17 | 10.15 | 10.13 | 10.17 | | 17.22 |
| R. S. Norris, Exp. P. | 9.98 | | 9.92 | | | |
| Station, work done by | 9.92 | 9.95 | 9.93 | 9.93 | | 16.75 |
| S. S. Peck. | | | | | | |
| F. R. Werthmueller, W. | 10.05 | 10.05 | 10.32 | 10.32 | 0.27 | 16.90 |
| A. E. Jordan, J. | 10.19 | 10.19 | 10.36 | 10.36 | 0.17 | 17.04 |
| and R. S. Norris. N. | 10.12 | | 10.35 | | 0.14 | |
| | 10.21 | 10.17 | 10.27 | 10.31 | | 16.93 |
| J. S. Burd, Univ. of Cal., | 10.18[1] | | 10.39[1] | | | |
| Berkeley, Cal. | 10.21[1] | | 10.43[2] | | | |
| 1/2 hr. before filtering | 10.26[2] | | 10.35[1] | | | |
| [1] 0.5 gram used | 10.24[2] | | 10.45[2] | | | |
| [2] 1 gram used | 10.25[2] | | 10.43[1] | | | |
| | | | 10.53[2] | | | |
| | | | 10.42[1] | | | |
| | | 10.23 | 10.46[2] | 10.43 | 0.20 | 16.71 |

Results of Co-Operative Work in Potash, Div. Fertilizer, Chemists (*Continued*).

| | Meth. No. 1. | Av. | Meth. No. 2. | Av. | Dif. in favor. Meth. No. 2 plus. | Mois. av. |
|---|---|---|---|---|---|---|
| B. L. Hartwell, R. I. State | 10.51 | 10.51 | 10.46 | 10.46 | | 16.95 |
| College, Kingston, R. I. | | | | | | |
| F. S. Hammett. | | | | | | |
| F. B. Porter, | | | | | | |
| Swift Fert. Works, | 9.93 | | 10.50 | | 0.43 | |
| Atlanta, Ga. | 10.00 | | 10.40 | | | |
| | 10.01 | | 10.48 | | | |
| | 10.08 | | 10.44 | | | |
| | 10.12 | 10.03 | 10.50 | 10.46 | | 17.15 |
| W. C. Dumas, A. M. Lloyd, | 10.38 | | 10.41 | | | |
| Lab., Atlanta, Ga. 1/2 | 10.22 | 10.30 | 10.55 | 10.48 | 0.18 | |
| before filter. | | | | | | |
| 48 hrs. before filtering. | 10.20 | 10.20 | | | | |
| 2 months later. | 10.40 | 10.40 | | | | 16.82 |
| B. W. Bang, Am. Ag. | 10.12 | 10.12 | 10.46 | 10.46 | 0.34 | 17.21 |
| Chem. Co., Carteret, | | | | | | |
| N. J. | | | | | | |
| Average for whole. | | 10.16 | | 10.31 | | 17.04 |
| B. W. Bangs, Am. Ag. | 10.12 | 10.12 | 10.46 | 10.46 | 17.21 | 17.21 |
| Chem. Co., Carteret, N. J. | | | | | | |
| Average for whole. | | 10.16 | | 10.30 | | 17.04 |

*Remarks.*—Cobalti Nitrite Method (Volumetric), 10.04 and 9.94 per cent. F. B. Carpenter.

The filter papers and contents after washing in Method 2 were found to contain 0.04 per cent. potash by Method 1.

Tests by Method 1 were not allowed to stand over 3/4 hours before filtering.

All the official samples were made by mixing 5800 gms. of acid phosphate and 1200 gms. muriate of potash analyzing; potash A. O. A. C. method acid phosphate 0.09 $K_2O$ muriate 60.16 $K_2O$.

Percentage $K_2O$ by theory 10.39.

In mixing and bottling, the samples undoubtedly lost enough moisture to account for Method 2 running slightly higher than that calculated. F. B. Porter.

Report on Moisture on Potash Sample, Dec., 1910, Meeting A C S.

| Name. | Wt. in gms. | Time in hrs. | | Temp. | | Moisture. |
|---|---|---|---|---|---|---|
| E. L. Baker. | 2 | 9 | Constant | 100° | | 17.76–17.61 |
| J. A. Bizzell. | 2 | 5 | Water oven | 97 | | 16.72–16.74 |
| E. O. Thomas. | 2 | 5 | | 99 | 1st | 17.16–17.22 |
| E. O. Thomas. | 6 days after first set. | | | | 2nd | 16.86–16.73 |
| Carlton C. James. | 5 | 5 | | 100–102 | | 18.57–18.46 |
| Stillwell & Gladding. | 10 | 5 | Water oven | 99 | | 17.25 |
| Stillwell & Gladding. | 5 | 5 | Water oven | 99 | | 17.26 |
| H. D. Young. | | 4 | Water oven | 98.2 | | 17.23–17.34 |
| H. B. Battle. | Watch glasses | 4 | Air oven | 105 | | 16.44–16.79 |
| Geo. W. Miles. | | 4 | | 99.5 | | 16.82–16.80 |
| F. A. Nantz. | 2 | 2 | Air oven | 105 | | 16.65–17.35 |
| F. B. Carpenter. | 2 | 5 | Water oven | 97 | | 17.11–17.05 |
| F. L. Parker. | 5 | 5 | Air bath | 98–100 | | 16.71–16.96 |
| W. H. Whitehouse. | 2 | 5 | Steam bath | 95–105 | | 17.09–17.07 |
| A. Lowenstein. | 5 | 5 | | 105 | | 17.12–17.32 |
| J. S. Burd. P. L. | 2 | 5 | Constant | 100 | | 16.73–16.77 |
| Mc Creary. | | | | | | 16.62 |
| B. L. Hartwell. | 2 | 6 | Water oven | 98 | | 16.93 |
| F B. Porter. | 10 | 5 | | 100–105 | 1st | 17.29–17.16 |
| F. B. Porter. | 10 | 5 | | 100–105 | 2nd | 16.73–17.34 |
| P. K. Nisbet. | 5 | 5 | | 100 | | 16.40–16.20 |
| | | | | | | 16.25 |
| E. W. Gaither. | 2 | 5 | | 100 | 1st | 17.27–17.05 |
| E. W. Gaither. | 2 | 5 | | 100 | 2nd | 17.17–17.11 |
| W. P. Colvin, diff. | 5–10 | 6 | Constant | 105 | 1st | 16.44–16.69 |
| | | | | | | 17.42 |
| W. P. Colvin, diff. | 5–10 | 6 | Constant | 105 | 2nd | 17.69–17.60 |
| | | | | | | 17.68 |
| R. S. Nossis | 2 | 5 | | 100–105 | P. | 16.67–16.83 |
| Double Watch Glasses | 2 | 5 | | | W. | 16.87–16.93 |
| | 2 | 5 | | | J. | 17.07–17.01 |
| | 2 | 5 | | | N. | 16.90–16.95 |
| W. C. Dumas | 5 | 5 | | 99 | | 16.82 |
| W. C. Dumas | 1 | 5 | | 99 | | 16.80 |
| W. C. Dumas | 1 | 5 | | 99 | | 16.83 |
| B. W. Bangs. | 5 | 5 | | 100 | | 17.21 |

*Moisture Remarks No. 3.*—Moisture determinations were made in an oven with a water jacket, the inside temperature of which was 98° C. Two samples of 2 grams each were heated for four hours, showing a loss of 0.3382 and 0.3368 gram. Upon heating for two subsequent hours, the total loss was 0.3386 and 0.3386. Further heating showed that the weights had become constant. Burt L. Hartwell.

10 gms. in a shoe blacking box dried 5 hours at 100 to 105° C. Thermometer buld near box in oven.

Oven No. 1.—10 × 12″ double wall oven with reflux ondenser using glycerine solution between walls. (E. & A. No. 3030).

Oven No. 2.—8 × 10″ single wall oven heated by single burner underneath. (E. & A. No. 3030).

| Oven. | No. 1. | No. 2. | Calculated. |
|---|---|---|---|
| Moisture in 5 hrs. at 100–105°....... | 17.29 | 16.74 | 15.95 |
| | 17.16 | 17.34 | |
| Total moisture shown after 3 additional hrs. at 130°................ | | 19.11 | 19.32 |
| | | 19.33 | |

The moisture tests at 130° were made to see whether the difference between the calculated and determined figures would still obtain at that temperature. It seems that the potash releases some of the moisture at 100° that would without its presence be shown only at higher temperatures.

F. B. Porter.

*Remarks.*—Proposed Method 2 gives more potash than official method, and approaches nearer theory.

Inasmuch as this method includes nothing but potash soluble in water and from the fact that the referee on potash of the A. O. A. C. reported same results it would seem that Method 2 gave better results than the official method.

J. E. Breckenridge.

## REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION OF THE DIVISION OF THE FERTILIZER CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY.

To the Executive Committee and Members of the Division of Fertilizer Chemists:

Your committee begs to report that their attention has been given largely to the subject of organic ammoniates in mixed fertilizers. Attached herewith are copies of correspondence on this subject among members of this committee and between this committee and the chairman of this division and the members of the committee made up of officials having in charge fertilizer inspection in their several states. This latter committee sent out a notice in March of 1910, which is attached hereto.

It will be noted in the circular above referred to that this committee contemplates publishing the solubility of the organic nitrogen in all the brands of commercial fertilizers examined, determined by a uniform method, and beginning this work with fertilizers examined on and after March 1, 1911. A sub-committee consisting of Mr. C. H. Jones, *Chairman*, Mr. J. P. Street, of Connecticut, and Mr. Burt Hartwell, of Rhode Island, have undertaken the study of a uniform method which is to be employed.

The chairman of this division and also the chairman of this committee wrote to Dr. Jones, chairman of this sub-committee, advising him of our interest in the matter and offering to coöperate if it should appear to be desirable to the sub-committee. As will be noted in Dr. Jones' letter, he states "that the matter of sending samples to others than those having fertilizer inspection directly in charge in the New England states has not been definitely settled. It is quite probable, however, that all interested parties will have a chance to take part in the work, and when things are ready, I will correspond with you further." Up to the present time, nothing further has been heard from Dr. Jones.

Inasmuch as there has been considerable controversy among agricultural chemists as to the value of the different methods for the determination of the availability of organic ammoniates, it would appear advisable that this matter be very carefully studied, and it is further recommended by this committee that the Committee on Nitrogen or a new committee be appointed, to study the methods for the determination of the availability of organic nitrogen in commercial fertilizers, either by itself or in coöperation with the Association of Official Agricultural Chemists, the above referred to a committee of New England chemists and other organized bodies making a study of this same subject.

Respectfully submitted,
A. LOWENSTEIN.

## REPORT OF THE COMMITTEE ON PHOSPHATE ROCK.

The progress of the work of the Committee on Phosphate Rock has been seriously delayed by the fact that the routine duties of most of the members are heaviest at this time of the year. Considerable progress has been made, however. The committee has been organized into sub-committees on Moisture, Phosphoric Acid, Iron and Alumina, and each sub-committee has drafted tentative methods covering its individual branch of the subject. These tentative methods have been sent out to all the members of the committee together with carefully prepared samples of phosphate rock. Some of the members have been able to accomplish considerable work, others, through no fault of their own, have been absolutely unable to begin their work on these samples and methods.

It is therefore not possible to do more than make this report of progress at present. Such results as have been received seem to bear out the opinion held by many chemists at the present time that all the various methods are not equally well adapted to all varieties of phosphate rock. It is, however, not feasible to quote any specific data resulting from the work done so far in support of this view. This should not be understood to mean that the committee is trying to formulate different methods, each of which shall apply only to certain varieties of rock. Every effort will be made to develop a method which shall be equally applicable to all commercial varieties of rock and produce results which shall be exact enough for commercial work.

Another important subject is the matter of standard samples. Preparations have been made and work is well under way towards the standardization of one or more samples of phosphate rock which shall be available to those interested at a nominal cost. This involves not only a careful preparation of a large supply of an absolutely uniform sample, but also the development of scientifically accurate methods of analysis, so that the exact composition of the rock may be determined. After this has been done, such standard samples will be of the greatest service in testing the methods for commercial work developed in the meantime in the work of this committee.

C. F. HAGEDORN.

## AMERICAN CHEMICAL SOCIETY. DIVISION OF PHARMACEUTICAL CHEMISTS.

The Division of Pharmaceutical Chemists of the American Chemical Society held its Minneapolis meeting in the Chemistry Building of the University of Minnesota on December 29th. The address of Prof. A. B. Stevens, *Chairman*, upon Pharmacopoeial Standardization was especially interesting and timely since Prof. Stevens is a member of the Committee of Revision, and Chairman of the Sub-Committee on Proximate Assays. The address outlined the work being done by the sub-committee mentioned and made clear the thoroughness and carefulness with which the Pharmacopoeia is being revised. The new and improved methods of committee work were also explained.

The Report of the Committee on Quantitative Methods gave a résumé of the analysis of mercury salts by six different methods. The committee has done valuable work and is being continued. The report, although merely a report of progress, was ordered published in order that the greatest benefit may be obtained from the work of the committee.

The papers read at the meeting were as follows:

A. B. Stevens. "Citro Compounds of Iron."
E. R. Miller and G. H. Marsh. "Camphor in Oil of Sassafras."
L. E. Sayre. "Assay of Gelseminum."
F. Klein. "Rapid Determination of Sulphuric Acid with the Porous Clay Crucible."
E. Kremers. "Chemical Problems suggested by the Cultivation of Medicinal Plants. (1) Stramonium."

The following officers were elected for the ensuing year:

B. L. Murray, *Chairman*,
A. D. Thorburn, *Vice-Chairman*,
F. R. Eldred, *Secretary*.
*Members of Executive Committee:*
A. B. Stevens,
L. F. Kebler.

Yours very truly,
B. L. MURRAY, *Chairman*.

## ABSTRACT OF REPORT OF THE COMMITTEE ON QUANTITATIVE METHODS.

Division of Pharmaceutical Chemists of American Chemical Society.

Your committee begs to offer the following report of work which has been done since the last meeting (July, 1910). In the search for suitable assays for the various mercury salts included in the U. S. P., for which a standard of purity is laid down and no assay process is given, investigation was made of a number of existing methods as indicated below.

In order that you may know the method of working of the committee, we give an outline of the plan pursued in this case. The chairman sent out requests to the members of the committee for suggestions as to methods suitable for general application to mercurous and mercuric salts. After going over the suggestions received, the following methods as proposed were again submitted to the committee, together with samples of mercurous chloride and mercuric iodide. The methods as submitted are as follows:

### Method 1.

Suggested by Mr. L. A. Brown.[1]

*Applicable to* mercurous iodide, chloride, bromide, and mixtures of mercuric and mercurous salts.

Weigh out sample of about 0.5 gram, place in Erlenmeyer flask of about 300 cc. capacity, add 10 cc. potassium iodide solution containing 2 grams KI; rotate and quickly add 50 cc. *N*/10 iodine solution by means of a pipette, agitate until all of the sample is in solution. Then run in *N*/10 $Na_2S_2O_3$ solution until all the free iodine has been removed, using starch solution if desired.

Reaction : $2HgCl + 6KI + I_2 = 2K_2HgI_4 + 2KCl$.

By mixing the HgCl with the solution of the potassium iodide immediately before adding the iodine solution, the insoluble salt goes into solution more quickly.

### Method 2.

Suggested by Mr. L. A. Brown.[2]

*Applicable to* mercuric chloride, iodide, cyanide, nitrate, oxide, ammoniated mercury, metallic mercury, and preparations of mercury such as ointment of mercury, ammoniated mercury,

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[1] See Schimpf, "Volumetric Analysis," p. 408.

[2] Merck's Report, **1908**, p. 57.

nitrate, oxide solution of mercuric nitrate, Donovan's solution, plaster of mercury, etc.

Dissolve one gram of the sample (*e. g.*, $HgCl_2$), using one or two grams of potassium iodide if necessary, in sufficient water to make 100 cc. of solution.

Take 20 cc. aliquot, add 1 gram Kl, 5 to 10 cc. of 10 per cent. KOH sol., and 10 cc. of water containing 2 or 3 cc. of formaldehyde solution. Mix thoroughly and place on water-bath for about 10 minutes, or until supernatant liquid settles clear; then decant off through a small filter, washing residue with two portions or more of water, decanting off through filter as before.

Dissolve the small amount of metallic mercury off the filter by means of a few drops of hot diluted nitric acid (1: 1), washing the filter with a few cc. of water to remove all traces of mercury. Collect filtrate and washings in the beaker containing the Hg, adding more nitric acid if necessary to secure solution of the mercury. Evaporate to about 2 or 3 cc. on a water-bath, then dilute with water and transfer to a 100 cc. flask, rinsing out beaker with successive amounts of water sufficient to make 100 cc. of the solution.

Take an aliquot representing about 0.100 gram of $HgCl_2$, add 25 cc. of water, then a slight excess of 5 per cent. iodic acid solution, 5 cc. being enough. This is added drop by drop, agitating all the while to secure complete agglutination of the curdy precipitate. As soon as the supernatant liquid is clear, filter and wash precipitate with three or four portions of water.

Dissolve precipitate off the filter with a few drops of diluted HCl, wash filter thoroughly, add 1 or 2 grams of KI, allow to stand for about 5 minutes, then titrate the liberated iodine with $N/10$ $Na_2S_2O_3$.

Each cc. of $N/10$ thiosulphate = 0.0022405 gram $HgCl_2$.

In the case of ointments such as official ointments of mercury and its salts, remove the ointment base by means of the proper solvent, dissolve the residue with nitric acid, and apply the method as given.

### Method 3.

Suggested by M. B. L. Murray.[1]

*Applicable to* solutions of mercury nitrate, the mercury oxides, metallic mercury, mercury with chalk, and possibly some of the other mercurial preparations.

*Not applicable* to calomel or corrosive sublimate.

Those preparations of mercury as found in the U. S. P., which can readily be brought into solution in nitric acid, are satisfactorily assayed for mercury by electrolysis.

The sample may well be of such a size that the final weighing of the metallic mercury will show a weight of about 0.250 gram. The mercury solutions, or the dried preparations dissolved, are acidulated with 3 cc. of concentrated nitric acid, diluted to 125 cc., heated to 70° C. and then electrolyzed with a current of $N. D._{100}$ = 0.06 ampere and two volts. The metal will be fully precipitated in from 2 to 4 hours, and may appear as a uniform metallic coating upon the platinum dish, which is used as a cathode, or it may appear in shiny droplets. After the deposition of the material is complete, the mercury is washed with water, then with alcohol, then with ether, and finally dried a short time in the desiccator and weighed. The electrolyte remaining may be tested qualitatively for mercury to show that the deposition was complete.

The time may be materially shortened by the use of the rotating anode and mercury cathode.

### Method 4.

Suggested by Mr. F. O. Taylor.[2]

A solution of the mercury salt, containing about 0.2 gram of mercury in 25 to 50 cc. of solution, is treated with excess of KI so that the $HgI_2$ formed redissolves. Render alkaline with NaOH; treat with 3 cc. of 40 per cent. formaldehyde solution diluted with 10 cc. of water and let stand with occasional stirring for about two minutes. Acidify with acetic acid; add 25 cc. of $N/10$ iodine and after all the precipitated mercury has combined with the iodine, titrate the excess with $N/10$ sodium thiosulphate solution.

Mercurous salts must be converted into mercuric before precipitation.

In the case of mercuric cyanide, sulphuric acid should be used instead of acetic in order to decompose any cyanogen iodide which may have formed.

### Method 5.

Suggested by Mr. F. O. Taylor.[1]

*Estimation of Mercury as Arsenate.*—The mercury must be present as a mercuric salt, and preferably as a nitrate, as the mercuric arsenate is not precipitated from the chloride solution. A small amount of free nitric acid does not interfere with the accuracy of the results. To a cold solution containing about 0.25 gram Hg in 100 cc. add 20 cc. of saturated solution sodium arsenate. The heavy yellowish white precipitate of mercuric arsenate immediately forms and settles rapidly, but for greater accuracy the author of the method recommends that the solution stand for several hours; then filter through a Gooch filter, wash thoroughly with cold water and dry at 100°.

### Method 6.

Suggested by Mr. F. O. Taylor.[1]

*Estimation of Mercury as Chloride.*—To a solution of the mercuric salt, preferably in the form of a nitrate containing about 0.25 to 0.4 gram Hg, add a slight excess of a mixture containing one drop of hypophosphorous acid to each cc. of $H_2O_2$, and then immediately an excess of solution sodium chloride. Let stand for one hour, filter off the precipitated HgCl, wash thoroughly, dry at 100° and weigh.

Below, in tabular form are given the results obtained by different members of the committee in using these methods.

ANALYSIS OF MERCUROUS CHLORIDE.

| Chemist. | Method No. 1 Per cent. | Method No. 4. Per cent. | Special method, Per cent. (*e*). |
|---|---|---|---|
| Mr. L. A. Brown. | 100.10 (*a*) | | |
| | 99.91 | | |
| Mr. B. L. Murray. | 98.94 (*b*) | | 99.62 (*e*) |
| | 99.33 | | 99.79 |
| | 99.25 | | |
| | 99.35 | | |
| | 99.23 | | |
| | 99.19 | | |
| Mr. L. D. Havenhill | 100.46 (*c*) | 99.84 | |
| | 99.71 | 100.04 | |
| | 100.01 | 99.62 | |
| | 100.04 | 99.84 | |
| | 100.18 | | |
| Mr. F. O. Taylor. | (*d*) | | |

COMMENTS.

(*a*) Method is entirely satisfactory if closely adhered to.

(*b*) Method worked well although some time was consumed in effecting solution in iodine.

(*c*) The factors seemed too large to permit of sufficient accuracy when working upon samples of close to 100 per cent. purity.

(*d*) (Mr. Taylor's results are unfortunately unavailable, but his comments are at hand.) The chief difficulty with this method is the dissolving of the mercury by the iodine solution, which is very often extremely slow. Aside from this the method seems very good.

(*e*) Samples were dissolved in sodium sulphide solution and

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[1] See Smith, "Electro-Analysis," pp. 90 and 94.

[2] See E. Rupp, *Berichte*, **39**, 3702 (1906); also *Chem.-Zeit.*, **34**, 229 (1910).

[1] See C. J. Pretzfeld, *Jour. Am. S. S.*, **1903**, p. 198.

electrolyzed $^3/_4$ hr. with 0.5 ampere, 4–5 volts, using mercury cathode and rotating anode.[1] Results very satisfactory.

ANALYSIS OF MERCURIC IODIDE.

| Chemist. | Method No. 2. Per cent. | Method No. 3. Per cent. | Method No. 4. Per cent. | Method No. 5. Per cent. | Method No. 6. Per cent. |
|---|---|---|---|---|---|
| Mr. L. A. Brown | 95.74(*m*) | | 99.67 (*l*) | | |
| | Highest of several | | 100.39 | | |
| Mr. B. L. Murray. | 79.17(*n*) | 98.68 | 98.57(*u*) | | |
| | 86.36 | 99.38 | 99.38 | | |
| | 81.50 | 98.52 | | | |
| | 86.04 | | | | |
| | 62.01 | | | | |
| | 80.82 | | | | |
| Mr. L. D. Havenhill. | 94.40(*o*) | 97.83 | 64.1 | | |
| | | (*i*)(*h*) | (*p*)(*v*) | 97.85(*x*) | 97.98 |
| | 94.19 | 97.94(*h*) | 98.64(*r*) | 93.10 | 97.84 |
| | 94.65 | 99.89(*k*) | 97.64(*r*) | 98.09 | 97.60 |
| | 91.88 | 98.86(*k*) | 98.80(*s*) | 94.00 | 97.51 |
| | 97.65(*f*) | | 98.86(*s*) | | |
| | 98.80(*f*) | | 99.58(*s*) | | |
| | 97.65(*f*) | | 99.98(*t*) | | |
| | 91.88(*g*) | | 99.80(*t*) | | |
| | 93.95(*g*) | | 99.70(*t*) | | |
| | | | 99.62(*t*) | | |
| | | | 100.50(*t*) | | |
| Mr. F. O. Taylor. | (*q*) | (*j*) | (*w*) | (*y*) | (*z*) |

NOTES.

(*f*) Precipitating and washing in dilute alcohol.

(*g*) Same solution as preceding (*f*) but washing with water.

(*h*) Dried at 50° C.

(*k*) Dried in desiccator room temperature.

(*p*) 30 seconds with stirring for reduction.

(*r*) 2 minutes with stirring for reduction.

(*s*) 4 minutes with stirring for reduction.

(*t*) 5 minutes with vigorous shaking.

COMMENTS.

(*m*) Mr. L. A. Brown, I got very poor results due possibly to two causes: (1) Mechanical loss of mercury in filtering after reduction. (2) Part of the mercury appears to come down in a colloidal condition and is lost in the filtrate. I have proven to my entire satisfaction that the reduction by formaldehyde in alkaline solution is quantitative, and what makes me believe that part of the mercury is in a colloidal form is that a *perfectly clear filtrate* will show the presence of mercury by hydrogen sulphide if completely saturated.

(*l*) Contrary to previous observations I find this method to give good results if the reduction is carried out in the cold and not allowed to stand too long before adding iodine solution. If the reduced mercury is allowed to coalesce and form large globules the solution of the mercury in the iodine solution is *very* slow.

(*u*) Mr. B. L. Murray, in using this method we found that two minutes was not sufficient time for the reduction of the mercury by formaldehyde. Even five minutes was too short a time and a little heat was used to complete the reduction; but this we found reduced the mercury to such a condition that it was very hard to dissolve in the iodine solution.

(*n*) The method gave us uncertain results.

(*o*) Mr. L. D. Havenhill, the amount of water used in washing the precipitate of mercury iodate tends to vary the results.

(*i*) Our work seems to indicate that there was a considerable loss of mercury, due to volatilization when the cathode was dried at a temperature of 50°.

(*v*) We found the time for reduction to be insufficient, also the stirring. Better, or at least higher results were obtained by vigorously shaking the mixture. The quantity of acetic acid used is indefinite. Our results, which are not herein reported, seem to show that the more acetic acid used, the lower are the results. We believe that the size of the factor is too large to permit of sufficient accuracy when working on samples that run close to 100 per cent. in purity.

(*x*) In this method the mercuric iodide was reduced with formaldehyde in the manner indicated by the method of E. Rupp, dissolved in nitric acid and precipitated with sodium arsenate. It was noted that the precipitate of mercuric arsenate was not of uniform color, and the higher results here reported were materially whiter in color than the lower results which were more yellow in color.

(*q*) Mr. F. O. Taylor, we find this method inaccurate because of the distinct solubility of the mercuric iodate in water, which solubility may be proved by testing the filtrate from the mercuric iodate by hydrogen sulphide, when a very decided test for mercury can be obtained.

(*j*) Unquestionably the electrolytic method is extremely accurate when used by one who is experienced and has at hand the proper apparatus, and it can also be made a very rapid method. It does not seem, however, to be suited to the requirements of pharmacopoeial estimation, as at the present time one is much more likely to find the requisite skill and apparatus for making other forms of assay than the electrolytic, among those to whom these assays would be chiefly valuable.

(*w*) Here again the difficulty of dissolving the precipitated mercury in iodine solution is the chief drawback. With care the method can be made accurate, but it usually requires more time than a process of this kind should.

(*y*) Inaccurate results here may be attributed to the slight solubility of mercuric arsenate in water, which seems to be sufficient to render the method not very desirable.

(*z*) No careful work was done by me on this method, but only some preliminary tests, and it would appear that special care must be taken in the reduction of the mercuric salts and it is therefore preferable to use phosphorous acid instead of hypophosphorous acid.

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

### THIRD ANNUAL MEETING, NEW YORK, DEC. 7–10, 1910.

The Officers of the American Institute of Chemical Engineers elected at the Third Annual Meeting in New York, December 7 to 10, 1910, are as follows:

*President*, Dr. F. W. Frerichs, Herf and Frerichs Chemical Company, St. Louis Mo.

*Vice-President*, George P. Adamson, Vice-President and General Manager, The Baker and Adamson Chemical Co., Easton, Pa.

Eugene Haanel, Director of Mines, Dept. of Mines, Ottawa, Ont., Can.

Dr. Leo. H. Baekeland, Yonkers, N. Y. Research Chemist and Chemical Engineer.

*Secretary*, Prof. John C. Olsen, Polytechnic Institute, Brooklyn, N. Y.

*Treasurer*, Henry S. Renaud, 159 Front St., New York.

*Auditor*, Herbert Hollick, Camden, N. J.

*Ex-Presidents*, Dr. Samuel P. Sadtler, Dr. Chas. F. McKenna.

*Directors*. H. F. Brown, Wilmington, Del.
Ludwig Reuter, Berkeley, Cal.
Thorn Smith, Detroit, Mich.
J. T. Baker, Phillipsburg, N. J.
Dr. W. M. Grosvenor, New York.
Richard K. Meade, Allentown, Pa.
William M. Booth, Syracuse, N. Y.
Edward G. Acheson, Niagara Falls, N. Y.
Prof. Edward Hart, Easton, Pa.

The American Institute of Chemical Engineers has voted to award a gold medal to the author of the best original contribution to the literature of applied chemistry, such contribution

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[1] THIS JOURNAL, **2**, 481.

to be presented only to the American Institute of Chemical Engineers with provisions as follows:

1. Members and non-members may compete.

2. The paper must be mailed by registered post to the secretary of the Institute, John C. Olsen, Polytechnic Institute, Brooklyn, N. Y., at least sixty days prior to the semi-annual meeting in June, 1911.

3. The papers will be examined by the Committee on Publication, of which William P. Mason, Rensselaer Polytechnic Institute, Troy, N. Y., is Chairman.

4. The first announcement of the award shall be made by the President of the Institute at the semi-annual banquet when the honor will be conferred.

5. If, in the judgment of the committee, no paper presented is worthy of the proposed honor, the award will not be made.

6. The first medal presented shall be given to the author of the best paper which shall have been presented to the Institute from its organization up to within 60 days of the next meeting. Subsequent medals shall be given for papers presented during the year.

A Medal Committee has been chosen to solicit funds for this purpose. The members of the committee are:

Samuel P. Sadtler, 39 South 10th St., Philadelphia, Pa.,
Joseph W. Richards, Lehigh Univ. South Bethlehem, Pa.,
Andrew D. Robertson, 2 North 9th St., Richmond, Va.,
Wm. M. Booth, *Chairman*, 710 Dillaye Bldg., Syracuse, N. Y.

It is proposed to raise by subscription Twelve Hundred and Fifty Dollars ($1250.00). This is to be invested for the Institute and shall be known as a "Medal Fund," the interest of which is to be used for the award. Any person or corporation may contribute. Any subject for investigation and report may be suggested. However, all moneys received will become a part of the general fund set aside for this purpose.

The members of the committee feel that some very valuable papers will be presented and that one of the main aims of the Institute will be accomplished, "to publish and distribute such papers as shall add to classified knowledge in chemical engineering and shall increase industrial activity."

Abstracts of papers read before the American Institute of Chemical Engineers at its Third Annual Meeting, Dec. 7 to 10, 1910:

## FITZGIBON BOILER.

JEROME ALEXANDER.

This paper gives a brief description of the construction and operating principles of the Fitzgibon boiler, a type combining vertical with horizontal tubular features. The boiler is internally fired, and is entirely without external or internal brick work, thus avoiding the annoyance and expense of repairs at inopportune times. A heavy asbestos or magnesia covering reduces radiation below that found in ordinary bricked-in boilers. The boiler is a quick steamer, economical in coal consumption, and can be easily moved about.

## EVOLUTION OF PORTLAND CEMENT PROCESSES.

DR. CHAS. F. MCKENNA.

The paper of the retiring president was a rapid review of the history of Portland cement from the day of Asdin's invention, portraying particularly the different stages in the pro ess from the crude method of Asdin's to the modern process of burning in rotary kilns and the fine pulverizing. The economy of the present day is such that for one cent twelve pounds of raw material can be taken from the earth, dried, ground, calcined and vitrified and the product ground again.

Considerable attention is paid to the old forms of wet processes, and the statement is made that present-day European practice in grinding to a semi-wet slurry hard materials, not marls, is the most important advance in modern times, and should be taken up more vigorously in America. The basis for this is the claim that the drier expense is saved, finer incorporation is obtained, better clinkering and easier grinding of the clinker. The critical feature of the modern semi-wet process is to secure the maximum of fineness of slurry with the minimum water. It is said that in good practice some materials can make with less than 35 per cent. of water a slurry which can be pumped, and as it dries in the upper end of the long kiln the extra coal consumption is not marked. Modern rotary kiln practice, particularly the long kiln, is touched upon, and the use of preheated air from clinker kilns and diminished indraft of cold air.

## SEWAGE DISPOSAL IN EUROPE.

RUDOLPH HERRING.

Disposal of sewage by dilution was first practiced. Of the sixteen largest cities in the world having a population of over one million inhabitants, every one without exception now employs the dilution method, where flowing water is available and a sufficient quantity of oxygen is dissolved in it, to represent a flow of fresh water equivalent to at least 3 cubic feet per second for every thousand persons discharging sewage.

Where a water supply is taken from a river, it must be purified even after any sewage entering above has been treated.

Where a river is not used as a water supply sewage may contaminate the food, fish, oysters, etc. The commercial value of such food is insignificant compared with the cost of removing all the conditions that would impair their hygienic qualities. It is therefore much cheaper to take them at a greater distance from the large cities wh re no dangers exist.

The nuisance to sight produced by sewage is almost everywhere in Europe prevented by keeping all plainly visible floating matter out of a river by screening. Screens with a mesh as small as one millimeter are used.

A nuisance to smell is prevented by constructing sewers with such smooth interior surface and good grade as will deliver the sewage practically fresh to the outfall and insure an immediate submergence of the sewage as far below the surface of the water as possible. This method is entirely successful in many continental cities.

The amount of sewage discharged into the Thames is so regulated that the dissolved oxygen in the water does not generally fall below 30 per cent. of saturation. No nuisance results under these conditions.

European experience justifies the conclusion that purification of sewage by the oxygen in flowing water is entirely satisfactory.

Sand purification of sewage requires the delivery of the sewage in fresh condition and a preliminary separation of the coarser suspended particles after which the finely divided matter may be oxidized in intermittent sand filters. The more recent developments involve improvements on the septic tank method of purification. Dr. Imhoff has developed a tank having two compartments. In the upper the suspended matter settles out and is drawn off through a slot. In the lower compartment the sewage is decomposed with the evolution of methane, carbon monoxide and dioxide. No sulphuretted hydrogen is produced. The decomposition is complete in from three to six months. The sludge which is removed dries quickly to a friable material similar to garden mold. The annoying question of the disposal of sewage may therefore be considered satisfactorily settled.

## PRINCIPLES OF SEWAGE DISPOSAL.

GEO. C. WHIPPLE.

The basic principl s underlying all methods of sewage disposal are to get rid of sewage without danger to the public health, with the least possible nuisance to the smallest number of people, with the least damage to property and at the smallest cost.

The process of purification is usually carried on in several stages: First, a partial removal of the suspended matter by screening or sedimentation or both, second, a process of oxidation using sprinkling filters, contact beds or sand filtration, and third, a final removal of bacteria by sand filtration or disinfection.

The term "sewage purification" is popularly applied to any or all of these processes. This has contributed not a little to confusion of ideas. Laymen innocently suppose that when sewage is "purified" it becomes pure, whereas the sanitary engineer may mean only that it is purer than it was before. How much purer depends upon the method used. It would be of decided benefit to the question of sanitation if more definite terms were used, such as sewage clarification, oxidation, deodorization, disinfection, filtration, etc.

The chief danger from sewage is the contamination of public water supplies. For the protection of public water supplies it is not safe to depend upon sewage purification works alone unless more than ordinary precautions are taken, for the reason that most of the processes cannot be depended upon to remove bacteria from the sewage to a sufficient extent, while with the combined system in use complete purification is impossible. Sewage purification is of advantage as it offers a second line of defense, and increased factor of safety. It also serves to prevent nuisances to sight and smell, which are of real damage to property and affect personal comfort. Sewage works themselves, however, may be the cause of similar nuisance.

What appears to be needed in this country at the present time is some method of coöperation by which needed sanitary reforms can be brought about at least expense. It is unbusinesslike to compel the purification of the sewage of a large upstream city in order to protect the water supply of a small city lower down, provided pure water can be furnished the latter in some better and cheaper way. Legislation that clothes the state authorities with power to prevent the pollution of sewage but does not give them power to compel the purification of water or to control pollution by trade wastes is unfortunate. It naturally leads to litigation rather than coöperation and may retard rather than hasten necessary sanitary reforms. If our state authorities cannot be trusted in this matter it may be that a proper solution of the difficulty will be found in the establishment of District Boards similar to those in England and Germany, such Boards having jurisdiction over the limits of particular water-sheds. In some respects these natural hydrographic boundaries have advantages over artificial state boundaries. In the near future also our national government will doubtless take a hand in the matter. In whatever form the authority may be constituted the idea of coöperation should prevail, and ironclad rules against steam pollution should give way to a rational distribution of the burden of purification of both water and sewage, and an equitable adjustment of cost made between the parties interested, thus decreasing the total expense of sanitary measures required, and utilizing natural resources for the purification of sewage in water as far as this is safe.

If the system of water carriage of sewage continues in use the time will some day come when the sewage of all of our cities will be purified, partially or completely, and all surface water supplies filtered. It is proper to anticipate this consummation as far as our means permit, but meantime it is good business and sound common sense to spend our money first where it will go furthest and do the most good, building water filters and sewage purification works, sometimes one, sometimes both, as they may be needed.

Adequate remedies against stream pollution from the standpoint of nuisance have been usually obtained by an appeal to the principles of common law. Cases involving bacterial pollution by sewage have been thus far too few to establish definite precedents. It will be interesting to see whether, in view of our increasing population, and especially the increasing growth of our cities, the courts will ultimately decide that the use of unfiltered river water as a source of water supply by riparian owners is a reasonable use of the water.

The writer is optimistic in regard to the improvements that are being made in methods of sewage disposal. He believes that the near future is to see extensive developments in the art. Important as are the recent improvements in the technical details still more important and necessary is a rational assignment of the means employed to the work at hand. The use that is to be made of the water into which sewage is discharged and the conditions tending to natural purification are to be studied with greater minuteness than ever before; the method of dilution is to be used more rationally, and the designs of the sewage disposal plants made to fit more closely the particular conditions. The general result will be the construction of more and simpler plants for the treatment of sewage, and where occasion makes necessary, the installation of yet more efficient devices for bacterial purification than those now employed.

## MANUFACTURE OF HYDRATED LIME.

RICHARD K. MEADE.

Hydrated lime is mechanically slaked lime. Just the correct portion of water is added so that the resulting product is a dry fluffy powder. Most of the hydrated limes on the market up to a few years ago were very crude products, usually containing considerable carbonate. Now, however, processes have been perfected which produce a lime consisting almost entirely of the hydrate. The process for the manufacture of hydrated lime usually consists of three stages: (1) crushing the lime; (2) mixing the lime and water, and (3) separating the hydrate from the unhydrated portion. In some processes instead of separating the hydrate from the unhydrated portion, the two are ground together in some form of pulverizing mill.

The hydrating plant itself is usually located adjacent to the lime kilns. The lime is drawn from the kilns and is immediately crushed in some form of rotary or pot crusher. From this it is conveyed mechanically to the hydrator, in which the slaking is done. There are several forms of this latter in use but all come under two heads, continuous hydrators and batch hydrators. The continuous hydrators most used is the Kritzer hydrator, which consists of a number of cylinders mounted one above the other on a steel frame work. Through the middle of each cylinder runs a shaft to which are fastened paddles. The lime is fed in at the upper cylinder and mixed with the water. The paddles stir it up and also force it to travel through the cylinder. It then drops into the next cylinder and here it is mixed up and passed on by the paddles in this and so on until it has passed all of the cylinders. The proportions of lime and water are determined by means of an automatic feed for the lime and a valve for the water.

The Clyde hydrator is a batch hydrator in which the lime and water are weighed in separate charges consisting of about 1500 pounds of lime and the proper amount of water for this much lime. The pan rests upon a ball bearing and is revolved by means of a gear and pinion on the under side of the pan, which is surmounted by a hood and a stack. Plows running across the surface of the pan are fastened to a stationary framework above the latter. The lime and water are fed into the hydrator through an opening in the side, and the plows stir it up and mix the two. When hydration is completed, the lime is discharged through an opening in the center of the hydrator, which during the mixing is closed.

After passing through either hydrator, that portion of the lime which has been slaked is in the form of a very fine fluffy powder, all of which will pass through a very fine sieve. Mixed in with this, however, are always some unslaked lime, unburned limestone and silicious ores. For the better grades of hydrate it is usual to separate out this foreign material by means of screens, although where the amount of these constituents is small they are sometimes ground in with the hydrate. Fuller, Lehigh and Raymond Mills are principally used for the grinding, while the separators most used are the Newaygo and the Columbian.

The packing of the hydrate is best done in cloth (100 lbs.) or paper (40 lbs.) bags automatically by means of the Bates system which consists of a valve bag and machine for filling the same. The bags are provided with a valve and are tied before being filled. This valve is made by ripping, folding and sewing one corner of the bag. The cement is inserted through the valve by means of a tube on the bagging machine which automatically fills and weighs the bag. The machinery for hydrating magnesian lime having a capacity of 2 to 3 tons per hour costs about $5000 and for high calcium limes $12000. The cost of hydrating lime is about 25 to 30 cents per ton. One ton of lime, however, will often make more than one ton of hydrate.

The advantage of hydrated lime are: it is a fixed product and does not deteriorate with age; it can be handled without risk of fire; it may be shipped by water and packed in cloth or paper bags; it can be used for all purposes for which lime is used and is more convenient than the latter. In addition to this it can be used for mixing with cement for which purpose quicklime cannot be used.

## BLEACHING OF OIL WITH FULLER'S EARTH.

David Wesson.

The literature of fuller's earth and its application is very meager. It appears to be first mentioned about 1889. From the best information obtainable fuller's earth was first used for bleaching fats and oils in Chicago on a large scale about 1878, or 1880, although it is said to have been used for a long time previous in Northern Africa for clarification of olive oil.

The first application was very cumbrous, the earth being stirred into the hot oil and allowed to settle, after which the oil was decanted and the residue boiled with water and pressed.

The filter press was first used between 1880 and 1882. The efficiency of a given sample of fuller's earth cannot be readily determined by chemical analysis. The best method is by making a bleach test on a small scale. In comparing the bleaching properties of two earths they should always be passed through sieves of the same size in order to obtain an accurate comparison.

Fuller's earth doubtless owes some of its bleaching properties to the presence of a certain amount of water of constitution. This, if driven off by either drying of the earth or by adding it to oil of too high a temperature, will prevent bleaching.

The reason why fuller's earth seems to bleach is not positively known. Fuller's earths differ greatly in their absorptive properties and show great differences in their liability to spontaneous combustion.

The arranging of filter plants is a matter of considerable importance. The place for filters is on the top of a refinery under suitable shelter. By having them at an elevation above the bleach tanks, oil can be allowed to run back to the same, or can be fed to any part of the building, or run easily to storage by gravity; besides, the fire risk is much less, and when the filters are steamed out the nuisance of the steaming is entirely done away with.

The mixing kettles for oil and fuller's earth are practically cylinders provided with mechanical agitation and suitable heating coils.

Filter pumps should be slow-moving, capable of working up to a pressure of 150 to 200 lbs. The operation of filter plant is quite simple. The earth is mixed with the oil at the proper temperature and then pumped through the filter press, the first portions of the oil being allowed to run back to the mixing kettle, or bleacher, as it is often called, until it comes up to the required standard, after which it runs directly to storage.

## UNSOLVED PROBLEMS OF SEWAGE DISPOSAL.

C. E.-A. Winslow, Associate Professor of Biology at the College of the City of New York, and Curator of Public Health at the American Museum of Natural History.

The three main ends of sewage treatment, the elimination of suspended solids, the oxidation of organic matter and the destruction of pathogenic bacteria can all be attained by practically efficient methods but there are minor difficulties to be overcome in each case. The pathogenic bacteria can be destroyed when necessary by disinfection with bleaching powder but the dosing devices available for use in small plants are very defective. The oxidation of organic matter can be economically effected by the use of sand, contact or trickling beds. Distribution systems for trickling filters require further study. The intermittent sand filter has possibilities of intensive action not attained in plants operated at present largely at haphazard. It is the accumulation of suspended solids on the surface which keeps the capacity of sand beds down to 100,000 gallons per acre per day and experiments carried out at the Sewage Experiment Station of the Massachusetts Institute of Technology show that the rate can be raised to 200,000 or 300,000 gallons if suspended solids are removed by careful preliminary treatment. Sludge disposal is still the most serious of the unsolved problems of sewage treatment. It has been minimized at the Technology Experiment Station by the use of a deep tank on the septic principle, but so operated that the sewage rises and washes the sludge continually, and thus keeps it from becoming overseptic. By this means the liquefying process is so accelerated that over 70 per cent. of the deposited total suspended solids have been liquefied. The utilization of sewage sludge though not yet economically realized furnishes promising possibilities to the industrial chemist in the future.

## SEWERAGE AND SEWAGE DISPOSAL IN NEW YORK AND VICINITY.

George A. Soper, Ph.D., M. Am. Soc. C. E. and President Metropolitan Sewerage Commission of New York.

For the most part, the sewage of New York is conveyed in crude condition by the shortest route to tide water and discharged at or near the surface of the water. There are over 500 sewer outlets discharging 600,000,000 gallons of sewage per day. In all parts of the harbor above the Narrows, the water is seriously polluted and rendered objectionable both to sight and smell. Along 175 miles of shore the water is so polluted as to be dangerous to bathe in. These conditions will rapidly become worse as the population increases.

A standard of purity for the water of New York harbor has been proposed by Col. Black and Prof. Phelps as a result of studies, estimate and apportionment. They consider that the dissolved oxygen in the water should not fall below 70 per cent. of what would be present if the water did not receive any sewage. This limit has already been exceeded.

A definite plan and program of main drainage, including outfall works and purification plants designed to improve the present unsanitary conditions, has been proposed by the Metropolitan Sewage Commission. The study of carrying out this plan so far as New York is concerned has been entrusted to this commission. This work is now progressing satisfactorily.

## SANITARY CONDITIONS IN THEIR RELATION TO THE WATER SUPPLY IN THE VICINITY OF NEW YORK.

Nicholas S. Hill, Jr.

This paper calls attention to the very unsatisfactory condition of the water supply in the suburbs of New York and emphasizes the fact that health conditions in New York City are very materially affected by sanitary conditions in the suburbs. The suburban territory adjacent to New York which is considered includes Northern New Jersey and Westchester County. It is shown that the very great growth of population in New Jersey tends to pollute the natural water supplies and on the other hand creates an increasing demand for a supply of pure water. In order to provide for this future demand, means should be taken at once to prevent further contamination of the New Jersey streams and to abate the nuisances already existing along these water courses.

Similar conditions prevail in Westchester County. The location of a large number of institutions in this county, such as sanitariums, hospitals, orphan asylums, etc., further tend to pollute the water-sheds. In many of the smaller towns there are no sewage disposal systems of any kind whatever. The remedies to be applied are proper sewage disposal and filtration of water supply.

It is impossible for a number of scattered communities to undertake the abatement of nuisances, the proper disposal and filtration of the water supply.

The necessary state supervision to procure efficient sanitary protection, under existing laws and with the funds at present at the disposal of the State Department of Health, is difficult to obtain. Pennsylvania appropriates Two Hundred Thousand ($200,000) Dollars per year and New York, Eighty-five Thousand ($85,000) Dollars.

Storage reservoirs of suitable size cannot be built because in a thickly populated section, like the one under consideration, the presence of villages and towns in valleys suitable for storage purposes makes the cost of condemnation excessive. Railways and highways also traverse reservoir sites in many cases. Such costs can be incurred only by large cities like New York. In other cases, a pure supply of water can only be obtained from Connecticut which will result in interstate complications if such sources must be largely drawn upon.

It would seem as if it would be necessary to organize a Metropolitan Water Board under whose direction a considerable supply of pure water and the enforcement of sanitary relations could be provided for these scattered communities. Otherwise New York City must be depended upon to arrange to furnish water in the necessary quantities to towns and villages immediately north of it, especially as the Metropolis has preempted the most available streams, namely the Croton, Byran and the Bronx.

## WESTERN SOCIETY OF TECHNICAL CHEMISTS AND METALLURGISTS.

After a career of six years the Western Association of Technical Chemists and Metallurgists has disbanded, and its journal, *The Western Chemist and Metallurgist*, published its last issue in December, 1910. Started as a little society in Denver, local sections were added in other parts of Colorada, in Utah, Montana, South Dakota and Mexico, and a volume of some four hundred pages was printed annually. With the lapse of time there came the disintegration due to a lack of interest on the part of the members—a lack of interest due partly to the nomadic habits of men connected with the mining and smelting industries, which renders anything like a permanent local membership next to impossible, and partly to the fact that the burden contributing to the journal fell on only a few of the members, and they could not with reason be expected to supply enough material to keep a technical journal up to the highest standard. The following extracts from a letter by President W. D. Engle are self-explanatory.

"To the Members of the Western Association of Technical Chemists and Metallurgists:

"For the past two years the Board of Control of your Association has endeavored to work out some plan whereby the original plan of the organization might be carried out more successfully. The original plan contemplated a strong organization of western and metallurgical chemists publishing a journal which would afford a means of exchanging ideas and make possible a comparison of methods and plans of work which would be of advantage to all. To some degree this has been realized, but not to that degree that will justify us in continuing.

"In Denver there has been, from the first, a strong section. However, outside of Denver it has been difficult, if not impossible, to arouse and maintain the desired enthusiasm, .........

"The disbandment of the Association is a source of much regret to many of us....The members of the Board are a unit in the desire to keep up the organization, but they are equally a unit in deciding that we must disband unless we can maintain the present degree of efficiency and have good prospects of making a stronger society and a larger and better journal.

"We have gained much in the way of recognition by other societies and scientific authorities ... and our journal is frequently quoted. It seems a waste that what has been gained must be abandoned, but we must not start a new year without good prospects of being able to complete it. It therefore becomes my disagreeable duty to announce to you that this will be the last issue of the journal, and that the end of the present year will close up the career of the Western Association of Technical Chemists and Metallurgists."

## BOOK REVIEWS AND NOTICES.

**Die Aetherischen Oele.** By E. GILDMEISTER AND FR. HOFFMANN. 2nd edition by E. GILDMEISTER. Vol. 1. 8vo. pp. viii + 697. Laboratory tables in pocket. 1910. Miltitz bei Leipzig: Schimmel and Co.

Gildmeister and Hoffman's work on the essential oils has long been one of the few books on this important subject. It has been well known and favorably received. The present second edition in two volumes by Gildmeister in conjunction with the firm of Schimmel will be welcomed. The general arrangement of the present edition is similar to that of the first. Since the publication of the latter, Semmler's great work in four volumes on the constituents of the essential oils has been completed. This work and the many researches of Wallach, Tiemann and others during the intervening years afford a foundation for a great extension of the part devoted to the components of the ethereal oils, and this part of the book covers 286 pages. The book is divided into four parts: 1. Historical, 258 pages; 2. Winning of Perfumes, 26 pages; 3. Components, 286 pages; 4. Testing, 100 pages. The historical chapters are very commendable, covering the spice trade in ancient times and during the middle ages, the general history of essential oils, history of special oils, and history of distillation. The methods of chemical and physical testing are adequate and excellent. The text and illustrations are well printed and the whole is well indexed.

Schimmel and Co's. Semi-Annual Report for October, 1910, contains some 204 pages $5^1/_4 \times 7^3/_4$ in. It contains the customary commercial and scientific review of the principal essential oils, descriptions of new essential oils and about 50 pages devoted to recent research work concerning terpenes and terpene derivatives.

**"Cement Age" and "Concrete Engineering" Consolidated.**—Cement manufacturers, engineers and chemists will be interested in the announcement that *Cement Age*, of New York, and *Concrete Engineering*, of Cleveland, two of the leading monthly publications in the cement field, have been consolidated. *Cement Age*, which was established in 1904, has been issued under the editorship of Mr. Robert W. Lesley, Vice-President of the American Society for Testing Materials, and an associate of the American Society of Civil Engineers, who is also one of the most prominent figures in the cement industry in this country. *Cement Age* has covered the popular features of cement construction, as well as the engineering and manufacturing side of the industry, and *Concrete Engineering* has been especially devoted to that branch of the industry indicated by its title. Beginning with the January, 1911, issue, the two magazines will be consolidated under the title "*Cement Age* with which is combined *Concrete Engineering*." The magazine will be slightly larger than the present size of *Cement Age*, and will have a type page 6 × 9 inches, thus retaining the distinctive magazine form which has been a popular feature of the older publication. The increased space will be more acceptable to both readers and advertisers. A two-column make-up will be a further innovation.

It is the purpose to preserve the best features of both the magazines, thus maintaining the prestige each has won. The use of cement from the architectural and engineering standpoints, as well as its manufacture, will be thoroughly covered, together with the popular features that are of such great interest to the general public.

Allen Brett, editor of *Concrete Engineering* for the past two years, will take the position as associate editor of the new publication, and Arthur E. Warner, formerly business manager of *Concrete Engineering*, will become the western manager. There will be no change in the present staff of *Cement Age*, Mr. Lesley continuing as editor, Frederic F. Lincoln as president of the Cement Age Company, in charge of the New York office at 30 Church Street and of the eastern advertising field, and Edward A. Trego as associate editor.

The *Mining World Index* conducted by the *Mining World* will mark an important inauguration in mining periodical literature. It aims at no less a project than to systematically index each week all the current periodicals and other literature relevant to any branch of the mining, mining engineering, metallurgical, and mineral and rock products industries. The value of this bibliographic work to technologists is self-evident.

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## RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., Washington, D. C.

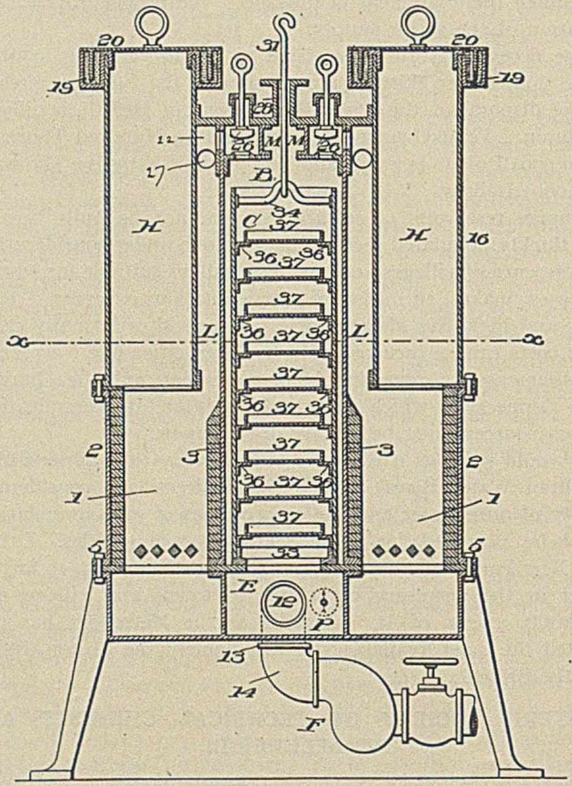
Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

**977,992. Process for the Recovery of the Paraffin Ingredients from Cannel-Coals.** HENRY WURTZ, Newark, N. J.

To obtain all hydrocarbon ingredients of cannel-coal, and other similarly constituted materials, and to recover them in a chemically unchanged condition, pantentee subjects such bituminous raw material, in an atmosphere of neutral gases, to a temperature only sufficient to render these hydrocarbons fluid, and then to suction by a strong, mechanically produced current of these neutral gases, whereby the hydrocarbons, having been rendered sufficiently fluid by the heating, are separated and removed from the solid constituents of the material treated. The suction, created by the current, materially reduces the pressure in the chamber, where the bituminous raw material is thus treated, thus creating a condition favorable to expansion and assists also materially in extracting the hydrocarbons of higher degree of consistency from among the fibers and pores of its carbon structure.

The neutral gases, enveloping the hydrocarbons thus extracted, constantly, during this transitory period, while they are in this heated and fluid state, prevent their oxidation, and neutralize their tendency to split and form other chemical compounds. Finally, the hydrocarbons are separated from the protecting neutral gases by condensation. This is effected by cooling the current of neutral gases, conveying the hydrocarbons in their fluid state, though a large proportion of the specifically heavier hydrocarbons is quite rapidly precipitated from the gaseous vehicle as soon as the velocity of the current is diminished. The chemical composition of hydrocarbon constituents of cannel-coal and of similar bituminous materials thus recovered is not changed, or in any respect materially modified. They are recovered in their crude state, and to render them available for further industrial uses, they must be separated from each other and refined. The processes for separating and for refining them are no part of the invention set forth and claimed herein, and therefore are not described.



An apparatus suitable for carrying on this education process is shown illustrating a vertical transverse section thereof, and consists, essentially, of an education chamber, B, designed to be hermetically closed after the charge of the cannel-coal or of a similar bituminous material was placed therein; an exhauster, F, connected by a conduit, 14, with the bottom part, E, of the education chamber; chambers 1 for producing or heating the neutral (deoxidized) gases; flues L for conveying these neutral gases into the education chamber; and devices (valves 26) for governing their admission.

### 977,996. Method of Smelting and Refining Copper Ores and Compounds. RALPH BAGGLEY, Pittsburg, Pa.

This is a method of extracting copper, gold, silver and other metals from ores, which consists in dissolving or melting ores that contain within themselves oxidizable elements, by submergence in a molten bath of matte and by the heat of oxidation produced by forcing air through the same, and eliminating the silica, alumina and lime, then separating the slag from the low-grade matte, then transferring the matte into a converter, oxidizing it therein, adding value-bearing silicious ore, and forming thereby silicate of iron slags, and then eliminating residual oxidizable impurities by forcing air into the bath.

Fig. 1.

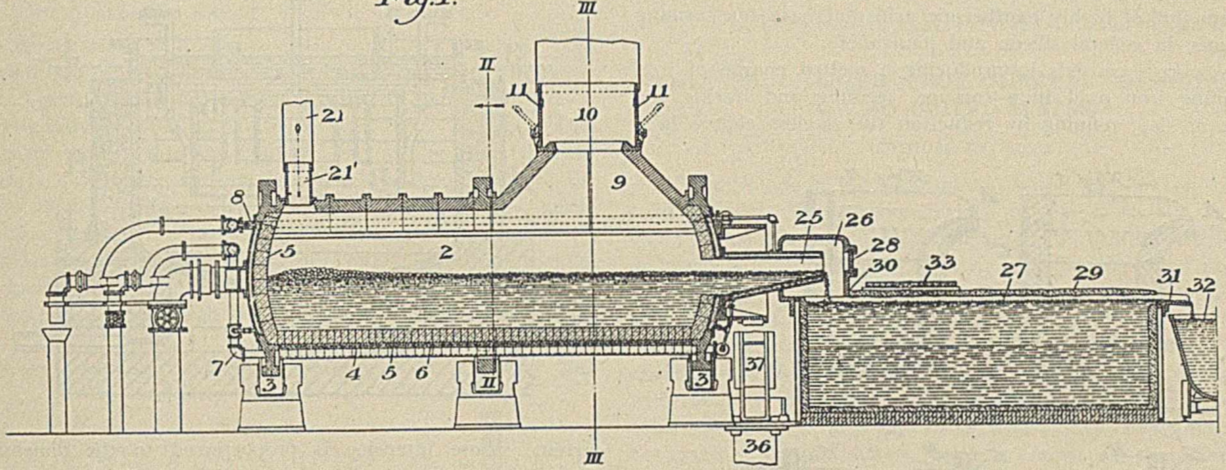
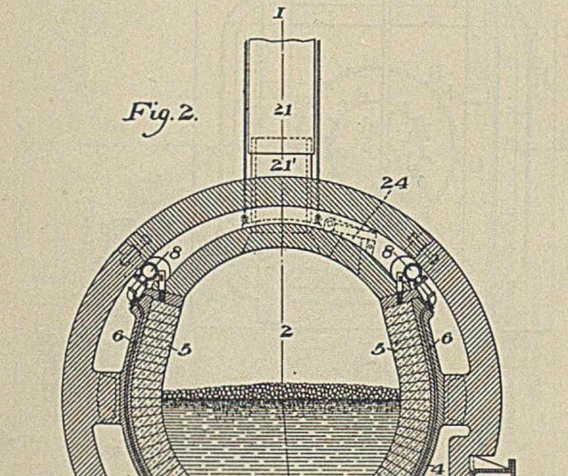


Fig. 2.

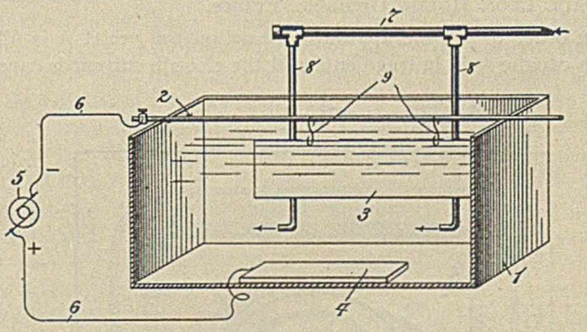


The accompanying illustration shows apparatus in which the patentees method can be carried out.

### 978,211. Art of Extracting Metals Electrolytically. JAMES HART ROBERTSON, New York, N. Y.

This invention is directed to a novel method of extracting gold and other precious metals from their ores after they have been reduced in a very minute or finely powdered state, and it has for its objects, first, to provide a method of effecting this result in as simple, efficient and inexpensive a manner as possible; second, to devise a method of extracting gold when found in other than a metallic state (chlorids, for instance) by the agency of electrolysis and in such manner that the gold is deposited on the cathode of the apparatus used in practicing said method.

The electrolyte which is illustrated as submerging the anode and cathode when used in the process of extracting gold may be cyanid of potassium or of any other such equivalent materials as are used in the art of electrolytic methods of extracting valuable metals and the anode and cathode may be located in the body of the electrolyte in any preferred manner, or may be of any preferred material and construction or shape, such matters coming well within the skill of those versed in the electrolytic art generally, the essential feature being that they shall be so located as to readily remove the cathode for the purpose of extracting the gold therefrom by fusion in the usual way.



The cathode is illustrated in the drawing as being suspended from the conducting rod 2 by good conducting metallic hooks, 9, 9.

The ore to be treated is first pulverized or ground to a fine powder and gradually fed into the electrolyte which is kept in an agitated condition or circulation by steam, hot air or gas issuing from the sources of supply, not shown, through the pipes 7 and 8. A relatively large amount of the powdered ore will remain in suspension while the liquid is in motion when it is placed in the vat and is simultaneously subjected to the action of electricity, motion and heat until the major part of the metal is deposited on the cathode 3.

**979,337. Manufacture of Steel.** ALLEYNE REYNOLDS, London, England.

This invention has for its object the economical production of steel ingots or castings of any desired analysis free from flaws. The patentee first produces a nearly pure iron free from foreign substances, and afterward, just previous to casting, alloy it with certain materials. For the overcoming of the oxidation unavoidable during casting, the extent of which may be ascertained by experience, there is always added the necessary amount of highly exothermic acid and basic-flue-forming additions, in general silicon and manganese.

The process consists in producing a melted charge of iron containing iron oxid in a furnace, teeming and freeing the charge of slag, refining by reduction the slagless charge in a second furnace teeming the refined charge and adding thereto melted alloys and a suitable flux heated in separate furnaces, and casting the charge into a mold.

Fig. 1.

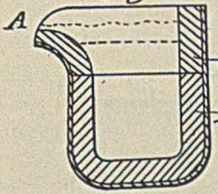


Fig. 2.

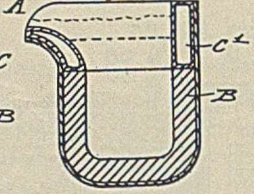


Fig. 3.

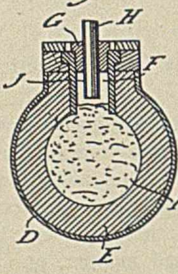
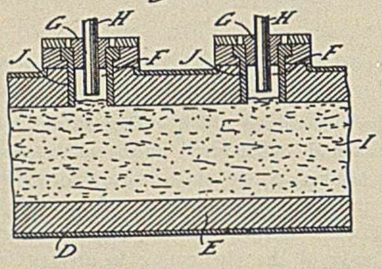


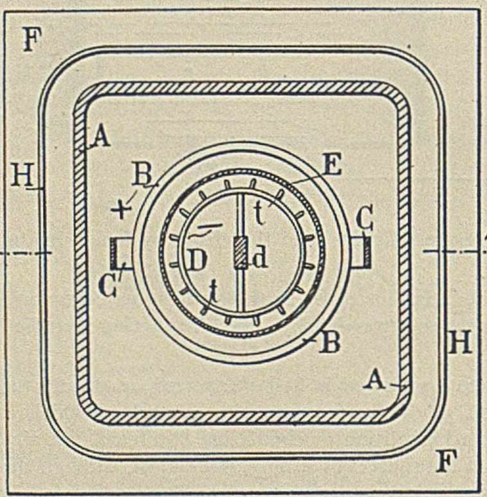
Fig. 4.



**979,497. Means for the Electrolytic Manufacture of Sodium.** PAUL LEON HULIN, Grenoble, France.

In order to set the apparatus in action the vessel A is filled with caustic soda in fragments and the electric current is caused to traverse the conductor G; the intensity of the current is regulated so as to bring the conductor to red-heat. The heat disengaged is absorbed by the metal of the vat, and the soda which it contains becomes fused. As soon as the vessel is full of liquefied soda the current is stopped flowing in the heating circuit G and the apparatus is ready for work.

Fig. 1



The production of sodium is initiated by passing a continuous current, whose intensity is proportioned to the dimensions of the apparatus and under a pressure of about 5 or 6 volts, the resistance which the current experiences in traversing the bath causing the development of sufficient heat to maintain the soda in the fused state. Under the electrolytic action of the current free oxygen is formed at the anode and is disengaged at the surface externally of the separator E, while the hydrogen

Fig. 2.

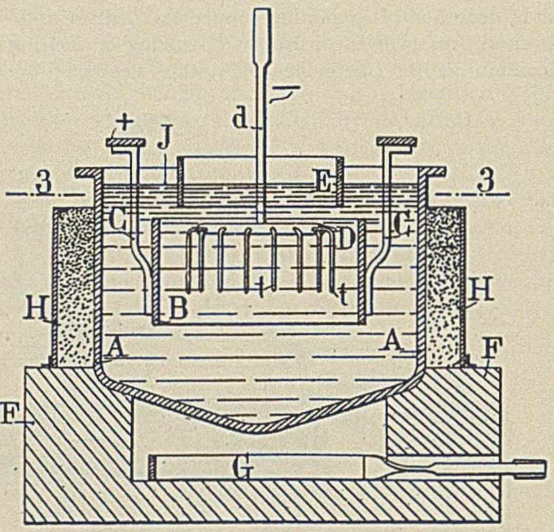


Fig. 3.

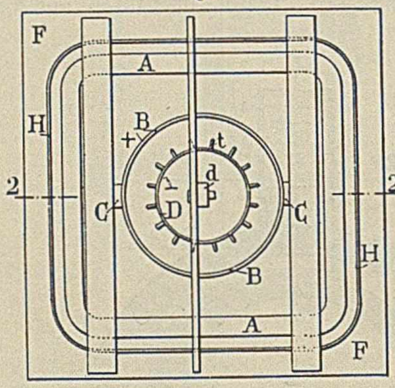


Fig. 6.

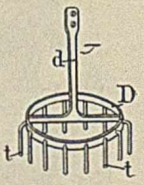


Fig. 4.

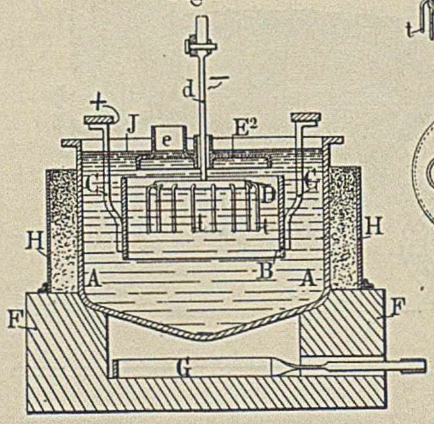
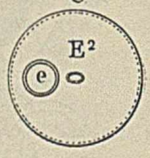


Fig. 7.



and sodium simultaneously escape from the cathode in globules and both appear at the surface of the bath in the interior of the ring E. The sodium collects in drops resembling melted white wax, and it is removed by means of a perforated ladle which only permits the passage of the fused soda.

The apparatus is charged periodically with soda to replace that which has been decomposed. The mean level of the bath is indicated at J.

The accompanying illustration shows the patentees apparatus.

979,663. **Electric Furnace.** BAYARD GUTHRIE, Pittsburgh, Pa., AND JOSEPH P. KARCH, Plainvill, Connecticut.

In the operation of this furnace the crucible 1 is charged, the car placed on top and the electrodes 2, 3, 4 and 5 are all moved up into contact with the crucible. Current is then turned on and the crucible and its contents are in the circuits. This warms up the crucible and contents but as the electrodes are purposely made large and as the crucible and contents are relatively good conductors the heat is not great. The handle 40 is then applied to the end of one of the screws, 38, and the electrodes are slowly withdrawn from contact with the crucible. Arcs immediately form between the pair of electrodes 2 and 3 and the pair 4 and 5 with the crucible in the center of intense heat.

The great heat soon melts the contents of the crucible. The electrodes are then closed into contact with the crucible, the arcs gradually decrease and the current is turned off. The mold 27 being hung on the hooks 26, 26, the hand wheel 15 is rotated so as to tilt the furnace and pour the contents of the crucible into the mold. The electrodes hold the crucible while pouring. When one mold is filled it can be quickly removed and another substituted and pouring continued until the crucible is empty. The furnace is then returned to its horizontal position and the operation repeated.

Fig. 1.

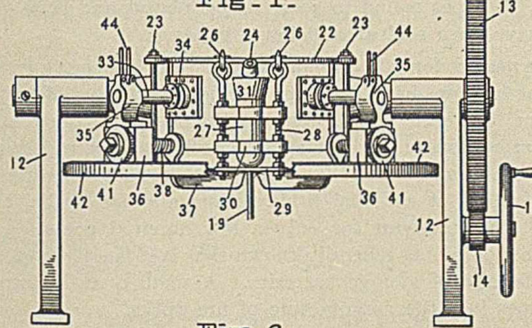
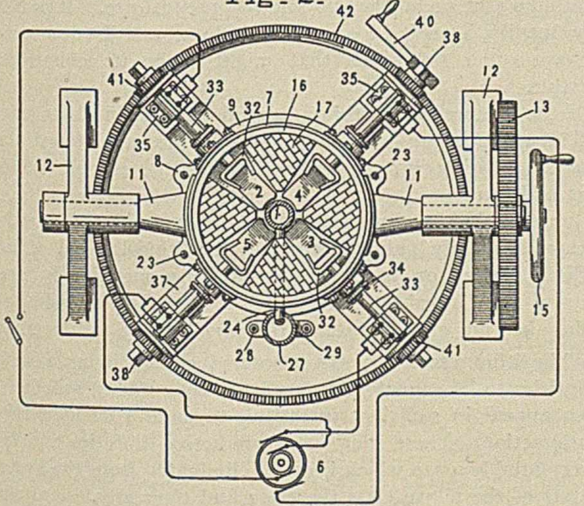


Fig. 2.



When it is particularly desired to avoid oxidation of the contents of the crucible a neutral or inert gas may be supplied through the pipe 19 and which will pass through the perforated stand 18, up around the crucible 1, and out through the opening in the top of the casing surrounding the crucible mouth. This will prevent the air from reaching the contents of the crucible. Similarly a combustible gas may be supplied and burned as it escapes from the opening in the top of the casing. This will have a tendency to withdraw oxygen from the contents of the crucible and thus act as a reduction agent.

## INDUSTRIAL AND TRADE NOTES.

### ADVANCE CHAPTER FROM MINERAL RESOURCES OF THE UNITED STATES.

### LITHIUM IN 1909.

Lithium is one of the alkali metals and is the lightest known solid element. Its specific gravity (0.585) is so low that it will float on kerosene. Although traces of lithium are found in nearly all igneous rocks[1] and in many springs, and notable quantities of several lithium minerals occur in the United States at widely separated points, such minerals are not at all common.

In all places where lithium minerals visibly occur they are associated with granitic rocks and generally, if not always, with the latest phases of granitic intrusions, either in pegmatites or in granites and adjacent rocks which have been altered by hot gaseous emanations—a process known as pneumatolysis or pneumatolytic action. In some places large masses of lithium minerals which can be worked commercially are found in pegmatites, but in the altered granites only minor quantities of lithia mica are found. The places of occurrence of lithium are practically those of tin, but the large deposits of tin seldom contain workable deposits of lithium minerals. In the pegmatites, which may carry large quantities of lithium minerals, the tin deposits are generally small.

*Lepidolite.*—Lepidolite ranges in color through glistening white, yellowish, violet and lilac tints. It occurs generally in small indistinct plates but in places forms six-sided crystals belonging to the monoclinic system. At Pala, Cal., and at other places it forms an outer rim around muscovite plates several inches across.

In the United States lepidolite is found in Hebron, Auburn, Norway, Paris, Rumford, and other places in western Main; in South Dakota in considerable quantities in connection with the tin deposits of the southern Black Hills; and in great quantity with the beautiful red tourmaline, rubellite, in the neighborhood of Pala, San Diego County, Cal. At the Stewart mine, 2 miles north of Pala,[2] a mass of delicately tinted lilac-colored lepidolite showed a lenticular surface exposure 90 feet broad and 25 feet thick. In 1907 a drift at right angles to the exposure had been driven 125 feet in the lepidolite. Several hundred tons were mined and shipped from this deposit. Rubellite, also containing lithia, forms beautiful radial aggregates enclosed in the mass of lepidolite. Many thousand specimens obtained from this locality are distributed through the mineral collections of the world. After the spodumene and amblygonite deposits in the Black Hills of South Dakota were opened up it no longer paid to operate the Pala deposits. In the Black Hills lepidolite also was at one time worked to a small extent for its lithia content. At many other localities lepidolite is found in occasional flakes or small masses. At Wakefield, Canada, lepidolite occurs in plates several inches across.

Other lithium micas are cookeite, zinnwaldite, cryophyllite, polylithionite, and protolithionite. Zinnwaldite containing

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[1] Clarke, F. W., "The Data of Geochemistry," *Bull. U. S. Geol. Survey*, **330**, 17 (1908).

[2] Personal communication from W. T. Schaller, U. S. Geol. Survey.

3.36 per cent. lithia was formerly worked at Zinnwald, Germany, for its lithium content.[1]

Triphylite occurs in small amounts at Peru, Me.;[2] Norwich, Mass.;[2] Grafton, N. H.;[2] and lithiophilite at Branchfield, Conn.,[2] and Tubb's farm, Me.[2] Minerals which probably belong to this group, but which are bodly weathered or of which no analyses are known, occur in the tin-bearing pegmatite dikes of Kings Mountain, N. C., near Pala,[3] and in the Black Hills. In the Black Hills such a mineral occurs in many pegmatite dikes, probably in all which carry either lepidolite, spodumene, or amblygonite. The masses are very irregular in size and shape and are of a brownish or blackish color, in the latter case probably owing to the oxidation of some of the manganese. In places, both in South Dakota and in North Carolina, surfaces are coated with a fine purple film of purpurite, a decomposition product. In the Etta mine, South Dakota, masses of the mineral 3 to 4 inches in diameter have decomposed, leaving cavities partly filled with lilac, blue, and dark green vivianite, probably accompanied by another iron phosphate, dufrenite. In both the Etta and the Peerless mines a lithiophilite-like mineral occurs in sufficient abundance to yield a few tons annually in the course of mining for other minerals. As stated it contains from 8.15 to 9.36 per cent. of lithia, and if it occurred in large quantity would be equal to amblygonite as a lithia ore.

Probably both triphylite and lithiophilite occur in the Black Hills.

Alluaudite is a mineral closely related to lithiophilite, but of no commercial value.

*Spodumene.*—Spodumene occurs in the same general localities mentioned for lepidolite, but is found in greatest quantity in the Black Hills. In the Etta mine, $1^1/_2$ miles south of Keystone, the crystals of spodumene are immense, and so far as known are approached in size by no crystals found outside of the Black Hills. One crystal was 42 feet in length, with a cross section of approximately 3 by 6 feet. Part was decayed and useless, but about 37 tons of spodumene were mined from it.[4] At many places mining has exposed cross-sections which are rectangles with truncated corners. Spodumene occurs—as do each of the other minerals mentioned—in pegmatite dikes. The dike at the Etta mine is oval in shape and about 150 by 200 feet in horizontal measurement. Tin was first discovered in the Black Hills in this mine, and previous to that the mine had been worked for mica. The crystals are considerably decayed, have an earthy appearance and the odor of a fresh clay pipe. Owing to the decay, the crystals have a fibrous, woody structure, and from this and their size the workmen ordinarily refer to them as "logs," which they much resemble. Cassiterite has been deposited along cracks in the spodumene and is evidently of later crystallization. It is an odd fact that amblygonite is almost wholly absent from this deposit, though in the Peerless claim half a mile away it occurs in large masses, with some spodumene.

Spodumene of an emerald-green color, when fresh enough to be glassy and clear, is known as hiddenite and sells for very high prices as a gem. As with most gems, the price is largely artificial. It is found at Hiddenite, N. C. A beautiful pink or lilac variety found near Pala and Rincon, San Diego County, Cal., is known as kunzite, and also sells at high prices. Some jewelers say that the stones lose their color, probably from strong light, and one jeweler showed the writer a stone which he said had faded in a comparatively short time. Kunzite when of a good clear color is one of the most beautiful of gem stones. In hiddenite and kunzite the refraction of light is high, so that the stones have considerable brilliancy. Both varieties are reported from Madagascar.[1]

Beta-spodumene, cymatolite, and killinite are alteration minerals formed from spodumene, which have only mineralogical importance.

Petalite, castorite, and hydrocastorite are lithium minerals related to spodumene, but are without commercial value as a source of lithia.

*Amblygonite.*—Amblygonite is found in the same general localities that have been noted for lepidolite and spodumene. It contains a larger percentage of lithia than any mineral except lithiophilite, and, as it occurs in masses large enough to be easily and cheaply worked, it is more valuable, other conditions being equal, as a source of lithia than either of the other minerals. As found in South Dakota and California, it is a pearly white mineral with one good cleavage, and looks like a very fresh feldspar. In other places it has pale greenish, bluish, yellowish, or brownish tints. In 1907 and 1908 Mr. Herman Reinbold, of the Western Chemical Reduction Company, Omaha, Nebr., mined a large deposit of amblygonite of excellent quality on the Peerless claim, half a mile northeast of the Etta claim and 1 mile from Keystone, S. Dak. The shoot or mass of amblygonite was about 20 feet wide and had been excavated more than 20 feet in depth and 20 feet in length. This mass is said to have produced a total of 900 tons.

After the mining of amblygonite began on the Peerless claim at Keystone, S. Dak., the price of lithium carbonate fell from $2 or $2.50 per pound to 50 cents per pound, and large quantities have been sold at still lower prices.

The market for lithium minerals and salts has been a restricted one, as few uses have been known and the number of large consumers has been small. The product most manufactured is lithium carbonate, and for some time it was not widely known what use was made of the bulk of the product. Its use in the manufacture of artificial lithia waters and for medicinal purposes would account for only a few hundred pounds a year. It is now becoming generally known that it is mainly used in the manufacture of storage batteries. A small quantity probably also goes into the manufacture of fire-works.

Lithium (the metal) has no known practical use. It oxidizes very readily, is soft, not very tenacious, and is not known to have other properties that might make it economically valuable.

Of the lithium salts, lithium bromide is used in photography and in medicine, and various other salts are used for lithiasis (gravel), arthritis (inflammation of the joints), chronic rheumatism, and gout.

By many the use of natural lithium-bearing waters for various diseases is highly valued, especially in lithiasis, and a large trade is carried on in water from "lithia springs" in many parts of the United States. Concerning the medicinal use of lithium-bearing spring waters, Haywood and Smith[2] remark:

> While lithium seldom or never occurs in waters in large enough quantities to be a predominating basic constituent, still it does often appear in sufficient quantities to have a decided therapeutic action. These compounds are active diuretics and form a very soluble urate which is easily eliminated from the system. Waters of the above class therefore find their greatest application in the treatment of rheumatism, rheumatic tendencies, and gout. In cases of gravel and calculi they are also valuable disintegrating agents.

The same authors found that among the various lithia waters, that from the Carlsbad Spring of Saratoga carried the largest proportion of lithium, namely, 31.8 parts of lithium chloride

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[1] Singewald, Jos. T., Jr., "The Erzgebirge Tin Deposits," *Econ. Geol.*, **5**, 173 (1910).

[2] Dana, *op. cit.*

[3] Personal communication from W. T. Schaller.

[4] Personal communication from A. M. Lane, Keystone, S. Dak.

[1] Sterrett, Douglas B., "Mineral Resources of U. S. for 1907," *U. S. Geol. Survey*, **2**, 826 (1908).

[2] Haywood, J. K., and Smith, B. H., "Mineral Waters of the United States," U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **91**, 12 (1905).

per million. Some of the so-called lithia waters contain only extremely small quantities of lithia.

In 1909 several carloads of amblygonite were shipped by the Western Reduction Company, of Omaha, Nebr., from its property near Keystone, S. Dak., and a few carloads of spodumene were shipped from the Etta claim by the Standard Essence Company to its works at Maywood, N. J. In view of the limited number of producers exact figures of production are not published.

## TUNGSTEN IN 1909.

With the recovery of the steel trade during 1909 prices for tungsten rose above those of 1908, and mining quickly responded. The mines in Colorado (Boulder County) and in California turned out quantities of ore comparable with those of 1907, and properties were developed at Deer Trail, Stevens County, Wash., and at Osceola, Nev., which promised a considerable effect in the near future upon the tungsten trade of the United States. Interest in and knowledge of tungsten minerals have become so wide-spread that prospectors generally are on the lookout for them, and new occurrences are reported from time to time.

Owing to errors in several returns of tungsten ore produced during the year 1909, the preliminary figures published in January, 1910, were too high. The figures as corrected by later returns indicate a production of 1,619 tons of 60 per cent. ore, valued at $614,370. The production of tungsten ores in the United States from 1900 to 1909, inclusive, has been as follows:

Production of Concentrated Tungsten Ores in the United States, 1900–1909, in Short Tons.[1]

| Years. | Quantity. | Value. |
|---|---|---|
| 1900 | 46 | $11,040 |
| 1901 | 179 | 27,720 |
| 1902 | 184 | 34,040 |
| 1903 | 292 | 43,639 |
| 1904 | 740 | 184,000 |
| 1905 | 803 | 268,676 |
| 1906 | 928 | 348,867 |
| 1907 | 1,640 | 890,048 |
| 1908 | 671 | 229,955 |
| 1909 | 1,619 | 614,370 |

The price of tungsten ores ranged from $5 to $9 per unit, depending upon quantity, quality, and the immediate need of the buyer. The average price was between $6 and $6.50 per unit.

Although the figures from all the countries producing large quantities of tungsten ores are not yet available, enough are at hand to show that the world's production for 1909 was larger than that for 1908, and was possibly equal to that of 1907. In very few of the returns, however, is the percentage of tungsten trioxide indicated and this is a prime necessity in comparing figures. It is probable that most of the exported ore is richer than 60 per cent. in tungsten trioxide, and that the figures are therefore low.

The World's Production of Tungsten Ore, 1905–1909, by Countries, Estimated as Far as Possible in Short Tons of Concentrates Containing 60 Per cent. of Tungsten Trioxide.

| Country. | 1905. | 1906. | 1907. | 1908. | 1909. |
|---|---|---|---|---|---|
| Africa: South Africa | ..... | 9 | 211 | 40 | 16[2] |
| Asia: | | | | | |
| Federated Malay States | ..... | 151 | 89 | 83[2] | 99[3] |
| Siam | ..... | ..... | 10 | ..... | ... |
| India | ..... | ..... | ..... | ..... | 7[1] |
| Australia: | | | | | |
| New South Wales | 251 | 270 | 451 | 269 | 431[2] |
| Sauth Australia and Nothern Territory | 71 | 230 | 177 | 40 | 49[3] |
| Queensland | 1,582 | 865 | 703 | 516 | 679[4] |
| Tasmania | 36 | 22 | 46 | 5 | 20[5] |
| Victoria | ..... | ..... | ..... | 3 | 15[6] |
| Western Australia | ..... | ..... | 1 | ..... | 6[7] |
| East Indies: | | | | | |
| Billiton | ..... | ..... | 4 | 11 | ... |
| Singkep | ..... | ..... | 1 | 14 | 23[8] |
| Europe: | | | | | |
| Austria | 65 | 63 | 50 | 44 | 43[9] |
| England | 193 | 304 | 361 | 261 | 421[10] |
| France | 28 | 20 | 67 | 124 | ... |
| German Empire | 42 | 57 | 68 | 46 | 106[11] |
| Italy | 36 | 28 | 18 | ..... | ... |
| Portugal | 320 | 629 | 702 | 684 | 609[12] |
| Spain | 413 | 222 | 303 | 249 | ... |
| Oceania: New Zealand | 64 | 121 | 153 | 87 | 78[13] |
| North America: United States. | 803 | 928 | 1,640 | 671 | 1,619 |
| South America: | | | | | |
| Argentina | ..... | 326 | 507 | 548 | 900[14] |
| Bolivia | 75 | 75 | 500 | 187 | 168[15] |
| Brazil | ..... | ..... | ..... | 16 | ..... |
| Total | 3,979 | 4,320 | 6,062 | 3,898 | 5,289 |

## NICKEL AND COBALT IN 1909.

The only metallic nickel and the only cobalt known to have been produced in the United States from ores mined in this country during 1909 came from Fredericktown, Mo., where the North American Lead Company operated a smelter for the extraction of nickel, cobalt and copper from sulphides accompanying galena. Both nickel and cobalt were produced in this country from Ontario ores during the year.

In refining copper by the electrolytic process, the electrolyte generally soon shows nickel sulphate in solution, and must be watched in order that more than 1 per cent. of the sulphate be not allowed to accumulate, as more than 1 per cent. is said to affect injuriously the deposition of the copper on the cathodes. Nickel is carried in minute quantities by crude copper from many places, but which ores produce it can not ordinarily be told, as the refineries which report a nickel saving refine pig copper from many localities and from several countries. In 1909 the United States Metals Refining Company at its Chrome, N. J., plant, the Nichols Copper Company at its Laurel Hill, Long Island refinery, and the Orford Copper Company at its refineries at Constable Hook, N. Y., and Bayonne, N. J., made large quantities of nickel sulphate and nickel ammonium sulphate. The total quantity of the two salts produced during 1909 was 3,101,505 pounds valued at approximately $62,000. It is

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[1] The production of tungsten ores in this country from year to year can be fairly compared in this table only since and beginning with 1906, as before that date no effort had been made to reduce the ores to a common basis of concentration. Since 1906 the ores have been, as far as possible, reduced to an equivalent of ore carrying 60 per cent. tungsten trioxide ($WO_3$), which is the ordinary commercial basis in the United States.

[2] Fourth annual statement of the trade and shipping of the colonies and territories forming the South African Customs Union, 1909, Cape Town, 1910, Table 44. The percentage of tungsten trioxide in the ores is unknown.

[3] *Min. Jour.*, London, **91,** October 8, 1910, p. 1174. Exports for 1908 and 1909.

[1] *Min. Jour.*, London, **91,** October 22, 1910, p. 1222.

[2] *Ann. Rept. Dept. Mines*, New South Wales, for 1909, Sydney, 1910, pp. 58–59. The figures given represent exports of 193.3 long tons of scheelite and 127 long tons of wolframite, a total of 320.3 long tons. Concerning scheelite the report states: "The prices realized locally ranged from £65 ($316) to £130 ($632) per ton for 72 per cent. ore." The tungsten ore has therefore been considered to carry 72 per cent. $WO_3$.

[3] *Min. Jour.*, London, **88,** February 26, 1910, p. 237.

[4] *Queensland Govt. Min. Jour.*, Bisbane, March 15, 1910, p. 122.

[5] *Progress Min. Ind. Tasmania*, Hobart, 1909 and 1910 (quarterly).

[6] *Ann. Rept. Sec. Mines for* **1909,** Melbourne, 1910, p. 25.

[7] *Min. Jour.*, London, **91,** November 19, 1910, p. 1320.

[8] Fiscal year June 30, 1908, to June 30, 1909. *Min. Jour.*, London.

[9] *Min. Jour.*, London, **91,** November 12, 1910, p. 1306.

[10] *Mines and Quarries*, Gen Rept. with Statistics for 1909, Home Office, London, 1910, p. 10.

[11] $WO_3$, *Min. Jour.*, London, **91,** December 10, 1910, p. 1409. Output of Saxony.

[12] *Boletim commercial e maritimo*, Dezembro, 1909, Lisbon, 1910, p. 791.

[13] Papers and reports relating to minerals and mining, Wellington, 1910, p. 17. The exports of scheelite for the year were 58 long tons thought to carry 72 per cent.

[14] *El Comercio Exterior Argentina*, Buenos Aires, 1910, p. 191.

[15] Communicated by Bureau American Republics, September 26, 1910.

difficult to estimate how much of the entire quantity should be credited as the production of the United States, possibly a third. The distribution of this quantity among the different States would be impossible.

At Webster, N. C., the North Carolina Nickel Company spent a large amount of money putting in a plant for the electrical reduction of low-grade silicate ores. It is the intention to make a ferronickel-silicon, and thus avoid complicated metallurgical processes. The ferronickel-silicon is to be sold for steel-making. The present steam plant and electrical machinery are reported to have cost $600,000. The company plans to utilize also a water power near at hand. Diamond drilling and trenches are said to show a sufficient supply of nickel ore on hand.

The imports for consumption of nickel into the United States since 1902, inclusive, as reported by the Bureau of Statistics, have been as follows:

Imports of Nickel for Consumption into the United States, 1902–1909.

| | Nickel, nickel ore, and matte, nickel oxide, alloys of nickel with copper, etc. | | Value of manufactured articles of nickel. | Total value. |
|---|---|---|---|---|
| | Pounds. | Value. | | |
| 1902 | 33,942,710 | $1,407,521 | $30,128 | $1,437,649 |
| 1903 | 36,217,985 | 1,456,605 | 37,284 | 1,493,889 |
| 1904 | 19,739,315 | 1,118,541 | 2,950 | 1,121,491 |
| 1905 | 31,072,206 | 1,958,840 | 3,291 | 1,962,131 |
| 1906 | 34,082,042 | 1,867,568 | 8,963 | 1,876,531 |
| 1907 | 18,598,638 | 2,233,867 | 9,159 | 2,243,026 |
| 1908 | 16,825,291 | 2,487,605 | 9,980 | 2,497,585 |
| 1909 | 22,194,102 | 3,034,407 | 1,866 | 3,036,273 |

The imports for 1909 were divided as follows:

Imports of Nickel for Consumption into the United States in 1909.

| | Pounds. | Value. |
|---|---|---|
| Oxides | 25,798 | $9,235 |
| Nickel, alloys, pigs, bars, etc. | 252,113 | 94,784 |
| Ore and matte (nickel content) | 21,916,191 | 2,927,975 |
| Sheets or strips | ...... | 2,413 |
| Total | 22,194,102 | 3,034,407 |

The imports for consumption of cobalt into the United States since 1901 have been as follows:

Cobalt Oxide, Ore, and Zaffer imported into the United States for Consumption, 1901–1909, in Pounds.

| Years. | Quantity. | Value. |
|---|---|---|
| 1901 | 71,969 | 134,208 |
| 1902 | 79,984 | 151,115 |
| 1903 | 73,350 | 145,264 |
| 1904 | 42,354 | 86,925 |
| 1905 | 70,048 | 139,377 |
| 1906 | 41,084 | 83,167 |
| 1907 | 48,013 | 74,849 |
| 1908 | 219,098 | 17,077 |
| 1909 | 12,132 | 11,696 |

### EXPORTS.

The United States refines much more nickel than it can use, so that although not an important producer it is a large exporter. Exports since 1901 have been as follows:

Exports of Nickel, Nickel Oxide, and Matte from the United States, 1901–1909, in Pounds.

| Year. | Quantity. | Value. |
|---|---|---|
| 1901 | 5,869,655 | $1,521,291 |
| 1902 | 3,228,607 | 924,579 |
| 1903 | 2,414,499 | 703,550 |
| 1904 | 7,519,206 | 2,130,933 |
| 1905 | 9,550,918 | 2,894,700 |
| 1906 | 10,620,410 | 3,493,643 |
| 1907 | 8,772,578 | 2,845,663 |
| 1908 | 9,770,248 | 3,297,988 |
| 1909 | 12,048,737 | 4,101,976 |

## VANADIUM IN 1909.

The larger part of the vanadium used in this country is obtained from ore imported from Cerro de Pasco, Peru, by the American Vanadium Company, of Pittsburg, Pa. The ore is largely patronite, a sulphide of vanadium, with which are various oxides in the weathered part of the deposit.

In this country vanadium was produced in 1909 by the Vanadium Alloys Company, at Newmire, Colo., from the roscoelite-bearing sandstone at that place. Much trouble has been experienced with the melting down of the furnaces in which the ore is given a chloridizing roast, and the percentage of recovery has not been all that could be wished. About the last of the year the plant passed into the hands of the Primos Chemical Company.

The Colorado Vanadium Company established a laboratory at Boulder and pursued experiments on the extraction of vanadium from the Newmire roscoelite, but produced no ore beyond a small quantity needed in its experimental work.

The General Vanadium Company shipped two cars of vanadiferous sandstone from the Jodandy claim in the Paradox Valley, 58 miles northwest of Placerville, Colo. Most of the vanadium in this sandstone is in a black mineral, probably an oxide, but not thoroughly investigated.

In New Mexico occurrences of vanadium minerals are said to have been prospected near Hillsboro and in the Caballos Range, but no production is known to have been made.

So many letters asking for tests for vanadium are received by the United States Geological Survey that the following tests, which have been found effective, are given:

To test for vanadium, the mineral may be digested, with nitric acid. If hydrogen peroxide be added to the resulting liquid, a brown color will appear if vanadium is present.

Some vanadium minerals are also attacked by hydrochloric acid and by sulphuric acid. To the solution resulting from the use of either acid, hydrogen peroxide may be added, and a brown solution will show the presence of vanadium, as when nitric acid is used. If either hydrochloric or sulphuric acid is used, metallic zinc may be added after hydrogen peroxide, and a bright blue color will be given by the reduction of vanadium compounds. The same effect can be obtained in a nitric acid solution by adding sulphuric acid, evaporating to white fumes, diluting, and adding metallic zinc. If preferred, hydrochloric acid instead of sulphuric acid may be added to the nitric acid solution, but in that case evaporation must be carried almost to dryness at least twice to get rid of the nitric acid. The liquid may then be diluted and more acid added, followed by zinc as described.

At times the tests given above are not wholly satisfactory. In such cases, if the apparatus is at hand, through a filtered solution made alkaline with ammonia pass hydrogen sulphide ($H_2S$) gas until the solution is saturated. The solution will take a fine garnet or deep wine color if vanadium is present. Copper, if present, is precipitated as a sulphide and does not interfere with the test.

If commercial iron sulphide for making hydrogen sulphide gas is not at hand, iron pyrites, galena, or zinc blende may be used with hydrochloric acid. The only accessories needed are two test tubes, one of which is closed with a cork in which is inserted a bent tube, the other end of which can be placed in the solution to be tested for vanadium.

## TITANIUM IN 1909.

During 1909 rutile (titanium oxide) was mined at two places in Nelson County, Va. The General Electric Company did a large amount of prospecting upon the Warwick farm, 7 miles northwest of Tye River postoffice during the winter, spring and summer, and later leased the American Rutile Company's mill and quarry at Roseland, about 4 miles farther northwest.

The rutile deposits on the Warwick farm were found to be so discontinuous that work was given up after more than a year's prospecting. About 100 tons of rutile ore, carrying

50 per cent. $TiO_2$, were shipped to a Pennsylvania company for concentration, and are reported to have yielded 35 tons of concentrates.

Eighty-six tons of concentrates, carrying between 80 and 90 per cent. $TiO_2$, were produced at the Roseland mill.

The concentrates from both places were further treated by a magnetic separator. The total value of the concentrates from both places is estimated at $10,000.

A carload of nelsonite, composed of ilmenite and apatite, was shipped from a dike near Roseland by the General Electric Company for experimental work.

The Titanium Alloy Manufacturing Company, of Buffalo, uses both rutile and ilmenite in making ferrotitanium. The company states that the ilmenite it uses comes from Canada.

No rutile is known to have been imported into the United States in 1909, but the American Rutile Company was an exporter of rutile concentrates. So far as is at present known its deposits at Roseland are the largest in the world.

The use of titanium in making steel rails increased considerably during the year. The New York Central lines have given rails treated with ferrotitanium a long trial, and concerning these rails W. C. Brown, the president of the system, makes the following statement in a published letter:

> Under the heaviest traffic we have ever had these rails are giving perfect satisfaction.
>
> We have subjected them to the most exacting service at the throat of the Grand Central terminal yard; and under traffic which made it necessary to change other rails within six or eight months, the ferrotitanium rails, which have been in service a year, show almost no appreciable wear.
>
> In this connection I would say that the Bessemer rails rolled by the Lackawanna Steel Company for our lines for the past two years (all of which have been treated with titanium) have been the best we have ever received, and in many respects we regard them as equal, if not superior, to the average open-hearth steel. While the quality is so much better the cost is insignificant, and we are now specifying titanium alloys in all of our rails.

The use of titanium in arc-light electrodes is also growing. Of these there are two principal types, one of which is an electrode made of finely ground titanium carbide, the other is composed of magnetite, chromium oxide and rutile.

## MOLYBDENUM, URANIUM AND TANTALUM IN 1909.

No production of molybdenum or uranium minerals and only a small output of a tantalum mineral is known to have been made in the United States during 1909. The demand is not large for either the metals or their salts.

The use of molybdenum in steel has not grown greatly, and no molybdenum deposits have yet been developed in this country to a point where they could be depended upon for any considerable production.

Up to the close of the year no one had established a method by which the low-grade carnotite deposits of Colorado could be profitably worked, though there are apparently large quantities of rock carrying from 1 to 2 per cent. of uranium oxide ($U_3O_8$), while smaller lots containing as high as 8 or 9 per cent. may be mined.

Tantalum incandescent electric lamps have such strong competition in tungsten incandescent lamps that the demand for tantalum minerals seems rather to have decreased than grown. A small tonnage of columbite (a tantalate and columbate of iron and manganese) was mined in 1909 by the Western Reduction Company, of Omaha, Nebr., from a claim near Keystone, S. Dak., which it was operating for amblygonite. The tantalum used in this country in 1909 was imported from Germany.

## TIN IN 1909.

Tin remains one of the few commercial metals of which the United States is not an important producer, although this country is the largest consumer of the metal, taking about 43 per cent. of the world's production.

*Alaska.*—On Cape Mountain, 5 miles southeast of Cape Prince of Wales, the Bartels Tin Mining Company continued prospecting work and reported having a considerable quantity of ore on their dumps. The company has been prospecting at this point since 1903. A 10-stamp mill with concentrating tables was erected in 1905, and the following year about 10 tons of concentrates were produced. Since then there has been no production.

Southwest of the Bartels Tin Mining Company's mine and near the top of Cape Mountain, the United States-Alaska Tin Mining Company has been working since 1903 or 1904. Since 1905 it has been driving a crosscut tunnel to cut a vein exposed near the top of Cape Mountain.

Only one company, the American Mining Company, operated on Buck Creek during 1909. Seventeen short tons of stream tin, carrying between 67 and 68 per cent. tin, equivalent to 19 tons of 60 per cent. ore, were taken out in the course of assessment and prospecting work. The ore was shipped to Penzance, England, and was sold for $33\frac{1}{3}$ cents per pound of metallic tin contained, a total of about $12,667. Prospecting is said to have shown that the tin extends farther into the tundra on both sides of Buck Creek than had been supposed, and the installation of a dredge is contemplated. The season of 1909 was short, cold, and stormy, and only assessment work was done on other claims along the creek.

Some prospecting for tin was done on Ears Mountain, Brooks Mountain, and Lost River.

*South Dakota.*—The Pahasa Mining Company took over in 1909 the properties of the old Harney Peak Tin Mining and Manufacturing Company near Hill City, which had been in the hands of the court for fourteen or fifteen years. Dumps were sampled, workings were examined, and shafts were unwatered and cleaned with a view to ascertaining the real value of the deposits.

The Gertie Mining and Milling Company continued work upon its mill just south of Hill City.

At Tinton, the Tinton Reduction Company has done further work both on the mill and in the mine, and 24 short tons of tin concentrates were shipped in 1909 to Chicago and smelted, giving a return of $4,832. The pegmatite in which the ore occurs is crushed dry and a steady blast of air is driven against a falling stream of the finely crushed ore, blowing out the flat leaves of mica, which is said to be a merchantable product. The ore is reported to average 0.5 per cent. tin.

*Texas.*—The tin deposits in the Franklin Mountains, 15 miles north of El Paso, which were owned and prospected by Mr. C. R. Morehead, of El Paso, and later by the Florella Mining Company, passed in 1909 into the hands of a new company, the El Paso Tin Mining and Smelting Company, which continued prospecting and reported having uncovered larger quantities of ore than were before known.

At Streeter, Mason County, P. H. Parker, whose discovery of tin ore was noted in the report for 1908, continued prospecting in 1909, but nothing of commercial value seems to have been developed.

*Other States.*—No work is known to have been done during 1909 on the deposits in North Carolina, South Carolina, Virginia, or Washington.

The world's supply of tin for the last three years, as shown by shipments and sales, has been approximately as follows:

Supply of Tin in 1907, 1908 and 1909, in Short Tons.

| | 1907. | 1908. | 1909. |
|---|---|---|---|
| Total shipments: | | | |
| Straits Settlements | 58,800 | 67,760 | 65,459[1] |
| Australia | 7,112 | 6,552 | 5,992[2] |
| Bolivia | 17,136 | 19,040 | 23,523[3] |
| South Africa | ... | 1,904 | 916[4] |
| China | 224 | ... | ... |
| Banka sales in Holland | 12,197 | 12,880 | 12,992[2] |
| Billiton sales in Java | 2,408 | 2,465 | 2,465[2] |
| Production in Cornwall | 5,488 | 6,048 | 5,802[2] |
| Total | 103,365 | 116,649 | 117,149 |

During the year 1909 the United States imported for consumption 47,662 short tons of metallic tin, valued at $27,558,546; 1,432 tons of cassiterite, valued at $68,462; tinfoil valued at $23,427; and other manufactures of tin, valued at $55,714. The quantity imported has been exceeded but once before, in 1906. The imports of tin for consumption into the United States since 1901 have been as follows:

Tin Imported and Entered for Consumption in the United States, 1901–1909, in Short Tons.

| Years. | Quantity. | Value. |
|---|---|---|
| 1901 | 37,280 | $19,024,761 |
| 1902 | 42,522 | 21,263,337 |
| 1903 | 41,567 | 22,265,336 |
| 1904 | 41,472 | 22,356,895 |
| 1905 | 44,188 | 26,316,023 |
| 1906 | 50,477 | 37,447,315 |
| 1907 | 41,257 | 32,074,263 |
| 1908 | 41,267 | 23,923,560 |
| 1909 | 47,662[5] | 27,558,546 |

The average price of tin as indicated by the imports for consumption during 1909 was 28.91 cents per pound. As given by C. Mayer[6] the average price in New York for the year was 29.69 cents per pound. "Metal statistics, 1910,"[7] gives the average price as 29.76 cents per pound.

There was a gradual, steady rise in the monthly average of prices from about 28 cents per pound in January to about 29$^{3}/_{4}$ cents per pound for December. The lowest price was 27$^{1}/_{4}$ cents in February, and the highest was 34$^{1}/_{8}$ cents, reached in December. Although the average price for the year was very little more than during 1908 (about 29.5 cents), the fluctuations were somewhat greater. During 1908 the lowest price was about 26.5 and the highest about 32.5 cents per pound.

Statistics gathered by John P. Dunlop, of the United States Geological Survey, indicate growth in the recovery of tin from tin scrap, used tin cans, old tin pipe, worn driving-box linings, drosses, old solder, bronze, sweepings, etc. From these materials the recovery of tin is commonplace and expected, except from used tin cans; in them the loss of tin is enormous, and in the recovery of tin from them must be the future growth in the comparative percentage of waste material treated.

At present the Vulcan Detinning Company is recovering tin from a considerable quantity of used tin cans. In a small way cans are treated by others for recovery of their solder. A common method of recovery is to throw the cans into a small sheet-iron vertical cylinder in which is a wood fire; such solder as runs down into the ashes is collected and remelted into more salable form.

The tin recovered during the year as tin amounted to 2,423 short tons; in the form of alloys, such as solder, babbitt metal, bronze, etc., 3,092 short tons were recovered, a total of 5,515 tons, equal to more than one-ninth of the tin imported into this country and worth at the average price for the year (about 29.75 cents per pound) $3,281,425. Besides the money value involved, the world's tin resources were increased by so much—a very real conservation.

In Europe there was also a large saving of tin from various wastes, but the quantity is unknown.

## ANTIMONY IN 1909.

No production of antimony ore in the United States during 1909 has been reported to the United States Geological Survey. There was, however, a considerable quantity of antimonial lead produced as a by-product in the smelting of other metals and in the refining of pig lead by the electrolytic process. As most of the antimony used goes into lead alloys, antimonial lead is a convenient form in which to handle antimony and there is no necessity for separating it from the lead. Besides the production of antimonial lead, a large quantity of antimony was recovered from various wastes, such as drosses, residues, old type, babbitt metal, journal bearings, etc.[1] Of this quantity, about 27 tons was recovered as antimony and 1,529 tons was recovered as a component of various alloys, a total of 1,556 tons of recovered antimony. Reports were received from 23 companies.

The production of antimony in the United States since 1903 has been as follows:

Production of Antimony in the United States, 1903-1909, in Short Tons.

| | Contained in antimonial lead of domestic origin. | | Contained in antimonial lead of foreign origin, but smelted in the United States. | | Antimony produced from domestic ore. | | Recovered from old alloys, scrap, dross, etc. | |
|---|---|---|---|---|---|---|---|---|
| Years. | Quantity. | Value. | Quantity. | Value. | Quantity. | Value. | Quantity. | Value. |
| 1903 | 2,558 | $445,092 | ... | ..... | 570 | $103,341 | ... | ...... |
| 1904 | 2,571 | 443,598 | ... | ..... | 486[2] | 61,926 | ... | ...... |
| 1905 | 2,747 | 588,354 | ... | ..... | 493 | 117,433 | ... | ...... |
| 1906 | 1,362 | 544,800[3] | ... | ..... | 404[4] | 58,149 | ... | ...... |
| 1907 | 1,561 | 508,886[5] | ... | ..... | 351[4] | 77,300 | ... | ...... |
| 1908 | 2,246 | 359,360[5] | ... | ..... | (7) | (8) | ... | ...... |
| 1909 | 1,617 | 252,252[8] | 743 | 115,908[7] | (7) | (8) | 1,556 | $242,736[8] |

Imports of antimony and antimony compounds entered for consumption during 1909 were large. The imports of antimony metals and regulus, 9,557,956 pounds, were larger than in 1908 and practically equal to the imports for 1907; but the value, $620,117, was less than that of the smaller quantity imported in 1908 (8,089,915 pounds, valued at $771,206), and not half of the value of the nearly equal quantity imported in 1907, when imports of 9,600,901 pounds were valued at $1,407,861.

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[1] Figures quoted from official sources by *Min. Jour.*, London, **88**, 1910, 65 (1910).

[2] Exports, as given by C. Mayer in "Annual Statistical Report of the New York Metal Exchange for 1909," p. 13.

[3] *Min. Jour.*, London, **88**, 336 (1910). Senor Ventura Farfan, inspector of custom houses (Bolivia), is quoted as giving the exports upon which duty was paid as 35,566.4 metric tons of barilla (concentrates) carrying 60 per cent. tin. Although a part was pig tin from Oruro, it was calculated to a basis of 60 per cent. concentrates.

[4] Fourth annual statement of the trade and shipping of the colonies and territories forming the South African Customs Union, Cape Town, 1910. Tin ore to the amount of 27,255 hundred weight was shipped during 1909. This is considered as giving a recovery of 60 per cent. tin.

[5] This item does not include the tin contained in imported ore, tinfoil, or other manufactures.

[6] *Op. cit.*, p. 17.

[7] *Ibid.*, p. 118.

[1] Figures collected by John P. Dunlop, of the United States Geological Survey.

[2] Estimated from the average content of the ore.

[3] Estimated from the prices current for the year.

[4] Figured as 60 per cent. of domestic ores only; direct figures from the smelters could not be obtained.

[5] Estimated, using 16.3 cents as the average price per pound.

[6] Estimated, using 8 cents as the average price per pound.

[7] None produced from domestic ore. Figures not collected for foreign ores.

[8] Estimated, using 7.8 cents as the average price per pound.

In the following table the imports of antimony and antimony ore for consumption are given since 1899 in order to show the great variation in both quantity and value of the imports from year to year. Importations of salts of antimony are given only since 1903, the earliest year for which the Survey has obtained statistics:

Antimony, Antimony Ore, and Salts of Antimony Imported and Entered for Consumption in the United States, 1899–1909, in Pounds.

| | Metal and regulus. | | Crude antimony and ore. | | Oxide and salts of antimony. | | |
|---|---|---|---|---|---|---|---|
| Years. | Quantity. | Value. | Quantity. | Value. | Quantity. | Value. | Total value. |
| 1899 | 2,990,915 | $241,685 | 3,968,654 | $47,427 | ....... | ... | $289,112 |
| 1900 | 3,654,822 | 287,937 | 6,089,134 | 75,866 | ....... | ... | 363,803 |
| 1901 | 3,640,505 | 254,529 | 1,682,301 | 22,720 | ....... | ... | 278,066 |
| 1902 | 5,388,739 | 333,601 | 3,129,069 | 62,968 | ....... | ... | 396,569 |
| 1903 | 4,694,309 | 260,144 | 2,714,617 | 54,316 | 916,468 | $66,469 | 380,929 |
| 1904 | 4,268,045 | 248,726 | 2,488,518 | 50,414 | 981,026 | 70,668 | 369,808 |
| 1905 | 4,941,247 | 431,228 | 1,970,788 | 53,026 | 1,010,228 | 80,130 | 564,384 |
| 1906 | 10,305,734 | 1,391,289 | 1,972,658 | 125,841 | 764,070 | 99,251 | 1,616,279 |
| 1907 | 9,600,901 | 1,407,861 | 2,771,387 | 180,903 | 682,192 | 98,038 | 1,686,802 |
| 1908 | 8,089,915 | 771,206 | 3,287,218 | 106,930 | 623,125 | 65,898 | 744,034 |
| 1909 | 9,557,956 | 620,117 | 3,453,542 | 94,249 | 955,360 | 60,353 | 774,719 |

The apparent consumption for the year is the sum of the antimony imported, smelted from imported crude antimony and ore, produced in antimonial lead of both foreign and domestic origin, and recovered from secondary sources, such as old alloys, scrap, etc. If the recovery from imported crude antimony and ore is taken as about 50 per cent. of the gross weight, the sum of the items named is 9,558 tons. This is exclusive of the antimony contained in oxide and salts, which would probably add 200 or 300 tons more.

The real consumption would have to take into account the stocks of antimony held at the beginning and the end of the year, and the imports and exports of type metal and of other antimonial alloys.

The price of antimony was fairly steady during 1909. According to the annual statistics issued by "The American Metal Market," of New York, the year opened with an average price for Cookson's of 8.11 cents during January. The price dropped until it averaged 7.95 cents during March. There was then a gradual rise, and during August the average price was 8.55 cents. Prices then gradually dwindled until November, during which month and December the average price per pound was 8.375 cents. The average price of Cookson's for the year was 8.27 cents per pound. Other brands were one-eighth to one-half cent less per pound.

## ARSENIC IN 1909.

In 1909, as in 1908, the only arsenic produced in the United States was the recovered in the form of white arsenic ($As_2O_3$) as a by-product in smelting. During 1909 white arsenic was saved at three smelters. Besides the arsenic-saving plant of the American Smelters Securities Company, at Everett, Wash., and that of the Anaconda Copper Mining Company, at Anaconda, Mont., a new plant was put up by the United States Smelting Company, at Midvale, Utah. The last company, which began producing during the year, smelts large quantities of Utah lead ores, which are highly arsenical, and from the flue dusts made in smelting these ores the arsenic is saved.

The arsenic mines at Brinton, Floyd County, Va., and at Mineral, Wash., did not operate, owing to the low price of white arsenic.

The total quantity of arsenic saved by the three smelters during 1909 amounted to 2,428,313 pounds or 1,214 short tons, valued at $52,946. The average prices received by the companies ranged from 2.05 to 2.4 cents per pound. The price in New York ranged around 3 cents per pound. The highest average monthly price was 3.25 cents per pound in January; the lowest, 2.725 cents per pound in October. The average price for the year was 2.97 cents per pound.[1]

The United States imported much more arsenic than it saved during the year, but most of the imported arsenic was in the form of sulphide.

The production and importation of arsenic, white arsenic, and arsenic sulphides and of Paris green and London purple since 1901 are given in the following table:

Production and Imports of Arsenic, 1901–1909.

| | | | Imports. | | | |
|---|---|---|---|---|---|---|
| | Production of white arsenic. | | White arsenic, metallic arsenic, and arsenic sulphides. | | Paris green and London purple. | |
| Years. | Quantity (short tons). | Value. | Quantity (short tons). | Value. | Quantity (pounds). | Value. |
| 1901 | 300 | $18,000 | 3,495 | $316,625 | ... | .. |
| 1902 | 1,353 | 81,180 | 4,055 | 280,055 | ... | .. |
| 1903 | 611 | 36,691 | 4,179 | 294,602 | ... | .. |
| 1904 | 36 | 2,185 | 3,400 | 243,380 | 28,498 | $985 |
| 1905 | 754 | 35,210 | 3,838 | 256,540 | 44,931 | 1,118 |
| 1906 | 737 | 63,460 | 3,987 | 350,045 | 311,293 | 21,347 |
| 1907 | 1,751 | 163,000 | 5,164 | 574,998 | 133,422 | 21,919 |
| 1908 | (2) | ... | 4,964 | 430,400 | 195,000 | 30,764 |
| 1909 | 1,214 | 52,946 | 4,036 | 303,728 | 183,765 | 20,370 |

The imports came from Canada, Europe and Mexico.

A large part of the white arsenic produced and imported is made into Paris green for use as an insecticide. The prices for Paris green have been held at high figures by the few manufacturers. Prices are said to be fixed in advance of the season. During 1909, prices from January to the middle of July, as quoted by the *Oil, Paint, and Drug Reporter*, of New York, were as follows:

Prices of Paris Green during 1909, New York, cents per Pound

| | 1909. | |
|---|---|---|
| | Before July 15. | July 15 to Dec. 31. |
| In bulk | 21½ | 17 |
| 100-pound to 175-pound packages | 22 | 17½ |
| 14, 28 and 56-pound packages | 23 | 18½ |
| 2- and 5-pound packages | 23½ | 19 |
| 1-pound packages | 24½ | 20 |
| 1/2-pound packages | 25½ | 21 |
| 1/4-pound packages | 26½ | 22 |

The cause of the fall in prices is not altogether clear, but the formation of a company to establish an independent factory at Norfolk, Va., which was to make Paris green from white arsenic made at the Brinton (Va). arsenic mine, was nearly coincident with the decline.

Paris green is protected by a duty of 15 per cent. *ad. valorem.*

## BISMUTH IN 1909.

*Production.*—The only production of bismuth in the United States during 1909 reported to the United States Geological Survey was made by the United States Metals Refining Com-

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[1] *Eng. and Min. Jour.*, 89, 137 (1910).

[2] There were only two producers of arsenic in the United States in 1908, so that the figures of production may not be given.

pany as a by-product at its electrolytic lead refinery (Betts process) at Grasselli, Ind. The bismuth is obtained from the anode muds of lead bullion. The bullion comes largely from the Utah lead ores smelted at the company's plant at Bingham Junction, Utah. Most of the lead ores carrying bismuth come from the Tintic district, but the company buys bismuth-bearing lead, gold and silver ores from other districts and States. More was recovered in 1909 than in previous years. As the output is that of a single firm, the figures may not be disclosed.

The Monsanto Chemical Company's electrolytic lead plant at St. Louis was idle during 1909. It was built to operate on bismuth-bearing bullion from Mexico, but the bullion produced at the mine on which it expected to draw was sent to England for refining.

Many tungsten ores carry bismuth, and one company is known to save it as a by-product when reducing the tungsten. Some bismuth is recoverable in the electrolytic copper refineries and experiments have been carried out toward this end, but no saving has yet been reported to the United States Geological Survey. It seems entirely possible that the United States may, in time, put its markets beyond foreign domination by saving the bismuth which at present goes to waste in various smelting industries.

Bolivia is the principal bismuth-producing country, and from it, during 1909, bismuth ore amounting to 481,215 pounds, valued at $188,574, were exported.[1] Smaller quantities were produced in Queensland, New South Wales, and Tasmania.

Other countries that are either actual or possible producers of bismuth are Bohemia, Mexico, Norway, Peru, Portugal, Saxony, and Spain.

*Imports.*—The imports of metallic bismuth for consumption during the last six years have been as follows:

IMPORTS FOR CONSUMPTION OF METALLIC BISMUTH INTO THE UNITED STATES, 1904–1909, INCLUSIVE, IN POUNDS.

| Years. | Quantity. | Value. |
|---|---|---|
| 1904 | 185,905 | $339,058 |
| 1905 | 148,589 | 318,007 |
| 1906 | 254,733 | 318,452 |
| 1907 | 259,881 | 325,015 |
| 1908 | 164,793 | 257,397 |
| 1909 | 183,413 | 286,516 |

*Prices.*—The price of bismuth and its compounds is closely governed by foreign firms. During 1909 the price of bismuth through the whole year was quoted at from $1.70 to $1.80 per pound. If the price of bismuth were materially reduced, the use would undoubtedly largely increase. Throughout the year 1909[2] bismuth compounds sold as follows, per pound: the citrate, $1.85 to $1.90; the salicylate, $1.25 to $1.30; the subcarbonate, $1.65 to $1.70; the subgallate, $1.35 to $1.40; and the subnitrate, $1.40 to $1.45.

## SELENIUM IN 1909.

Selenium is known to have been made during 1909 at only one place in the United States, where a comparatively small quantity was saved. It was sold at an average price of $3.43 per pound. The uses are at present very limited, and should they so increase as to create a demand for large quantities of the element, it could be profitably sold at a much lower price. As the output is that of a single company, the figures of production may not be given.

## MERCK & CO'S NEW QUARTERS.

Merck & Co. have moved into new quarters at 45 and 47 Park Place, Manhattan, after fourteen years spent in the Merck Building at University Place and Eighth Street. This move into the wholesale business center of New York, near the Hudson Terminal buildings, has been in contemplation ever since the Merck works were established in Rahway, N. J. The new location is within three minutes' walk of the Jersey ferries, so that office and factory are brought into close connection. The firm's auto truck service several times daily between New York and Rahway effects a considerable saving in time by reason of the change.

Besides being in close proximity to the McAdoo tunnels and the west-side ferries the new Merck headquarters are only a half block from the Sixth Ave. L. and are within a few minutes walk of the subways, the Brooklyn Bridge, the General Post Office, and are hardly more than a block from Broadway.

Merck & Co. have a tract of 120 acres at Rahway, a considerable portion of which is already taken up by their extensive works, warehouses, and the cottages of superintendent and chemists. Here the shipping facilities are of the best, with a half-mile of railroad sidings alongside the main tracks of the Pennsylvania Railroad.

The western branch office of Merck & Co. remains at St. Louis, Mo.

## PHOSPHORUS SUBSTITUTE PATENTS.

It is stated that the American Association for Labor Legislation has induced the Diamond Match Co. to assign its patent for the most available substitute for poisonous phosphorus in the manufacture of matches to three trustees: Prof. Seligman of Columbia University, and Commissioner Neil and Attorney Ralston of Washington. The trustees are empowered to deal with all future applicants who may wish to use the substitute in such manner as they may think just. The Esch phosphorus bill, which was prepared by the American Association for Labor Legislation and later endorsed as to method by President Taft in his recent message, at this writing is not reported out of the Ways and Means Committee.

## TURPENTINE AND TURPENTINE SUBSTITUTES.

### ENGLAND.

(From Consul-General John L. Griffiths, London.)

There are a number of substitutes for turpentine upon the English market, the price ranging, according to a local dealer, from 24 cents to within a few cents of the price of pure spirits of turpentine. The bulk of these substitutes is sold direct to the painters and paint manufacturers, who do not guarantee their paints as mixed with pure spirits of turpentine. The manufacture of these substitutes has been in progress for a long time, and is particularly active when the price of turpentine goes above 50 cents per gallon in the United States.

The imports of turpentine into the United Kingdom during 1909 amounted to 589,880 hundredweights of 112 pounds, valued at $3,405,610. Of this amount the United States furnished 476,484 hundredweights, valued at $2,979,875; Russia, 77,382 hundredweights, valued at $242,585; France, 31,084 hundredweights, valued at $150,117; Germany, 2,290 hundredweights, valued at $6,399; and other countries, 2,640 hundredweights, valued at $26,634. (A list of importers and dealers in turpentine is filed for reference in the Bureau of Manufactures.)

(From Consul Horace Lee Washington, Liverpool.)

Regarding the prospects of introducing a turpentine substitute into this market, it appears from inquiry made of several firms, who handle the larger part of the imports of paint, turpentine, etc., in Liverpool, that substitutes for turpentine are manufactured by many of the distillers in this locality. A substitute which is well thought of by the trade, and which is manufactured in this country, commands a good sale at the price of $136.26 per ton, f. o. b. Liverpool. The imports of turpentine into Liverpool from the United States in 1909 amounted to 48,422 hundredweights, valued at $390,823.

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[1] Figures furnished by the Bureau of American Republics, Washington, D. C.

[2] *Paint, Oil and Drug Reporter*, weekly prices.

(The names and addresses of the firms who do a large business in turpentine are listed for reference in the Bureau of Manufactures.)

### SOUTH AFRICA.

(From Consul Edwin N. Gunsaulus, Johannesburg.)

There is considerable sale for turpentine substitutes in this market owing to the prevailing high price of turpentine. With good local agencies it would appear that a satisfactory trade might be established by those not selling such products in this territory, while those already in the market should be able to increase their sales.

It should be borne in mind that shipment of goods of this description must be in tins, known as "American packing," and not in barrels. The packing is usually in tins of 5 gallons each and smaller, as required. (A list of some of the leading importers and dealers in turpentine and similar products in this district is on file in the Bureau of Manufactures.)

### SWITZERLAND.

(From Consul George Heimrod, Berne.)

The imports of turpentine oil into Switzerland in 1909 amounted to 3,044,260 pounds, distributed among the following countries: United States, 13,660; Belgium, 8,150; France, 1,518,000; Spain, 1,515,000; Austria-Hungary, 440; England, 660; Germany, 5,950; and Italy, 2,400. The average price delivered at the Swiss boundary was $15.63 per 220.46 pounds. There is no customs duty. The oil is usually shipped in metal receptacles containing 352.7 pounds and its specific gravity is 900. (Names of dealers at Berne may be obtained at the Bureau of Manufactures.)

### JAPAN.

With reference to the experiments in turpentine extraction in Karafut (Japanese Sakhalin) the British consul at Hokodate reports that, preliminary experiments having proved very successful, the manufacture of turpentine by the Government is shortly to be begun. Machinery for the purpose to the value of about $75,000 has been ordered. It is hoped eventually to produce a very large amount of turpentine, as the sources of supply are almost inexhaustible, and consequently more machinery will doubtless be required later. In connection with the manufacture of turpentine at the government laboratory, experiments are to be made in the manufacture of guncotton. The consul has forwarded to the British Board of Trade at London samples of raw turpentine, extracted from the tree "Larix dahurica Turez," known in Karafuto as the "Rakuyosho," of refined turpentine oil produced at the government experimental laboratory and of the rosin left after the extraction of the oil.

## ALCOHOL FROM THE CAROB BEAN.

(From Consul General Herny H. Morgan, Barcelona, Spain.)

The discovery that alcohol can be extracted from the fruit of the carob tree has caused this article to be looked upon as much more valuable than formerly. This tree is a leguminous evergreen found in Spain, Italy and the Levant, and its fruit, commonly called the "carob bean," is about 1 inch wide and from 6 to 8 inches long, and when dried has hitherto been used as food for animals.'

Experiments have lately been made in Spain to obtain alcohol from this bean. After triturating the fruit it was immediately placed in hot water to steep and the sugar or glucose extracted by means of a current of water. The liquid resulting from the process was then allowed to ferment, the glucose thus being transformed to alcohol, which was later distilled. It was found that 2.3 quarts of pure alcohol could be obtained from 22 pounds of the beans.

A factory has been established at Faro, in Portugal, furnished with a triturator of 4,408 pounds capacity per hour. Here the practice is to steep the beans in four or five times their weight of water at 70° C. for one hour. The quantity of water depends upon the amount of glucose contained in the beans, which must be determined chemically. In the Faro factory 3 to 5 per cent. of sulphuric acid are added to the water. The sugared liquid is fermented by adding the leaven of figs or beer, usually the latter. The fermentation, which takes three days, is made in wooden casks at 25° C., and is very tumultuous. The distilling is with the most modern apparatus, because the alcohol from the carob bean, unless very pure, emits a peculiar odor and has a disagreeable taste.

Owing to the great quantity of carob trees (algarrobos) in Spain, this discovery will likely establish another important industry in this peninsula, as well as in other Mediterranean countries. Large quantities of the bean are grown in this district and in the Provinces of Valencia and Castellon, and in the south the production is even greater. It is used chiefly as food for horses, sheep, and goats, and the current price is 90 cents per hundredweight.

## MANUFACTURE OF CELLULOID IN JAPAN.

(From Consul George N. West, Kobe.)

There are two plants in course of erection in Japan for the manufacture of celluloid, one of which, located a few miles from Osaka, is expected to begin operations during the present month (November), and the other, located at Aboshi, which is now installing its machinery, is expected to be completed by the end of December.

According to the *Japan Chronicle*, the two companies show a wide divergence of oppinions as to the success of this new undertaking. The Aboshi company's opinions as expressed in the *Chronicle*, are as follows:

One of the principal materials used in the manufacture of celluloid can not be obtained in Japan and has to be imported entirely from Germany. Neither can the nitric acid or strong alcohol required be produced in Japan. When celluloid made in Japan from material imported from Germany is exported to China, India, and other countries, the freight and customs duty on the product amounts to 12 sen (6 cents) per pound. Under these circumstances it will cost more to produce celluloid in Japan than in Germany.

The Osaka Company holds that—

The principal materials required for celluloid can be procured in Japan cheaper than in Germany. Alcohol strong enough to meet the requirements for the industry can be produced in Tokyo. Of the materials necessary for the production of celluloid, it is contended that nitric acid is the only one that must be imported from abroad. In these circumstances the cost of raw materials will be smaller in Japan than in Europe. This advantage, combined with the lower price of labor in Japan, will, it is thought, place the Japanese product in a position to successfully compete with the foreign product in the oriental market.

### POSSIBLE EFFECT ON THE AMERICAN INDUSTRY.

The first company holds that the cheaper labor in Japan can not compensate for the higher price of materials which must be imported, and that state aid, in some form, will be necessary for the success of the new enterprise.

It is apparent that if the manufacturers here are successful, and that celluloid can be produced in Japan at less cost than in the United States, either through state assistance or through the Japanese being able to secure camphor, which so largely enters into the manufacture, at a less price than is paid by the American manufacturers, the industry of the latter will be seriously affected.

## NITRATE INDUSTRY OF CHILE.

According to the report it is estimated that the nitrate fields of Chile contain 242,150,000 tons of 2,000 pounds, and that, with an annual exportation of 2,000,000 tons, they can supply the world's consumption for 120 years.

The annual exportation of nitrate from Chile has been, in tons of 2,000 pounds: 1,814,585 tons in 1907, 2,236,973 tons in 1908, and 2,319,571 tons in 1909, of which the United States took 132,570 tons in 1907, 369,294 tons in 1908, and 503,889 tons in 1909. Unofficial figures for 1909 and 1910 show a consumption by the United States of 639,949 tons, which represents an enormous increase.

## NITRATE PRODUCTION ORGANIZED.

(From Consul Alfred A. Winslow, Valparaiso, Chile.)

The nitrate of soda producers of Chile have an organized Nitrate Propaganda working to increase the consumption of nitrate of soda throughout the world. During the nitrate year ended June 30, 1910, the propaganda expended $438,000 (United States gold) in this work, the Government of Chile contributing $195,000.

From the following table it will be seen that the propaganda succeeded in increasing the exports for 1909–10 about 25 per cent. over those for 1908–9, and from reports since July, 1910, it would seem that the association's work continues effective. The following export figures represent Spanish quintals of 101.6 pounds each:

| Country. | 1908–9. | 1909–10. |
|---|---|---|
| Argentina | 21,978 | 21,875 |
| Australia | 15,400 | 75,600 |
| Austria-Hungary | 136,525 | 72,825 |
| Ecuador | 163 | 448 |
| Belgium | 1,177,885 | 2,295,046 |
| Bolivia | ...... | 32 |
| Brazil | 3,269 | 4,183 |
| British Columbia | 189,728 | 215,194 |
| Chile | 26,708 | 23,316 |
| China | ...... | 14,190 |
| France | 2,244,120 | 1,477,476 |
| Falkland Islands | ...... | 22 |
| Egypt | ...... | 235,755 |
| Germany | 9,661,896 | 13,801,523 |
| Great Britain | 15,276,071 | 16,670,308 |
| Holland | 1,589,336 | 1,759,061 |
| India | ...... | 11,000 |
| Italy | 339,369 | 496,931 |
| Japan | 56,100 | 259,050 |
| Mediterranean countries n. e. s. | 391,562 | 611,272 |
| Mexico | 11,000 | 76,960 |
| Panama | 66 | 6 |
| Peru | 10,427 | 5,709 |
| Sandwich Islands | 190,582 | 443,139 |
| Spain | 330,580 | 193,982 |
| Sweden | 55,000 | 53,800 |
| South Africa | 537,396 | 490,596 |
| United States | 7,988,121 | 12,672,262 |
| Total | 40,263,282 | 51,981,561 |

The nitrate interests do not seem to be quite satisfied with the result and propose to expend $500,000 next year to further extend the business. (A list of the permanent nitrate committee is filed for reference at the Bureau of Manufactures.)

## CORRECTION.

In my note on "Dissolving Silicon Alloys" in the January, 1911, issue for "(21 per cent. Si; 39 per cent. Mn; 42 per cent. Cr)" read "(21 per cent. Si; 39 per cent. Mn; 0.42 per cent. Cr)."