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EDITORIALS

THE INVENTION OF CELLULOID.[1]

Never has the Perkin Medal been better awarded than to John Wesley Hyatt. He created a distinctly American industry, chemical in its very essence, although the inventor never claimed to be a chemist. He not only invented the fundamental principle on which this important industry is based, but he gave his fertile inventive genius and the better part of his life to the development of the many details which built up the technique of celluloid.

The technique of celluloid is strikingly different from that of rubber and all other plastics. This explains why rubber technologists ordinarily fail when they attempt celluloid manufacturing. It provides an excuse why the hard rubber concerns of this country failed to see the coming importance of celluloid when the new material was offered to them.

I believe it was Rudyard Kipling who, in one of his writings, refers to a fisherman who was specially successful because "he could think as a cod-fish would think." I have observed in meeting celluloid or rubber manufacturers that the former cannot think but "celluloid," and the latter "rubber," and are much at sea when they are confronted with the technique of a new plastic.

The history of the discovery and industrial development of celluloid by Hyatt has been described in detail by E. C. Worden, in "The Nitrocellulose Industry," Van Nostrand, New York, 1911.

I may mention here, from conversations with the inventor himself, that celluloid and the celluloid industry with all that it implies, after all meant merely a big parenthesis in the life of Hyatt in his quest of a perfect billiard ball which would replace the expensive ivory article. This is so true that even during his later years, when he is well in the seventies, he has spent considerable time in the study of other plastics in his effort to still further perfect billiard balls. Celluloid and the celluloid industry are by no means the only inventions which Hyatt has to his credit; the famous Hyatt Roller Bearing which has developed into a large and successful manufacturing enterprise, his methods of water purification (with Isaiah S. Hyatt), his process for crushing sugar cane, and his many other patents testify to the abundance as well as the diversity of his inventive achievements.

The invention of celluloid is an excellent example of how sometimes it is a real advantage for a man of genius not "to know too much;" not to be hampered by too much book knowledge if the latter tends to petrify the mind into a too one-sided point of view. In all his work Hyatt's keen observing mind was his sole guide. He tried things for himself. He did not rely overmuch on what others told him to be the facts, or on what was written in books. He wanted to be his own "authority." He had found by experience that there are many things printed in books and chemical treatises "that ain't so."

He thus discovered the important fact, on which the whole celluloid industry is based, that a mixture of nitrocellulose, camphor and a small amount of alcohol, when properly prepared, becomes thermoplastic. In other words, it becomes soft when heated, can be molded in a hydraulic press, and after cooling to ordinary atmospheric pressure, it becomes again hard and strong.

His predecessors all used nitrocellulose in presence of relatively large amounts of solvents, and used a solution, or a relatively soft mass, from which the solvents were left to evaporate. This not only meant a considerable loss of solvents, but restricted enormously many possible technical applications. The mass shrunk in the act of drying, and rapid molding was impractical, if not totally impossible.

Some of his predecessors had even used camphor in their solutions, although Hyatt knew nothing about this until it came out later in his patent suits. But his predecessors had used camphor merely as any other solvent. They had failed to observe or to grasp the great technical importance of the fact that camphor could make a solid solution with nitrocellulose and produce a thermoplastic mass.

This seemingly simple observation might have left very little imprint on any other but the actively constructive mind of a Hyatt. He saw right away that from that moment on, he could employ purely mechanical means for molding rapidly and effectively, and develop the technique of nitrocellulose plastics, for purposes never dreamt of before. The principle was simple and the available methods seemed simple enough. But as usual, when one tries a process commercially, it was found that there were endless details which conspired to render the industrial and commercial development a far more difficult problem than the mere discovery of the new principle in the laboratory. Here the whole problem might have suffered shipwreck in the hands of any other man than Hyatt. The whole technique of celluloid was then developed painstakingly by him, in all its endless details. Special machinery was invented, new methods were conceived. All this is shown by the numerous subsequent Hyatt patents.

It is an axiom that the test of a valuable invention is that it should be infringed, or attacked by those whose thinking cells are passive until some inventor arouses them out of their mental drowsiness.

Hyatt, in his patent suits, had plenty of experience of the kind. Fortunately, his financial backers could afford to defend his rights in the absurdedly long and expensive patent litigation, which is a proverbial characteristic of the inefficient administration of the patent laws of this country.

I believe it was George Westinghouse who reminded us that every successful invention passes through three

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[1] The Perkin Medal for valuable researches leading to the establishment of industries was awarded on January 23rd to Mr. Hyatt. A full report of the meeting is published in this issue of THIS JOURNAL.

stages: The *first*, when it is said: "Such a thing is absurd or impossible." The *second* stage, after the patent descriptions have become public, and have given others the means to imitate and try to find loopholes in the patent claims, begins when it is said: "The thing is not new." And *finally*, after the usefulness of the invention has become so obvious and the details connected therewith have penetrated through the hard skulls of the laggards, then it sounds: "There is no invention at all."

Lawyers are great in this game. Hyatt's invention went through every one of these three stages and were it not for the Perkin Medal, many of us might have forgotten that there ever was such a man as Hyatt, and that there was a time when celluloid did not exist, or involved very difficult problems.

His patents were assailed on the ground that others before him had used solvents and camphor in conjunction with nitrocellulose, but it was studiously omitted that his predecessors had used these ingredients under entirely different conditions, for entirely different purposes, and could not produce in that way, Hyatt's valuable technical effect. The very solvents which proved a bar to any important applications for molded plastics, Hyatt did away with, when he conceived his thermoplastic mass.

Some of the early drawbacks in the technical applications of Hyatt's discovery were none other than chemical experts with which his financial backers surrounded him. Hyatt knew no chemistry, but he knew well observed facts intimately connected with the details of the work he had undertaken. His knowledge of nitrocellulose was obtained piece-meal by his own experimenting. Facts found in books he accepted only after he had verified them. It so happened that he frequently noticed that printed statements did not agree with his own observations. One of the chemical experts insisted that "cellulose was cellulose," regardless of the source of supply, provided it was sufficiently purified, and that nitrocellulose made from any kind of pure cellulose had the same properties. Hyatt knew better when he found that the article made from ramie, the strongest and most expensive cellulose, was incomparably superior to that obtained from cheap cotton or cheap pulp cellulose.

Some chemical experts also made the positive statement to his backers, that his process would surely lead to terrific explosion because he was heating in a hot press nothing less than guncotton, which was known to be a violent explosive. Though Hyatt stated that he had been using his process for quite a time and still was alive, it was objected that this was simply due to sheer good luck which would cease at some time; if ever it happened that by accident or carelessness, the heat in his presses rose a little higher, a violent explosion was bound to occur, and this would be the end of the celluloid industry. These arguments were not by any means without logic. At that time, it is doubtful whether any chemist who knew the chemical properties of nitrocellulose would not have thought it the height of folly to heat this substance under pressure.

Hyatt not being a chemist, preferred to try and see for himself what would occur. He took a good-sized block of celluloid and heated it in the hydraulic press at a temperature far superior to the relatively low temperatures he was using in practice. He tells me that he was sufficiently impressed by all the threatening talk of the chemical experts to screen himself from the press by means of several thicknesses of cross boards behind which he could peep on and see what was going to occur. After the temperature rose to the point when the celluloid began to be destroyed, the block started sizzling on account of the emission of gaseous products. But he continued the experiment until he made sure that nothing worse occurred than to spoil the material.

The pessimistic chemical experts had failed to take into consideration that the introduction of such a large proportion of camphor had profoundly modified the properties of nitrocellulose. They had also overlooked the fact that soluble nitrocellulose is not nitrated so much as the more explosive higher nitrated cotton.

L. H. Baekeland

ORIGINAL PAPERS

THE COMPOSITION OF PAINT VAPORS

By Henry A. Gardner[1]

Received December 18, 1913

Freshly painted surfaces give to the surrounding air a peculiar odor. In closed rooms, this odor is pronounced. Its nauseating effects are well known. Painters are in the habit of stating that the vapors of fresh paint have a "leady smell." This is probably due to the fact that white lead is used as the base upon which the majority of paints are prepared. The painter has therefore always associated this pigment with the characteristic odor of fresh paint. Some cases of illness among painters have been ascribed to the effects of paint vapors. People occupying freshly decorated sleeping rooms which are not well ventilated, have at times complained of illness from the same cause. E. C. Baly[1] examined spectroscopically the vapors from basic carbonate-white lead paint, and found evidences of metallic lead therein. The vapors from basic sulfate-white lead paint or zinc oxide paint, when examined in a similar manner, showed the absence of metallic constituents. Some cases of lead poisoning among painters could be ascribed to the vapors from basic carbonate-white lead paints, if lead compounds could actually be found present in such vapors. Armstrong and Klein,[2] after conducting an elaborate series of tests, concluded that lead is not present in the vapors from white lead paint, but that the toxic effects produced by such vapors are due almost entirely to the volatile substances given off by the turpentine present.

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[1] Assistant Director, The Institute of Industrial Research, Washington, D. C.

[1] *The Oil and Colour Trades Journal*, May 6, 1911, p 1518

[2] *J. S. C. I.*, **32**, 320 (1913).

The writer has made a series of tests which confirm those of Armstrong and Klein, insofar as their results are concerned with the non-metallic constitution of paint vapors. The writer's tests, however, show that the vapors from paint apparently contain carbon monoxide, the poisonous nature of which is too well known to be commented upon. The amount of carbon monoxide evolved is also shown to be directly influenced by the type of pigments used in the paint. The definite presence of aldehydes and organic acid substances in paint vapors has also been established by these tests. The data presented has brought forth considerable information regarding the phenomenon of oxidation as applied to linseed oil and linseed oil paints. The results are given with a view to awakening further research work of a similar nature. An outline of the tests made is herewith presented, together with a summary of the results obtained and in some instances a discussion of the data. Many of the tests outlined were made in duplicate.

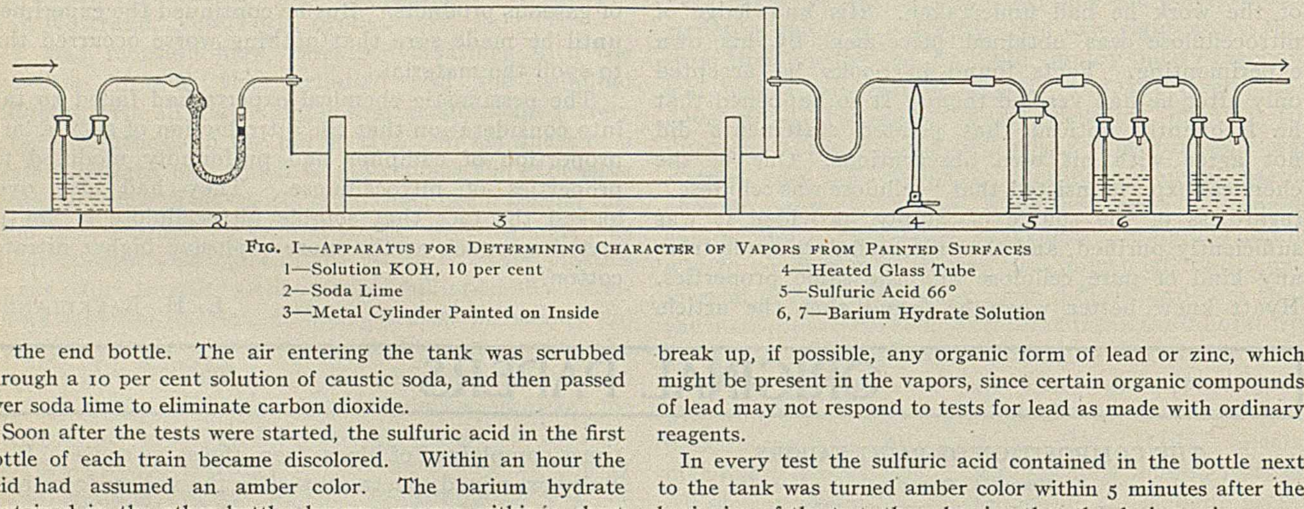

FIG. I—APPARATUS FOR DETERMINING CHARACTER OF VAPORS FROM PAINTED SURFACES

1—Solution KOH, 10 per cent
2—Soda Lime
3—Metal Cylinder Painted on Inside
4—Heated Glass Tube
5—Sulfuric Acid 66°
6, 7—Barium Hydrate Solution

EXPERIMENT I.—Four cylinders each 30 in. long and 9 in. in diameter, were formed of galvanized sheet iron. One end of each cylinder was fitted with a removable lid. The other end was closed. The seams were all soldered. The tanks were numbered from 1 to 4. The interiors of the tanks were brush-coated with raw linseed oil, soya bean oil, tung oil, and menhaden oil, respectively. The tanks were weighed previous to and subsequent to the application of the oil, in order to determine the amount of oil applied. The tanks were individually connected up to a train of three Woulff bottles, the first of which contained 66° sulfuric acid, the second and third containing a saturated solution of barium hydrate. Vacuum was applied to the end bottle. The air entering the tank was scrubbed through a 10 per cent solution of caustic soda, and then passed over soda lime to eliminate carbon dioxide.

Soon after the tests were started, the sulfuric acid in the first bottle of each train became discolored. Within an hour the acid had assumed an amber color. The barium hydrate contained in the other bottles became opaque within a short time. At the end of a 2-day run, the sulfuric acid was dark red, and the barium hydrate solutions contained a dense white precipitate which proved to be barium carbonate. Each series of apparatus was disconnected and the coatings on the interior of the tanks examined. The amount of air passing through the tanks in 2 days was evidently insufficient to complete the oxidation of the oils which under normal conditions would have been quite dry in that time. The linseed oil was very soft and tacky. The soya bean oil was but slightly oxidized. The fish oil was somewhat tacky, but it had dried to a greater extent than the other two oils mentioned. The tung oil was very hard and dry. The smell emanating from the tanks was most unpleasant, being somewhat characteristic in each instance of the type of oil used. A certain nauseous smell, however, was common to each tank. The discolored sulfuric acid from each test had an acrid odor. The bottles containing barium carbonate had an odor suggestive of aldehydes.

RESULTS: These tests indicate that the phenomenon of oxygen absorption which takes place when oils are spread in thin layers and exposed to the air, is accompanied by the evolution of considerable amounts of organic substances. Large quantities of carbon dioxide are simultaneously evolved.

EXPERIMENT II.—A series of paints was prepared from those opaque white pigments which are most widely used in the manufacture of exterior and interior paints (basic carbonate-white lead, basic sulfate-white lead, zinc oxide, and lithopone). The oil used was raw linseed oil. No turpentine or drier was added. The lead pigments were ground to a thick paste with 10 per cent of oil. The zinc pigments were ground to a paste with 15 per cent of oil. Oil in the proportion of about 7 gals. to the cwt. of paste was then added to each paint, the quantity of oil added in each instance being sufficient to make paints containing approximately 60 per cent pigment and 40 per cent oil. Each of the four iron cylinders described in Experiment I was then cleaned and painted on the inside with one of the four paints. An effort was made to spread the same amount of paint in each tank. After painting, the tops were placed upon the tanks and they were connected up to Woulff bottles containing various reagents as shown in Fig. I. Uniform vacuum was applied to the end of each apparatus, and a 48-hour run was made. The air passing into the apparatus was scrubbed through a 10 per cent solution of caustic soda and then passed over soda lime in order to remove the carbonic acid present. The glass tubes coming from the ends of the cans were bent as shown in the illustration, to hold back any particles of paint which might be carried over, although such occurrence seemed highly improbable and such precautions unnecessary. A part of each exit tube was heated with the flame of a Bunsen burner, in order to break up, if possible, any organic form of lead or zinc, which might be present in the vapors, since certain organic compounds of lead may not respond to tests for lead as made with ordinary reagents.

In every test the sulfuric acid contained in the bottle next to the tank was turned amber color within 5 minutes after the beginning of the test, thus showing that the drying paints were giving off considerable organic matter. After a 48-hour run, the acid in each bottle was dark red. The amount of carbon dioxide evolved in each test was considerable. No quantitative determination of carbon dioxide was made in any case. At the end of the experiment, the cans were re-weighed to determine the amount of oxygen absorbed. To the writer's surprise, there was recorded a loss of weight in one test, and but slight, if any, gains in the other tests. The basic carbonate-white lead paint lost 2 per cent by weight. The basic sulfate-white lead paint and the zinc oxide paint neither gained nor lost, the weight of the films remaining constant. The lithopone paint showed less than 1 per cent gain.

The bottles containing the sulfuric acid were removed from each train and the contents examined. Upon dilution with water, the acid in the bottle, through which the fumes from the drying basic carbonate-white lead paint had been passed, became opaque. It was at first thought that this cloudiness of the diluted acid might be due to the presence of lead sulfate, formed by the absorption of volatile lead compounds eliminated by the drying paint. Alcohol was added to a portion of the liquid. It immediately became clear, thus indicating the absence of lead. A very thorough examination of the liquid was then made, and not a trace of lead was found. The sulfuric acid through which the vapors from the other paints were passed, was also examined. No metallic compounds were found. The experiments were repeated, the only refinement being that of introducing in front of the sulfuric acid bottles in the trains connected to the lead-painted cylinders, a bottle containing strips of filter paper saturated with sodium sulfide solution. The papers were not darkened in either case, thus giving further indication of the absence of lead compounds. In another experiment, one of the cylinders was painted with basic carbonate-white lead paint and the gases evolved were passed through a heated tube, finally being drawn through a 2 per cent solution of nitric acid. The test was run for forty-eight hours. The acid was evaporated on a steam bath. The residue was taken up with dilute acetic acid and a few drops of water. It was tested microscopically[1] for lead after the addition of copper acetate and potassium nitrate. No response for lead was shown in the test.

RESULTS: The results of these tests indicate that drying paints, containing zinc or lead pigments, do not emit volatile compounds of a metallic character.

When spread as thin films, oil-pigment paints are capable of evolving considerable amounts of organic substances without showing any material increase in their respective weights.

EXPERIMENT III.—Experiment II was repeated after cleaning the interior of the tanks and applying fresh coats of paint. The first Woulff bottle in each train contained distilled water. The second bottle contained 66° sulfuric acid. After a 48-hour run, the contents of the first bottle in each train were examined. The water in each instance was acid in reaction. There were required for neutralization from 1 cc. to 14 cc. of $N/10$ KOH. The water in the bottle connected to the cylinder painted with lithopone showed the lowest amount of acid, while the water connected to the cylinder painted with basic carbonate-white lead showed the largest percentage of acid. The presence of carbon dioxide in the water may partially account for the acidity of these tests. A portion of the neutralized acid was tested qualitatively for the presence of aldehydes. Small amounts of aldehydes were found present. Formates were also found present. The sulfuric acid in each of the four bottles was diluted with water and titrated with $N/10$ potassium permanganate to determine the amount of reducing substances present. The acids in the trains connected to the cylinders painted with white lead paints each required about 100 cc. permanganate solution. The acids in the trains connected to the cylinders painted with zinc paints required from 19 to 39 cc. of permanganate, that connected to the lithopone cylinder requiring the least amount. The solutions of acid thus oxidized were transferred to separatory flasks and shaken with ether. The ether solutions were thoroughly washed with water and then evaporated. In each instance a dark substance which had the appearance of heavy oil was left as a residue. This substance was found to be soluble in alcohol, in which solvent very acid reactions were given. No attempt was made to identify the acids present. Their complex nature would make such determination rather difficult, especially when working on small quantities.

RESULTS: 1. The above experiments indicate that the vapors from drying paints contain acids of a water-soluble nature. These acids apparently contain formic acid. The amount of such acid evolved may be influenced by the type of pigment present in the paint. The basic pigments are apparently more active than the neutral or inert pigments.

2. Organic acids of a fatty or aromatic nature are apparently evolved from drying paints. The amount evolved may bear some direct relation to the pigment present in the paints. The basic pigments apparently are most active in this respect.

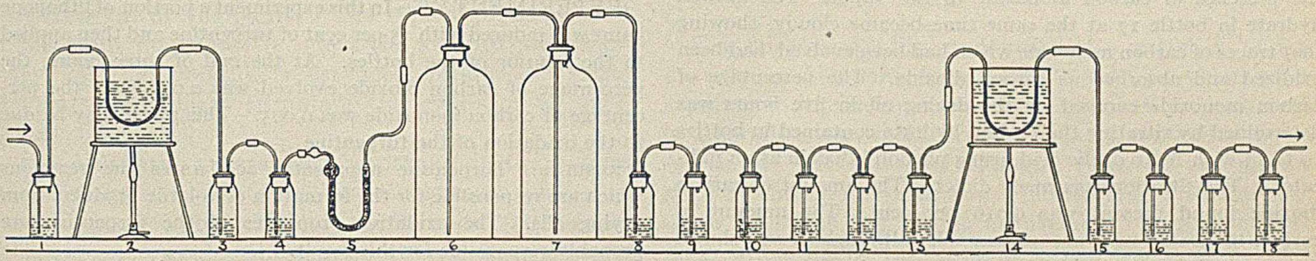

FIG. II—APPARATUS FOR DETERMINATION OF CO_2 AND CO IN VAPORS FROM PAINTED SURFACES

1—Solution KOH, 10 per cent
2, 14—Iodic acid in tube; Soya Oil Bath
3, 4, 15, 16—1 per cent KI Solution
5—Soda Lime
6,7—Bottles Painted on Inside
8—Fuming Sulfuric Acid
9—Distilled Water
10–13, 17, 18—Barium Hydrate Solution

The aldehydic reducing substances and the acids which are evolved from paints are, no doubt, responsible for the odors which are coincident to the drying of paints. In the writer's opinion, however, there are also evolved substances of a more poisonous nature. Inasmuch as large percentages of carbon dioxide are formed, it is at least possible that carbon monoxide may also be produced. The following experiments were designed to determine whether this gas is really formed

EXPERIMENT IV.—After many attempts to devise a suitable apparatus in which to determine the percentage of carbon dioxide or carbon monoxide which might be evolved by drying paints, the apparatus shown in Fig. II was found to be most satisfactory for the purpose. The first experiment made with this apparatus was conducted upon raw *linseed oil*. The interiors of two carefully weighed glass bottles, each having a capacity of one gallon, were coated with linseed oil. The oil was poured into each bottle and allowed to flow over the entire area of the interior, this being accomplished by revolving the bottle. After draining out the superfluous oil, the bottles were re-weighed to determine the amount of oil used for the test. Cork stoppers carrying glass air-tubes, were then inserted. The stoppers were thickly coated with paraffin to make them air-tight. The apparatus was connected up as shown in Fig. II. Vacuum was applied at one end. As the purpose of the experiment was to determine the presence and amount of carbon dioxide or carbon monoxide in the vapors from the oil, the air entering the bottles was first freed of its content of carbon dioxide and carbon monoxide. This was accomplished by first

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[1] Page 167, "Lead Poisoning and Lead Absorption," Legge and Goadby. Longmans, Green & Co., Publishers.

scrubbing it through a solution of caustic soda in order to remove the carbon dioxide. The air was then run through a U-tube containing iodine pentoxide heated in a bath of soya oil to 150° C. at which temperature carbon monoxide is oxidized to carbon dioxide.[1] The iodine liberated was absorbed in a 1 per cent solution of potassium iodide and the carbon dioxide formed was taken up by the caustic soda and soda lime in the subsequent train of apparatus.

After the tests had been running for 15 minutes, the fuming sulfuric acid in bottle 8 was turned amber color, showing that organic substances evolved by the oil were being absorbed. The absorption of these organic vapors by the sulfuric acid prevented such vapors from interfering with the subsequent train of liquids in which the percentage of carbon dioxide and carbon monoxide were to be determined. Bottle 10 containing saturated barium hydrate, the strength of which was determined by titration, showed a slight precipitate of barium carbonate at the end of the first 10-minute run. At the end of a 5-hour run, bottles 10–11 and 12 showed quite a noticeable deposit of barium carbonate. Bottle 15, containing potassium iodide, did not change color until the tests had been under way for over an hour. At that period the reagent became slightly yellow, showing that some iodine had been carried over into this bottle, thus indicating the presence of carbon monoxide in the vapor. The barium hydrate in bottle 17 at the same time became cloudy, showing that traces of carbon monoxide which had been evolved, had been oxidized and absorbed as carbon dioxide. The percentage of carbon monoxide evolved by the drying oil in five hours was determined by titrating the barium hydrate contained in bottles 10 to 13 with $N/10$ oxalic acid, using phenolphthalein as an indicator. The titration was made direct. The amount of carbon dioxide found present was 0.016 per cent. The amount of carbon monoxide was not measurable, although it was shown to be present in traces.

RESULTS: This experiment indicates that linseed oil in drying gives off traces of carbon monoxide.

EXPERIMENT V.—Experiment IV was repeated, coating the interior of the bottles in this case with basic carbonate-white lead paint in place of raw linseed oil. The test was run for five hours. The amount of carbon dioxide produced in that time was 0.0305 per cent. The carbon monoxide evolved amounted to 0.006 per cent. The experiment was made with basic sulfate-white lead paint in place of basic carbonate-white lead. The experiment was accidentally interrupted.

The experiment was again repeated, using zinc oxide paint in place of the white lead paint. The amount of carbon dioxide evolved was 0.0292 per cent. The amount of carbon monoxide evolved was 0.0039 per cent.

The experiment was again repeated, using lithopone paint in place of the zinc oxide paint. The amount of carbon dioxide evolved was 0.022 per cent. A mere trace of carbon monoxide was found.

Experiment V was repeated with a basic carbonate-white lead paint. The first bottle leading from the painted bottles contained fuming sulfuric acid to intercept and collect the organic vapors. The second bottle contained water. The third bottle contained alkaline bisulfite solution to collect any traces of aldehydes which, if evolved by the paint, might possibly escape absorption by the sulfuric acid. The fourth and fifth bottles contained water and caustic soda solutions, respectively, the latter to collect the carbon dioxide or phenols evolved. The vapors passing from the last bottle were passed through a U-tube containing small lumps of caustic potash. The U-tube was immersed in hot soya oil. At the end of a 5-hour test, the U-tube was removed from the hot oil and the lumps of caustic potash removed and examined for the presence of formates which, if present, would indicate that absorption of carbon monoxide had occurred. After dissolving the potassium hydrate in water, making acid with tartaric acid and distilling over barium carbonate suspended in water, the filtrate from the barium carbonate was treated with a small percentage of bichloride of mercury. After the solution had stood over night, a very faint precipitate of calomel was observed, indicating the presence of carbon monoxide.

RESULTS: These experiments would tend to show that the highly basic pigments stimulate the evolution of organic substances from linseed oil paints, especially influencing the amount of carbon dioxide and carbon monoxide evolved.

The amount of air entering the painted bottle in a 5-hour run was insufficient to cause any marked oxidation. This explains why such small amounts of carbon dioxide and carbon monoxide were obtained. The extremely small quantities present made the analytical determinations a matter of great care. Tests extending over a greater period should be made, in order to substantiate the figures presented. The writer is designing another type of apparatus in which it is hoped more accurate determinations may be made.

EXPERIMENT VI.—In this experiment a portion of lithopone paint was reduced with 15 per cent of turpentine and then applied to the interior of the bottles. At the end of three hours, the percentage of carbon dioxide evolved was 0.04, while the percentage of carbon monoxide was 0.003. This result may be due to the oxidation of the turpentine.

RESULTS: Turpentine apparently accelerates the reactions which are responsible for the formation of volatile products from drying oils. The oxidative properties of the turpentine are probably responsible for this result.

GENERAL DISCUSSION OF RESULTS

The results obtained in Experiment II, in which the paint films showed but slight if any increase of weight at the end of the tests, are interesting. They may be partially accounted for by assuming that the amount of air passed through the tanks in 48 hours was very small. It will be well at this point to discuss the experiments on linseed oil and oil-pigment paints, as made by Sabin.[1] He describes a series of tests in which various paints were applied to small glass plates, the increase in weight shown by the paints being recorded at different periods. At the end of 7 days, raw linseed oil showed a gain in weight of 18 per cent, while white lead paint showed a gain of approximately 15 per cent.

The writer carried out a similar series of tests with a set of paints made up with 60 per cent of pigment and 40 per cent of raw linseed oil. The gain in weight of the films at the end of 7 days was as follows:

	Per cent
Linseed oil	14.0
Corroded white lead	6.4
Sublimed white lead	7.1
Zinc oxide	5.4
Lithopone	5.9

These tests indicate that oil-pigment paints do not gain in weight to the same extent as raw linseed oil. Heretofore, however, investigators have not given consideration to the possibility that pigments may stimulate not only those processes which cause the oil to increase in weight through the absorption of oxygen,

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[1] "Method Used for Examination of Tunnel Gas," by Dr. A. Sydell, Hygienic Laboratory, Washington, D. C.

[1] THIS JOURNAL, 3, 84.

but also those processes and reactions which cause the oil to eliminate volatile substances, which might detract materially from the weight of the paint. In this connection it is of interest to cite the tests of Olsen and Ratner[1] upon the drying of linseed oil. They record a gain in weight of 18 per cent at the end of approximately 10 weeks. They also showed the elimination of approximately 5 per cent of carbon dioxide and 15 per cent of water.

SUMMARY OF CONCLUSIONS

I. When linseed oil or similar drying oils are spread in thin layers, the absorption of oxygen which takes place is accompanied by the evolution of considerable amounts of carbon dioxide and organic substances. Carbon monoxide is also evolved in small amount.

II. Oil paints containing lead or zinc pigments do not emit volatile compounds of a metallic nature.

III. Drying paints evolve water-soluble acid substances such as formic acid, as well as acid substances which are apparently of a fatty nature. Carbon dioxide and carbon monoxide are also present in the vapors from the drying paint. The type of pigment used in the paint may directly affect the amount and character of the volatile substances produced. Basic pigments apparently stimulate the evolution of such products.

IV. Aldehydic substances are present in the vapors from drying oil paints. These substances probably have a marked bactericidal effect upon pathogenic bacteria and would thus account for the sanitary value ascribed to oil-pigment paints.

The writer desires to thank H. C. Fuller, L. G. Carmick and the staff of The Institute of Industrial Research for their assistance in carrying out the above experiments.

Institute of Industrial Research
Washington

METALLOGRAPHY AS APPLIED TO INSPECTION

By Wirt Tassin

Received December 11, 1913

The sudden failure of engineering structures of metal, the static physical tests of which, before use, pointed to the good quality of the materials, is well known. Such failures have usually been attributed to a so-called deterioration known as "fatigue."

Whether or not repeated stresses below the elastic limit of the metal can set up such a deterioration may be questioned. One fact has however been proven beyond all question, and that is that in any metal there are always present certain structural conditions, the influence of which are either favorable or unfavorable to "fatigue."

The character of these structural conditions is indicated in part only, and then often by chance, by the static and dynamic tests. It may, however, be completely revealed by metallographic methods, that is, by the study of the structure of the metal as seen on the etched surface under the microscope.

The possibilities of metallographic methods as an additional safeguard to determine quality have been recognized, but their usefulness has been limited by the lack of protability in the appliances necessary for their use. This has made it difficult, if not impossible, to study the forging, the casting or the bar as a whole, with the result that the metallographic field has been limited to the examination of more or less small specimens cut from the piece and which, like the bar used for the machine tests, may or may not be representative of the whole.

It is the purpose of this paper to describe a complete metallographic outfit which is portable and may be used either in the mill or the laboratory and is serviceable for the study of the forging, the bar or the casting as a whole; to give certain types of structure found in the ferrous metals; to give a list of certain probable causes for failure and to outline a scheme for their detection and thus supplement other methods of testing.

THE APPARATUS

The apparatus[1] consists of a microscope, illuminating device and a camera, all self-contained, Fig. 1, *A*, *B* and *C*.

The microscope, Fig. 2, consists of a barrel, *b*, and a draw-tube, *d*, mounted on a handle arm provided with a coarse and a fine adjustment. Attached to the barrel is a shoulder, *c*, which holds a rod, *r*, controlled by a set screw. The base of this rod rests on the pinion head of the handle-arm and when locked with the set-screw prevents the coarse adjustment from overrunning when using the camera. The whole is carried on a base which is the stage. Through the center of the stage is a 1-inch circular opening which affords free space for the objective when examining large masses below it. Leveling screws are provided, one in each of the four corners of the stage, which permit the adjustment of the microscope perpendicular to nearly any surface.

The illuminating device consists of an arm, *a*, in Fig. 2, which locks into the microscope barrel by means of a threaded collar. The arm serves to carry the condensing arrangement made up of a telescope tube, *tt*, which carries the lenses. The tube is mounted in a sleeve, *y*, provided with a set-screw to lock it in any position. A hanger, *h*, from the arm is attached to this sleeve by means of a trunnion controlled by a set-screw which permits the tube as a whole to be tilted at any angle. A vertical adjustment is provided for by a set-screw at the outer extremity of the arm. The rear of the telescope tube carries a shield, *xx*, provided with clips to hold the source of light when electricity is used and is slotted to hold a rod and a movable lamp carrier when gas is used.

The source of light may be an acetylene jet or an electric lamp.

When acetylene is used the gas may be obtained from a generator or from a prestolite tank. The support for the lamp is a rod which locks into the slot in the shield of the illuminator. On the rod is placed the movable carrier for the source of light, see *B*, Fig. 1.

When electricity is used the lamp is carried in a socket fixed in an insulated metal hood and held in

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[1] *J. S. C. I.*, **31**, 937 (1912).

[1] Manufactured by Bausch and Lomb, Rochester, N. Y.

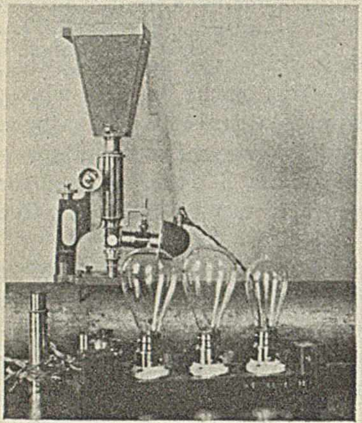

Fig. 1—*A*

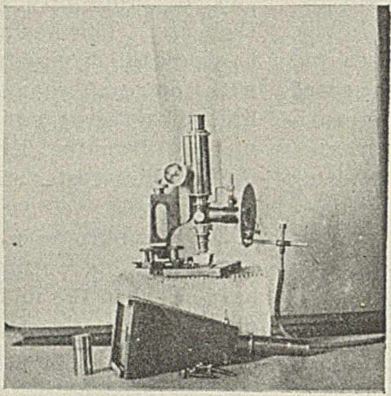

Fig. 1—*B*

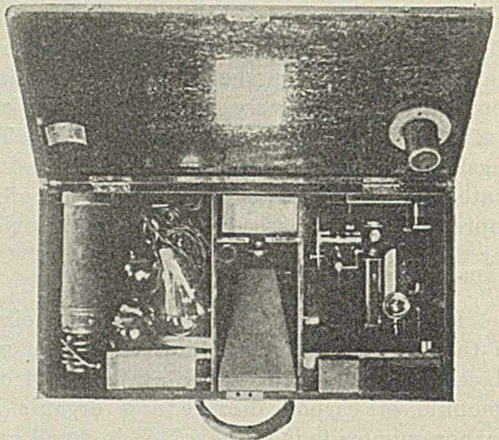

Fig. 1—*C*

position with reference to the lenses of the condensing train by clips fastened to the shield of the illuminator; see *A*, Fig. 1.

The current may be obtained from an accumulator or by cutting down the lighting current. A lamp bank to reduce a 110 volt current is wired as in Fig. 3. The lamp resistance needed for the various candle power 6 volt tungsten miniature lamps is:

Two 32 and one 16 c. p. carbon lamps for a 6 volt, 16 c. p. tungsten miniature.

One 32 and one 8 c. p. carbon for a 6 volt, 8 c. p. lamp.

One 32, or two 16, and one 4 c. p. carbon lamps for a 6 volt, 6 c. p. tungsten miniature.

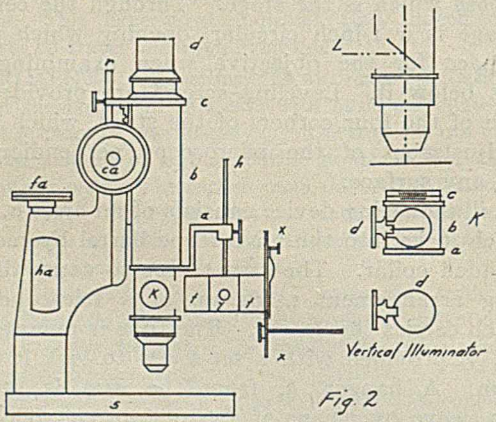

Fig. 2

One 16 and one 4 c. p. carbon for a 6 volt, 4 c. p. tungsten.

Any of these candle power tungsten lamps may be used but the one recommended is the 6 volt, 16 c. p. lamp known as "Headlight Mazda, No. 68, 12 G., candelabra base."

To get the light from the condensing train through the objective use is made of a device known as a "vertical illuminator," *K* in Fig 2. This device screws into the barrel of the microscope below the hanger which carries the condensing train. Turning the plate *d* of the illuminator to some desired angle reflects the illuminating ray, which enters the aperture, down upon the surface of the metal. This in turn reflects the light up through the barrel to the eye.

A "quick-acting nose piece" is fitted to the lower end of the vertical illuminator. This device permits of a ready change of objectives without an unscrewing motion and consists of a clamp operated by a spring controlled by two handles. Pressing the handles opens the clamp and permits the insertion of a ring, one of which is provided for each objective and to which it has been previously fastened.

The camera, see Fig. 1, is connected with the barrel of the microscope by a tube which slips in and out like the draw tube of the microscope and may be removed with the same ease. The camera moves with, and becomes part of the barrel and any degree of focusing is possible. The distance between the eye piece and the ground glass is a constant so that the amplification is standard for each magnification. To use the camera the draw tube of the microscope is removed and the tube of the camera inserted.

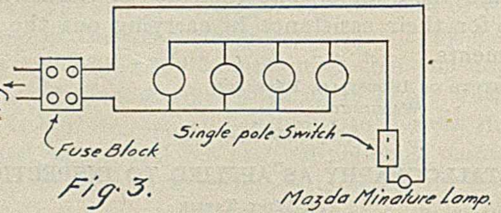

Fig. 3.

The apparatus lends itself readily to all forms of metallographic work and is adapted to the needs of the inspector, the engineer of tests and the metallurgist. It may be used in the mill or the laboratory and is equally adapted for the study of the mass, Figs. 4, 5 and 6, or the small specimen. It is used both for visual examinations and for making photographic records. It is portable, self-contained and compact.

METALLOGRAPHIC METHODS

SAMPLING.—By sampling is meant the location and number of areas to be polished. It is not necessary nor practicable to polish the entire surface of the mass provided that a sufficient number of small areas be taken which shall properly represent it. In selecting these areas it is desirable to follow some fixed rule and always prepare the surface at definite positions which shall be the same for the same kind of objects so as to be of value for comparison. This is especially desirable when grain size is to be taken into consideration as the grain may vary greatly in different parts of the work as from the thick to the thin parts of a casting.

In billets the cross section at each end should be taken, together with several areas parallel to the direction of the work and preferably on two or more sides. With rounds prepare a cross section at each end and several others parallel to the direction of the work. With flats take along the center lines of the several sides. With hollow forgings and similar material areas along the outer and inner surfaces in the direction of the work should be chosen together with two or more cross sections at each end. With castings both thick and thin parts should be selected and where the cope and drag can be distinguished, sections along each should be taken together with areas in those parts which have to take the major part of any sudden load, as trunnions.

Sections should never be prepared too near any distorted part as a sheared edge or punched hole. With annealed material, especially with castings where the soaking has been prolonged, care should be taken to get below that part decarbonized by the action of the flame.

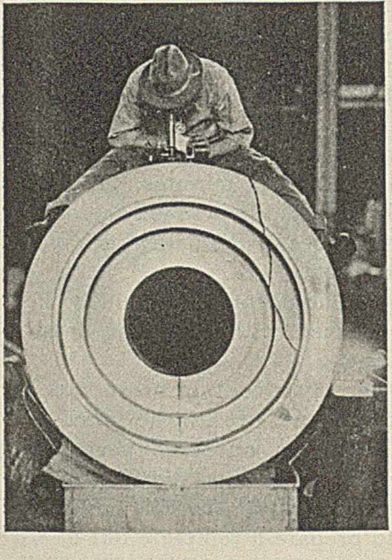

FIG. 4

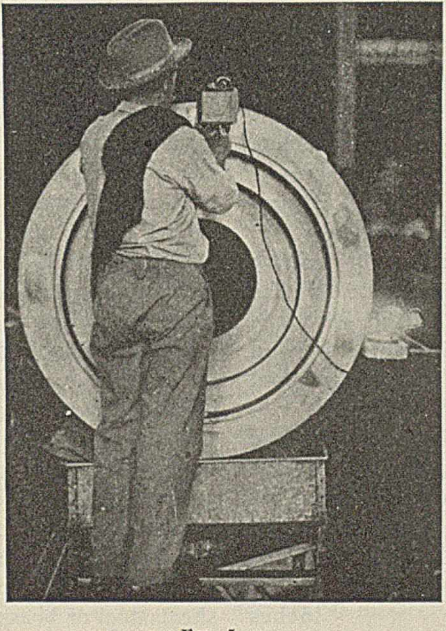

FIG. 5

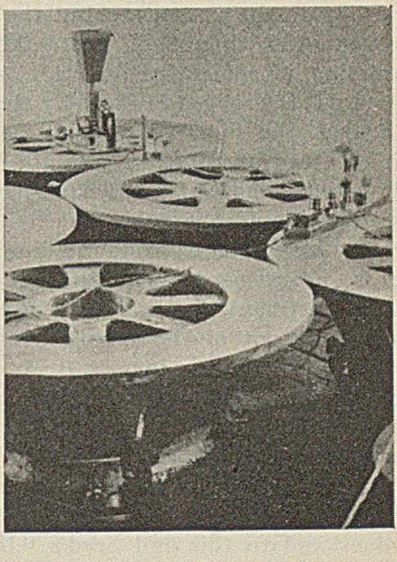

FIG. 6

The size of the sections polished should be about three inches wide by about twelve inches long.

POLISHING.—This is done by wheels and buffs driven by an electric or a pneumatic grinder, one or the other of which is usually to be found in any mill. When preparing a surface the following treatment has been found satisfactory for most purposes: If the surface is very rough grind down with a 24 grain emery wheel, follow with a cloth wheel charged with 60 emery, then use a similar wheel charged with 120 emery, follow with a buff charged with washed flour emery paste and finish with a buff charged with rouge.

The above procedure requires about 15 minutes to finish an area 3 inches by 12 inches and will give a surface that is perfectly satisfactory if the etching is done with picric acid or iodine. It is not necessary that the surface should be free from scratches but it is necessary that the scratches should all lie in the same direction.

CLEANING.—After polishing and before etching clean the surface with cotton moistened with alcohol or gasoline.

ETCHING.—After cleaning, the surface is now ready to have its structure developed. This is usually done by means of some reagent which attacks or colors some constituent of the metal more than it does others. For the ferrous metals a 10 per cent solution of picric acid in 95 per cent alcohol will be found the more useful. Soak some absorbent cotton in the solution. Take up the cotton with a pair of tongs or tweezers and allow the excess acid to drain off. Place the cotton on the surface to be etched and move it back and forth till the desired depth of etch is obtained. The degree of temperature affects the speed of etching, the colder it is the longer the time; with 55 to 70 degrees of temperature about 20 seconds is sufficient.

After etching wipe off the acid with cotton or clean, soft waste, then clean thoroughly with cotton moistened with alcohol.

Care must be taken that the etching fluid covers the whole area and that the saturated cotton is moved back and forth with a rapidity sufficient to insure the even distribution of the acid over the surface at all times as otherwise there may be variations in the character of the etch which may give rise to false conclusions. This variation in the etch is less likely to happen with picric acid than with other etching mediums.

THE VISUAL EXAMINATION.—With the unaided eye look for streaks or areas which are differently colored. Carbon-rich areas will usually appear darker and carbon-lean areas lighter than the rest of the surface. In general the segregations of the alloy elements will also be indicated by a color difference. Heat and forging cracks are commonly rendered visible as well as pipes, seams, shakes, flow lines, cold shuts, welds, etc.

When making the microscopic examination the instrument should be leveled, if necessary, by means of the screws on the stage.

The field should be clear, distinct and free from any haze, glare or image of the lamp. Should any of these appear the illumination is faulty and must be corrected. To adjust the illumination the condensing train as a whole should be raised or lowered so that the plane of its lenses is centrally in line with the opening of the vertical illuminator. Then shift the angle of the mirror in the illuminator, or the source of light.

It is recommended that but three sizes of objectives and one size eye piece be used, a 32 mm., a 16 mm., and an 8 mm. Bausch & Lomb objective and a 7.5x eye piece. These will give magnifications of 30, 65 and 150, respectively. Where higher magnifications are desired eye piece magnifications are preferable to the use of higher powered objectives and a magnification of 315 can be obtained with a 15x eye piece and the 8 mm. objective.

Care should be taken that the entire area etched should be gone over and that part selected for the photograph should be strictly representative.

PHOTOGRAPHING.—When inserting the camera it is advisable to rack the tube of the microscope well up away from the surface of the metal before removing the draw tube and attaching the camera. This will prevent the chance of damaging the objective by jamming it against the metal. After attaching the camera it is brought in focus by the coarse adjustment. The rod *r*, in Fig. 2, is brought squarely down on the pinion head and locked with the set-screw; this prevents a change of focus when changing plate holders. Further should the tube rack too easily, tighten it by setting down the screws holding the pinion of the coarse adjustment. The final focus is fixed with the fine adjustment, the sharpness of the image as seen on the clear spot of the ground glass being determined with a pocket magnifier.

All photographs should be taken with the eye piece in the camera and it will be found convenient to have two 7.5x eye pieces, one for the draw tube of the microscope and one to be kept in the tube of the camera.

The plates used should be fast and give good color values and to this end Seed's "L Ortho" are recommended. The size of the plate is $3\frac{1}{2} \times 3\frac{1}{2}$ inches and the image is about $3\frac{1}{4}$ inches.

The time of the exposure depends upon the character of the surface and the plates used. For steel, using the above plates it will not average over 10 seconds.

After exposing it is always well to verify the focus by looking through the ground glass and thus make sure that it has not been overrun as a result of changing the plate holder.

DEVELOPING.—The plates may be developed in the ordinary way with any of the developers on the market. It is suggested that "Ingento edinol hydrochinon developing tablets" be used because of their adaptability for dish and tank developing and for printing.

Where a dark room is not available an Ingento changing bag will be found an efficient substitute while loading and changing plates. Such a bag together with two tanks makes it possible to develop and fix the plates without leaving the work.

For tank developing in addition to the Ingento developer referred to the following formulas may be used for 20 minute developing at 60 to 70 degrees:

Hydrochinon	90 grains
Sod. sulfite (anhydrous)	400 grains
Sod. carbonate (anhydrous)	390 grains
Water	30 ounces

To each part of this stock solution add three parts of water before using.

Edinol	145 grains
Sod. sulfite (anhydrous)	300 grains
Sod. carbonate (anhydrous)	300 grains
Water	40 ounces

To each part of this stock solution add three parts of water before using.

The plain fixing bath of 4 ounces of "hypo" to 16 ounces of water may be used with any of these formulas; the following is, however, to be preferred:

Sol. 1	Water	96 ounces	Sol. 2	Chrome alum	32 ounces
	Hypo	2 pounds			
	Sod. sulfite	2 ounces		Sulfuric acid	$\frac{1}{4}$ ounce

Dissolve 1 and 2 separately, then slowly pour 2 into 1 with constant stirring.

It should be remembered that for the permanency of the negative, a complete fixing followed by a thorough washing and a slow drying is an essential. Occasionally prints are desired as soon as possible. Then the plate after fixing may be quickly rinsed with water, soaked in alcohol and dried in 15 minutes. After the prints are made the plate should be washed thoroughly in water to remove any traces of the fixing bath which may remain and again dried.

CARE OF NEGATIVES.—The negatives should be kept in envelopes plainly marked with sufficient data to identify them at any time.

Most micrographic negatives contain areas that are not needed or are out of focus. It will be found convenient to use a mask to cut out such parts when printing from them. Time will be saved if each negative is matted out permanently. To this end it will be found convenient to prepare a template out of $\frac{1}{16}$" sheet steel or brass which shall be a 3 inch square with a $2\frac{7}{16}$ inch circular central opening. Laying the template and a suitable piece of paper on a sheet of glass any number of masks may be quickly and easily cut with a sharp knife. One of these masks is then pasted on the film side of the negative thus always ensuring the same field.

PRINTING.—Any of the gaslight papers may be used. The glossy papers give better detail but they are liable to be scratched during manipulation and require squeegeeing to get the best results and are to this degree not so desirable as the velvet or satin finishes.

In printing, where electric light is available, a printing or developing lantern as shown in Fig. 7 will be found convenient. Throwing the switch one way gives the exposure, the other way gives the developing light. With two 100 c. p. Mazda lamps the time of exposure will rarely exceed 12 seconds.

The prints after developing should be thoroughly fixed and washed and preferably dried between blotters. If they are needed quickly they may be soaked in alcohol and dried within 15 minutes.

RECORDS.—It is always well to make notes at the time of the examination as the eye is better than the best of photographs.

The records should include remarks as to appearance, opinion as to what the area indicates and other details. Note the number and description of the piece, location of the area examined, the etching medium and the time of etching, the number of the objective and eye piece and the magnification.

TYPES OF STRUCTURE

The structure of steel may be profoundly modified by the rate of cooling from a high temperature, the degree of re-heating and the amount and kind of work to which it has been subjected. The several structures so obtained may each be referred to a type.

In a steel obtained by the simple solidification of the liquid metal followed by a slow and undisturbed cooling the grain size will be large; Fig. 8. If now the metal be re-heated to some temperature below its melting point and cooled slowly without mechanical work being applied, there will be a corresponding change in the grain; Fig. 9.

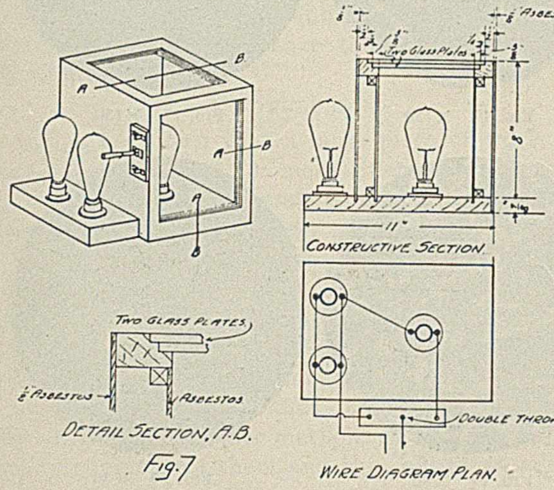

Fig. 7

In any steel, other things being equal, the smaller and more uniform the grain the better the physical properties and the size and uniformity of the grain is influenced by heat and by work.

Steel is heated to give the plasticity required for rolling or forging. It is heated to relieve internal stress but an improper heating or an interrupted cooling may set up such stresses and even cause rupture. It is heated to give hardness or to take it away. The higher the temperature from which it cools the larger will be the grain. Heating to some certain temperature will give the finest grain possible and all previously existing structures, however coarse, will be obliterated. Heating for a longer period or a shorter time at too high a temperature, or a long heating at too low a temperature will coarsen the structure. Too rapid heating or too rapid cooling or an unequal rate of cooling may set up internal stresses and cause rupture.

With steel castings the effect of these conditions is shown by Fig. 10, the structure of the metal as cast; Fig. 11, the structure as properly annealed; Fig. 12, the effect of annealing at too low a temperature.

With rolled or forged material they are shown by Figs. 13, 14 and 15 which show the normal grain as properly annealed and the effect of higher temperatures upon it.

The size of the grain and its uniformity is also affected by the amount and kind of work to which the metal has been subjected. Work may be applied in two ways, hot or cold. Hot working when finished at some certain temperature gives a small grain and the most tough and ductile metal. If the finishing temperature be too low the grain will be more or less distorted and if the work be carried far enough the metal will have a tendency to become brittle or to split along the direction of the work. The higher the finishing temperature the coarser the grain and the weaker and more brittle the metal. Cold working distorts the grain and renders it fibrous.

The effect of work can be seen best on the cross section. Thus in a hammer-forged piece if the work be applied during the proper temperature and is vigorous enough, each blow will penetrate the center and the grain will be practically uniform throughout. If the work is not vigorous enough, or the metal hotter in one portion than in another there will be more or less marked differences in grain and there may be alternate layers of hard and soft metal if the heating be followed by work with portions of the interior colder than the exterior or if the work be applied locally when the exterior is much colder than the interior. Fig. 16 shows the fracture of a hammered piece having the interior much hotter than the exterior.

The tendency of the several constituents of steel to segregate is known and in general they are to be regarded as elements of weakness. Figs. 17 and 18 show the appearance of such segregations to the unaided eye after etching; Figs. 19 and 20 their appearance under the microscope. These areas are in general relatively large and they can be seen best with the lowest powers; in fact the higher powers, because of the smallness of the field, often fail to show the structural differences between the segregated and non-segregated areas.

Slag is liable to be found in any steel and when sparingly distributed in isolated particles may be disregarded, but when occurring in any amount it is always a source of weakness. Fig. 21 is an illustration of its occurrence under conditions where it is an element of danger.

Sulfides, Figs. 22 to 24, like slag, may be found in any steel and when sparingly distributed in isolated or minute particles may be disregarded, but as the amount increases the element of weakness increases.

STRUCTURE OF SOUND STEEL.—Steel of normal composition and treatment will show after etching a surface free from segregations and laminations. The structure will be regular and uniform and the grain will show a gradual increase in size from the outside to the center as the result of work. The boundaries of the grain will be quite regular in outline with little or no signs of ingotism, or incomplete grain refining. Slag

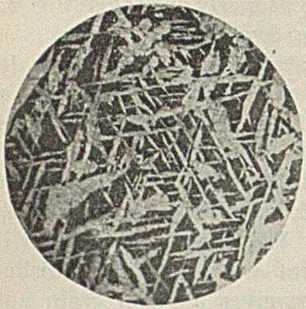
FIG. 8 ×65

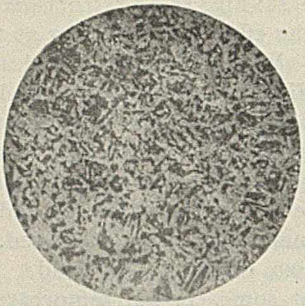
FIG. 9 ×65

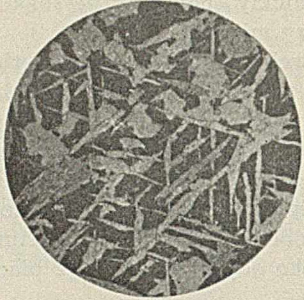
FIG. 10 ×65

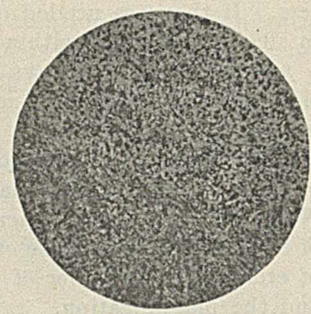
FIG. 11 ×65

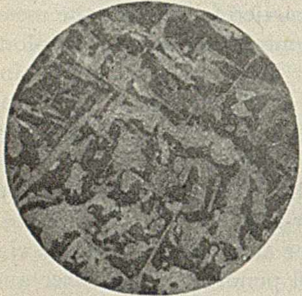
FIG. 12 ×150

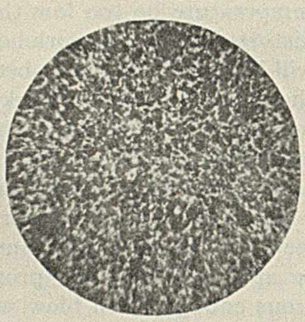
FIG. 13 ×65

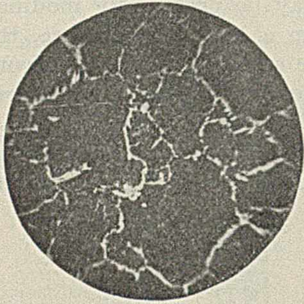
FIG. 14 ×150

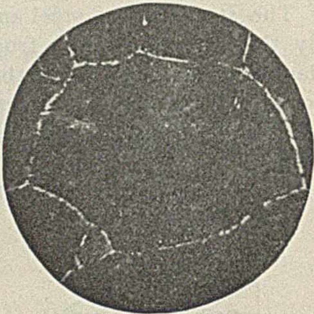
FIG. 15 ×150

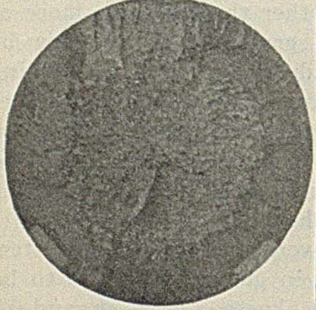
FIG. 16

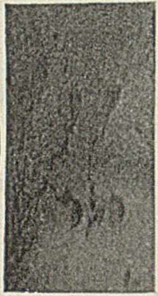
FIG. 17

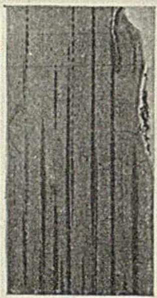
FIG. 18

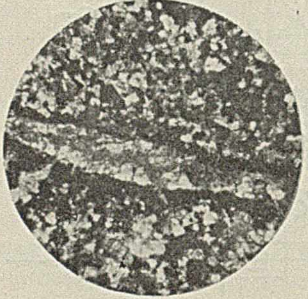
FIG. 19 ×30

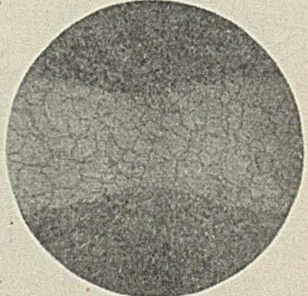
FIG. 20 ×30

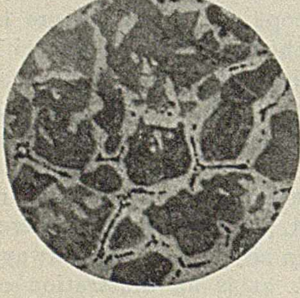
FIG. 21 ×150

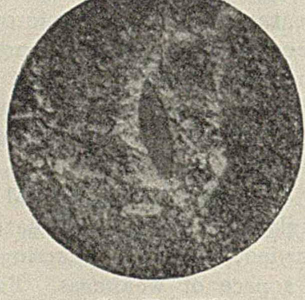
FIG. 22 ×150

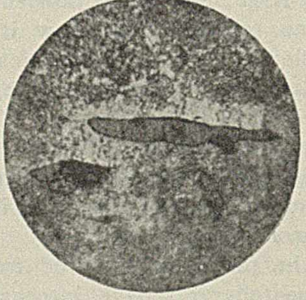
FIG. 23 ×150


FIG. 24 ×30

and sulfides are absent or only sparingly present and in isolated particles.

When cold rolled or drawn the grain will be distorted in those parts affected by the work but there will be no cracks or fissures either in or between the grain nor any "loosening."

STRUCTURE OF UNSOUND STEEL.—The causes which may give rise to unsoundness and failure are sand splits, seams, pipes, blowholes, cavities and honeycomb, all of which during work are extended as cracks. Etching develops these defects and usually renders them plainly visible to the unaided eye.

Ingotism, incomplete grain refining and failure to destroy an existing coarse structure—these conditions if present to any extent imply internal stress, lack of cohesion, liability to cleavage and brittleness.

Lack of uniformity of the grain in which those nearer the center are smaller than those further away from it—such a structure is common to material which has been heated either too high or too long. Too high heating coarsens the grain; Figs. 13, 14 and 15. In general any marked lack of uniformity of the grain implies a lowered resistance to a repeated or a suddenly applied load.

Segregations of certain essential components of the steel as the carbon or the alloying elements—Figs. 17 and 18—give rise to areas each of which have different physical properties. The presence of such areas implies a lack of continuity in the metal, since the junction lines between them are more or less sharp; Figs. 19 and 20. Such areas when under a load have a tendency to slip one upon the other, thus setting up a rupture. Their presence is revealed microscopically and macroscopically by etching. When studying them under the microscope the use of the lowest powers is advised.

Layers, streaks or patches of various impurities as slag, sulfide, etc.—all of these are less ductile and more brittle than the steel.

METHOD OF EXAMINATION

Sample, polish and etch. Examine macroscopically for pipes, cracks, seam, laps, blow-holes, honeycomb or sponginess, welds, segregations and laminations (especially on the cross section), flow lines, excessive slag and sulfide areas, cinder, etc., Examine microscopically for lack of uniformity of grain, coarseness, ingotism or incomplete refining. Look for slag and sulfide areas with reference to their abundance and distribution.

CONCLUSION

It can be shown that a large piece of work can be spot polished in eight or more different places with but little, if any, more expense and time than it takes to prepare a standard test bar; that there is a relation between structure and physical properties. It follows that given sufficient experience and a set of standards, metallographic methods will give information that cannot be obtained conveniently by any other method of inspection.

It should be stated that metallography is not intended to replace other methods of test and inspection but to supplement them and thus afford an additional safeguard against failure.

1423 R. St., Washington, D. C.

MAHONE PETROLEUM

Its Recent Origin, and the Origin of Petroleum in General

By Charles F. Mabery

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Six years ago I was invited to visit a section of the Valley of the Mahoning River in Mahoning County, Ohio, where a deposit of petroleum had been known in Milton Township for several years, and where an open well was still to be seen from which oozed a small stream of thick oil. At the time of this visit, several wells had recently been drilled over an extended area, and were producing a considerable supply of oil. But on account of faulty operation and mismanagement, these wells soon afterward became inoperative and the entire field was closed until some years later. Several wells were then to be seen on a farm bordering on the river valley, the property of Mr. R. Wiesener, from which some years earlier oil had been pumped freely and sold as a lubricant without refining.

On learning of the shallow depths at which this petroleum was reached, my interest was naturally aroused with reference to its origin, and I made several subsequent visits to become better acquainted with its occurrence, in connection with a laboratory study of the oil which seemed especially inviting, for it evidently differed very materially in its composition from the other well known varieties of petroleum. It had the further attraction that, associated with the petroleum in or near the river valley, there were extensive beds of high-grade bituminous coal, sections of which in the adjoining Township of Palmyra, were mined on an extensive scale. In a narrow section of the valley, approximately one hundred feet in width, where the river had cut its way down from a considerable height, exposing an abrupt vertical section of the geological formations, a vein was exposed, three or four feet in thickness, of partially weathered carboniferous deposits with the accompanying shales so friable that they were easily crushed in the hands. Analysis showed that these deposits contained nearly fifty per cent of pure carboniferous material. It, therefore, seemed probable that the coal and the oil were of a common origin, which, in connection with the shallow depths of the oil strata, less than 150 ft., presented an inviting opportunity to study the origin of petroleum at close range.

GEOLOGICAL OCCURRENCE OF MAHONE PETROLEUM

The Mahoning River rises in Columbiana County, and flowing sinuously through Portage, Trumbull, and Mahoning Counties, finally enters the Ohio River. In Mahoning County the valley is a few miles in length, and its greatest width is 2800 ft. The wells drilled for oil vary in depth from 135 to 150 ft.; in one well the oil sand was reached at a depth of 115 ft. According to the report of the driller, the surface layer extends in a depth of 20 ft. to a bed rock of shales that are continuous to the oil-bearing sand. These shales are partly light and partly dark in color, and just above the upper layer, below the surface silt is a bed of sand and below that a bed of shale impregnated with bituminous carbon. The oil sand composed of rather coarse granules of very pure quartz is overlaid by a soapstone shale 14 ft. thick, and it extends to a depth of 105 ft., of which the upper coarser layer, 16–18 ft. thick, carries the oil above a large volume of water. Below this sand is a brown shale sixty feet thick, and below this a lighter shale extending to the Berea Grit.

So far as it appears from the 25 or more wells that have been drilled by the Mahone Oil and Gas Company, there are no restricted pockets in the oil strata, but a somewhat regular anticlinal and synclinal formation, the anticlinals approximately 20 ft. in height and 200–300 ft. in diameter. On account of the inertness of the crude oil, special care is necessary in drilling, and particularly in pumping: it is raised with some water into large settling tanks and the water drawn off. The daily yield from a single well is small; the largest daily output from any one well has been 8 barrels. There is evidently nothing especially striking in the formations connected with the occurrence of this petroleum, except the shallow depths at which the oil is found, and the absence of any complicated conditions connected with its origin.

As mentioned above, the Berea Grit appearing in this section as an underlying formation suggested the probability that the abundance of oil and gas elsewhere in this oil strata should likewise promise similar yields in this field. Accordingly a well was started with the intention of drilling to a sufficient depth to reach any possible deposits in this section of the Berea Grit. This well has been carried to a depth of 1800 ft. and will be continued with the expectation of reaching an abundant flow of gas and the lighter Berea Grit oil.

PHYSICAL CHARACTERISTICS AND COMPOSITION OF MAHONE PETROLEUM

Soon after the first wells were drilled, specimens of the oil placed in my hands for examination appeared to be so unlike any that had been brought to my attention, that I undertook a thorough study of the crude oil and the products to be obtained from it, both on account of its interest from a scientific point of view and the possibility of the preparation from it of commercial products. After three years with the aid of two assistants, although much has yet to be done on the composition of its constituents it seems advisable to place on record the accumulated observations on the nature of the crude oil.

This petroleum is quite dark, approaching black in color and it has scarcely any odor. In consistency it is very thick and viscous; its specific gravity taken from samples pumped at different times during three years gave, at 20° C., in four samples:

I	II	III	IV
9057	9036	9040	9036

showing practically no variation in different sections of the field during this period. Its extremely high viscosity—928—explains its former use as a lubricant without refining. Its refractive index as determined by the Abbé refractometer is 1.4878, a value unusually high as compared with other varieties of petroleum. So much attention has recently been given to the optical activity of petroleum, and rotation has been observed in so many varieties of crude oil and products of refining, that it became necessary to ascertain whether this petroleum was also optically active; but in neither the crude oil nor in any products separated from it could the slightest effect on the polarized ray be detected. Perhaps this is what should be expected in view of its composition which is much less complex than that of other varieties of petroleum, in fact consisting (as will be shown later) of a comparatively few hydrocarbons, so far as examined only of the series C_nH_{2n-2} and C_nH_{2n-4}.

In testing the crude oil for sulfur by decomposition with sodium and comparing the color given by potassium nitroferrocyanide with colors obtained from oils containing known percentages of sulfur, it gave a color corresponding to less than 0.01 per cent.[1] Inasmuch as petroleum dissolves sulfur to the extent of 3 per cent there are probably few crude oils that do not contain this element or its hydrocarbon derivatives. A wide range of crude oils tested by this method all gave colors for sulfur except such light varieties as those from Pennsylvania, West Virginia and the Berea Grit oils of southern Ohio, all of which consists very largely of the series C_nH_{2n+2}, including the solid paraffine hydrocarbons, none of which showed a trace of sulfur.

Nitrogen is a significant element relating to the formation of petroleum, since it has been assumed that nitrogen compounds in petroleum could have had their source only in organic matter of animal origin. In most varieties of American petroleum nitrogen has been identified—to the largest extent in California oils. It therefore seemed interesting to ascertain whether Mahone petroleum contains nitrogen: 5 grams of the oil were subjected to the Kjeldahl method with the precaution necessary to convert all the nitrogen of the possible pyridine or chinoline compounds into ammonia, and the resulting solution distilled, and Nesslerized. No trace of color appeared, thus excluding nitrogen as a constituent. A specimen of Pennsylvania petroleum tested in the same way gave not a trace of nitrogen as ammonia. The question as to the presence of nitrogen in other varieties of American petroleum will be determined in this manner.

Mahone petroleum is unique in composition in that it contains no hydrocarbon of the series C_nH_{2n+2}, gasoline or kerosene, and none of the series C_nH_{2n} that constitutes so large a proportion of Pennsylvania lubricants. So far as it can be distilled *in vacuo* this oil consists very largely if not entirely of the series C_nH_{2n-2}, and the series C_nH_{2n-4}. As to the composition of the residue of distillation above 350° under 30 mm. pressure nothing can be said, for at this point or perhaps somewhat lower in temperature the hydrocarbons simply fall asunder, having reached the limit of their capacity to maintain molecular composition, and the distillates come over as thinner oils. These changes are readily and accurately detected by the viscosity and cold tests of the distillates which without warning may change in viscosity from 250 to less than 100, and the cold test from —20 to +10°. Under atmospheric pressure the crude oil begins to distil at 230°, and at 250° it begins to decompose, breaking down into thinner oils. It will be interesting to ascertain the composition of these products of decomposition. If the distillation be continued beyond this point, the residue consists of a thin tar which, *in vacuo*, may be run down to within two per cent of residue without coking. The general distinction of the varieties of petroleum, those with a paraffine base and those with an asphaltic base, does not apply to Mahone petroleum, which contains neither paraffine nor the so-called asphaltic hydrocarbons. While the crude oil contains no crystalline hydrocarbons (at least none were observed at a temperature of —20°) when decomposition is caused by distillation, crystalline hydrocarbons appear in the residue, and in the higher distillates. There is a close connection between the formation of these

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[1] This is an extremely delicate test for sulfur in petroleum oils, and extremely accurate quantitatively based on the comparative depths of color given by oils with 0.1, 0.01, and 0.001 percentages as standards.

crystalline bodies and changes in the cold test. These changes are directly the opposite of those which occur under similar conditions in other petroleums where the tendency is toward a breaking down of the crystalline hydrocarbons into thin oils. Nevertheless the hydrocarbons in Mahone petroleum are remarkably stable in distillation when air is excluded and under diminished pressure. Distillates prepared in the course of this work were carried apparently unchanged as shown by analysis through fourteen repetitions, and as it seemed, the distillations could have been continued indefinitely without decomposition.

Determinations of carbon and hydrogen in the crude oil gave percentages corresponding to the series C_nH_{2n-2}: C, 86.42; H, 13.31. Assuming a mean composition represented by the formula $C_{20}H_{38}$, the proportions of carbon and hydrogen are: C, 86.33; H, 13.67. To separate the constituents of the crude oil, so far as it can be done by distillation *in vacuo* without decomposition, the light and heavy fractions from five gallons, separated first in iron stills, were carried through a prolonged series of distillations and finally collected within limits of single degrees under 30 mm. The lowest fraction came over in the vicinity of 90° and in quantity only 15 grams. Its odor resembled that of the terpenes—quite unlike the odors of the petroleum hydrocarbons. A somewhat larger amount, 35 grams, collected after the twelfth distillation at 97°–98°. Fractions also collected in much larger amounts at quite regular intervals of 10° as the distillation proceeded, as follows: 109°–110°, 40 grams; 120°–121°, 79 grams; 130°–131°, 143 grams; 138°–139°, 207 grams; 151°–152°, 300 grams; 161°–162°, 425 grams; 171°–172°, 500 grams. At higher temperatures there was still a tendency for quantities to accumulate but at somewhat longer limits, 15°. Hitherto, good evidence of the series C_nH_{2n-2}, and C_nH_{2n-4} in petroleum has been obtained in this laboratory, but the results herewith presented are conclusive and more comprehensive. The series in Mahone petroleum is defined by analysis, and the individual hydrocarbons by determinations of their molecular weights, which gave very satisfactory results by reason of the prolonged distillations on which an assistant was engaged nearly all his time during twelve months. All molecular weights were determined by the Beckmann freezing-point method.

The fraction 97°–98° was examined with considerable interest, for if any hydrocarbon of the series C_nH_{2n} were present in the crude oil it should appear at this point. But its molecular weight was found to be 153; calculated for the formula $C_{11}H_{20}$, 152; specific gravity at 20°, 0.8549. A combustion gave percentages required for the same formula: Carbon, 86.76; Hydrogen, 13.26; required for $C_{11}H_{20}$: Carbon, 86.84; Hydrogen, 13.26. It is, therefore, safe to conclude that the series C_nH_{2n} is not present in this petroleum. The fraction collected at 109°–110° gave as its specific gravity at 20°, 0.8576, and as its molecular weight, 166; required for the formula $C_{12}H_{22}$, 166. A combustion gave: Carbon, 86.49; Hydrogen, 13.44; required for the formula $C_{12}H_{22}$: Carbon, 86.74; Hydrogen, 13.26.

Hydrocarbons of this series with such low molecular weights have not hitherto been separated from petroleum. A hydrocarbon, $C_{13}H_{24}$, was identified in this laboratory as a constituent of Santa Barbara, Cal., petroleum, and several of the same series with much higher molecular weights from Ohio and Pennsylvania oils as constituents of lubricants prepared from these oils.

The composition of the fraction 120°–121° was shown by its molecular weight, 180.4; required for the formula $C_{13}H_{24}$, 180, and by combustion: Carbon, 86.72; Hydrogen, 13.33; required: Carbon, 86.66; Hydrogen, 13.34; specific gravity, 0.8614. Since the hydrocarbon separated from Santa Barbara oil was collected under 60 mm. and none of that product is still on hand, it cannot be compared with the one now under examination.

The molecular weight of the fraction 130°–131° was found to be 194; required for $C_{14}H_{26}$, 194. By combustion it gave: Carbon, 86.48; Hydrogen, 13.64; required: Carbon, 86.60; Hydrogen, 13.40; specific gravity at 20°, 0.8654.

A molecular weight determination of the fraction 138°–139° gave 206.7; required for $C_{15}H_{28}$, 208. It gave by combustion: Carbon, 86.38; Hydrogen, 13.64; required for $C_{15}H_{28}$: Carbon, 86.54; Hydrogen, 13.46; specific gravity at 20°, 0.8662. The fraction 151°–152° gave as its molecular weight, 218.7; required for the formula $C_{16}H_{28}$, 218. It gave by combustion the following percentages of carbon and hydrogen: Carbon, 87.07; Hydrogen, 12.88; required: Carbon, 87.28; Hydrogen, 12.72; specific gravity at 20°, 0.8692.

For the fraction 171°–172° was found the molecular weight 235; required for the formula $C_{17}H_{30}$, 234. A combustion gave the following percentages of carbon and hydrogen: Carbon, 87.02; Hydrogen, 12.90; required for $C_{17}H_{30}$: Carbon, 87.18; Hydrogen, 12.82; specific gravity at 20°, 0.8716. Of the higher fractions to be more fully examined later, that collected at 212°–214° gave as its molecular weight 263; corresponding to the formula $C_{19}H_{34}$, molecular weight 262. It gave, by combustion, percentages of carbon and hydrogen required by this formula: Carbon, 87.12; Hydrogen, 13.01; required for $C_{19}H_{34}$: Carbon, 87.03; Hydrogen, 12.97; specific gravity at 20°, 0.8790. The series C_nH_{2n-4} is, therefore, established as constituting much the larger part of Mahone petroleum so far as this examination extended. It appears also that as commercial products lubricants may be prepared from this crude oil that shall contain four hydrocarbons, and even only two, of this single series. This applies likewise to Texas petroleum since it has been found in this laboratory that the most valuable lubricants separated from that crude oil are composed of hydrocarbons of this series, C_nH_{2n-4}, as has also been shown for lubricants prepared from California petroleum.

These results are summarized in the following table:

Distillation temperatures	Sp. gr. at 20° C.	Actual determinations			Required			
		Mol. wt	C	H	for	Mol. wt.	C	H
97°–98°	0.8549	153	86.76	13.26	$C_{10}H_{20}$	152	86.84	13.16
109°–110°	0.8576	166	86.49	13.44	$C_{12}H_{22}$	166	86.74	13.26
120°–121°	0.8614	180.4	86.72	13.33	$C_{13}H_{24}$	180	86.66	13.34
130°–131°	0.8654	194	86.48	13.64	$C_{14}H_{26}$	194	86.60	13.40
138°–139°	0.8662	206.7	86.38	13.64	$C_{15}H_{28}$	208	86.54	13.46
151°–152°	0.8692	218.7	87.07	12.88	$C_{16}H_{28}$	218	87.28	12.72
171°–172°	0.8716	233	87.02	12.90	$C_{17}H_{30}$	234	87.18	12.02
212°–214°	0.8790	263	87.12	13.01	$C_{19}H_{34}$	262	87.03	12.97

The higher fractions will be more fully examined later.

INDEX OF REFRACTION

Three specimens of the crude oil collected in different years and from different wells gave the following indices of refraction in an Abbé refractometer at 26°:

I	II	III
1.4878	1.4878	1.4882

Fractions obtained by prolonged distillation as described above gave the following indices:

80°–81°	1.4499
97°–98°	1.4570
120°–121°	1.4625
138°–139°	1.4645
151°–152°	1.4688
230°–265°	1.4820
265°–315°	1.4879

These results were obtained after treatment with sulfuric acid; the indices were the same before and after this treatment.

ORIGIN OF MAHONE PETROLEUM

The question of the origin of petroleum has received profound attention both from geologists and chemists, but it is yet elusive on account of the difficulty of securing reliable data that should explain the conditions under which it was formed, and of accounting for the several series of hydrocarbons of which it is composed. Then, further, the absence of organic material as a possible source, and the geological disturbances associated with its present situation afford too meager information for its complete elucidation. In the petroleum under consideration several of these uncertain features were eliminated. In the first place, the shallow depths of the oil strata and its apparent common origin from vegetation with the extensive beds of coal close at hand indicate a more recent formation of these oil deposits than can be assigned to other well known varieties that occur at greater depths. In the Mahone field, the oil sand has evidently not been disturbed since the oil was therein accumulated. The neighboring coal strata suggested a coincident formation of the oil as an intermediary product between vegetation and coal and that subsequent geological conditions of heat and pressure forced out the liquid hydrocarbons forming the oil deposits as they now appear. This view of its origin is supported by recent experimental evidence. Pictet and Bouvier[1] distilled Montrambert (Loire) coal under 15–17 mm. pressure, and fractionated the tar. They isolated two hydrocarbons, $C_{10}H_{20}$ and $C_{11}H_{22}$, which they found to be identical with hydrocarbons separated from Canadian petroleum. After giving the closely agreeing values as to specific gravity, molecular weights, and refractive indices, they summarized the comparison as follows:

"Vergleicht man nun die von Mabery engegebenen Eigenschaften dieser beiden Fraktionen mit dienen unserer Kohlenwasserstoffe $C_{10}H_{20}$ und $C_{21}H_{22}$ aus dem Vakuumteer, so sieht man, dass sie sich ebenfalls fast genau decken. Die Uebereinstimmung ist eine so gute, dass man daran nicht zweifeln kann, dass es sich nicht mehr um isomere, sondern um identische Korper handelt, und dass im canadischen Petroleum und im Vakuumteer der Steinkohle von Montrambert dieselben Kohlenwasserstoffe $C_{10}H_{20}$ und $C_{21}H_{22}$ vorhanden sind. Mit andren Worten werden durch Vakuumdistillation gewisser Steinkohlen Korper gewonnen, die sich anderswo als Bestandteile gewisser Erdole vorfinden. Somit ist zum ersten Mal ein chemischer Zusammenhang zwischen den beiden Naturprodukten auf experimentellen Wege dargetan."

The last important statement may be translated as follows:

Therewith for the first time is a chemical connection between both these natural products (coal and petroleum) established by experiment.

The complete absence of the series C_nH_{2n+2} is not unusual; those hydrocarbons are wanting in most heavy varieties, but the series C_nH_{2n} is more frequently present. In composition, Mahone petroleum evidently stands between varieties with the so-called paraffine base, such as Pennsylvania and Ohio on the one hand, and those with an asphaltic base such as the Texas and California varieties on the other. The absence of paraffine is significant since it shows that the oil as originally formed has all been converted into series with less hydrogen. Likewise the absence of asphaltic constituents is significant as indicating that the changes in formation have not been such as to include these bodies poorer in hydrogen, either through the agency of heat or pressure, or by the prolonged action of sulfur on the atmosphere, which no doubt are concerned with the formation of natural asphalts.

The determining influence of sulfur and oxygen in the primary formation of the principal constituents of petroleum evidently cannot be disregarded in attempting to account for their origin. As mentioned above, the heavy varieties of petroleum dissolve sulfur to the extent of three per cent of their weight. I found that one variety of Texas oil, the "Humble Crude," contained three per cent of sulfur, the greater part as the element in mechanical solution. Much the larger proportion of the world's supply of petroleum contains sulfur in considerable quantities, in part, in the form of hydrocarbon derivatives, such, for example, as compounds of the series $C_nH_{2n}S$ which were identified in this laboratory as constituents of Ohio, Indiana, and Canadian petroleum.

In a paper published several years ago I expressed the opinion which was quoted by Engler in "Das Erdöl," that petroleum containing sulfur probably had its source in organic remains of animal origin. But more recent study of the relations of sulfur and petro-

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[1] *Ber. d. chem. Ges.*, Nov., 1913, 3342.

leum hydrocarbons especially in connection with crude oils from the Texas fields makes it plain that any petroleum may contain sulfur whatever its origin, provided it comes in contact with native sulfur which is widely distributed.

As is well known any hydrocarbon heated with sulfur loses hydrogen and evolves H_2S; if the hydrocarbon be of the series C_nH_{2n+2} it is pretty certain under carefully regulated conditions that the hydrocarbon nucleus will combine with more of the sulfur but this feature of its action has not been fully verified. In the study of the hydrocarbons distilled from coal by Pictet and Bouvier it was found that H_2S was evolved when the hydrocarbons were heated with sulfur and that sulfur derivatives were formed. On account of the instability of the sulfur derivatives of the hydrocarbons, unless special care is exercised, it is probable that the principal products should be hydrocarbons poorer in hydrogen, such as the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, that constitute the main body of petroleum. The formation of the great quantities of hydrogen sulfide that escape from many oil wells takes place freely under the influence of heat and pressure; it may be by simple contact under pressure in long geological periods. Experimentally by prolonged heating with sulfur the lighter hydrocarbons may be converted into solid asphalts.

All natural asphalts contain sulfur to a greater or less extent, and in view of its ready action on the hydrocarbons it is safe to conclude that it has had much to do with their formation. What most impresses a visitor to the great asphalt lake on the Island of Trinidad, is the question as to its formation. On observing close at hand, however, numerous petroleum wells with a large output, and bearing in mind the large amounts of sulfur contained in these immense beds of semi-solid bitumen, the answer is not far to seek.

The instability of the petroleum hydrocarbons in presence of air is a matter of common observation in the manipulation of crude oil and its products. In lighter refined oils on standing color reappears. During distillation the heavier constituents increase in gravity, finally forming asphaltic residuum and coke. The difficulties arising from this influence of oxygen are the most perplexing of all that beset the arduous duties of the refiner. This action of oxygen on the hydrocarbons is taken advantage of in the Byerley process for the conversion of residuum into hard asphalts by passing air through the residuum at carefully regulated temperatures. Evidently all changes of this nature with oxygen as with sulfur depend on the abstraction of hydrogen; it is doubtful whether under these conditions oxygen enters at all into combination with the hydrocarbon nucleus.

While a full explanation of the origin of petroleum should include a plausible source of all its constituents, sulfur and nitrogen derivatives, phenols, acids, and aromatic hydrocarbons, the fundamental demand is for a clear statement based on experimental data concerning the principal series of hydrocarbons. The unquestionable source of the petroleum hydrocarbons is organic remains either of vegetable or animal origin, it matters little which, for either is experimentally known to yield hydrocarbons by decomposition. In one section of oil territory it may have been the enormous growth of the carboniferous age that gave the coal; in other sections it may have been the extensive beds of sea weeds, and in still another the organic remains of the great masses of shells that have formed the limestones and dolomites.

Reichenbach was the first to recognize the presence of paraffine in the products of decomposition of organic matter, and it has since been frequently obtained with its lower congeners from various animal and vegetable sources. Breaking down of paraffine into lower members of the same series under the influence of heat and pressure was observed by Thorpe, and no doubt this experimental formation is a close duplicate of similar changes produced in long periods of time under natural agencies. Even when heated with exposure to air, paraffine gradually breaks down to lower hydrocarbons. It is certain that these changes are not possible in the reverse order, that is, the production of paraffine from lower hydrocarbons. In such molecular decompositions by a simple break in the hydrocarbon chain, a paraffine hydrocarbon, for example, $C_{25}H_{52}$, should give one $C_{12}H_{26}$, and one $C_{13}H_{26}$, or by simple loss of hydrogen it should give $C_{25}H_{46}$ of the series C_nH_{2n-4}. Evidently in such decompositions other bodies are formed even proceeding as far as marsh gas. A great variety of such changes are experimentally possible especially with the aid of sulfur or atmospheric oxygen, and in the earth with the aid of natural heat and pressure, yielding as final products the asphalts, or proceeding directly from vegetation to the beds of coal. These changes together with possible evaporation doubtless explain why the series C_nH_{2n+2} is not found in the heavier varieties of petroleum.

In studying the characteristics of these series as they appear in extended distillation up to the breaking point, together with their behavior toward oxygen and sulfur, one can hardly escape the conviction that the hydrocarbons which constitute the main body of all varieties of petroleum have been formed from organic matter in nature's laboratory by these progressive changes. Certainly any attempt to account for the origin of petroleum must be based on its composition which includes principally the series of hydrocarbons above mentioned, and the fact that changes in composition are always in the direction of the lower series and lower members, with loss of hydrogen.

In the origin of Mahone petroleum the influence of sulfur was precluded, for the oil is practically free from this element. By reason of the shallow depths of the porous strata, contact with air was possible with its influence in removing hydrogen, but this action did not continue beyond the formation of the few series of hydrocarbons which the crude oil contains, since the oil is free from the asphaltic hydrocarbons. These porous conditions were likewise favorable for the escape of the hydrocarbons C_nH_{2n+2} and C_nH_{2n}. Its proximity to the coal, its shallow occurrence, and the experimental results of Pictet and Bouvier are pretty conclusive evidence that the oil was exuded from the coal doubtless long subsequent to its formation, and perhaps with later changes in composition. This connection between Mahone petroleum and the neighboring coal will receive further attention in this laboratory, together with the products of distillation of the natural asphalts.

On account of the simple composition of Mahone petroleum and its freedom from deteriorating bodies it is especially adapted for the preparation of superior lubricants. In the absence of gasoline and kerosene hydrocarbons, paraffine or other crystalline bodies, with due precautions, distillates may be obtained with extremely low cold tests. So long as the hydrocarbons C_nH_{2n-4} remain intact they constitute the most durable body in lubrication that it is possible to prepare from petroleum. The lighter hydrocarbons of the series C_nH_{2n-2} with lower viscosity, 100° to 125°, have similar qualities. This petroleum, therefore, yields a range of lubricants especially adapted for delicate mechanism from a chronometer to a sewing machine, and they are widely in use as prepared by the Eagle Lubricant Manufacturing Company.

With reference to the formation of petroleum in general, no additional evidence concerning its geological occurrence has been forthcoming within recent years. More extended knowledge as to its composition and the relations of its constituents have an important bearing on its origin. All published results and opinions bearing on the chemical aspects of its origin were recently thoroughly reviewed by Engler ("Das Erdöl", Leipsic, 1912). The theory of its formation from carbides, suggested by Mendeléeff and more forcibly presented by Moissan and accepted ten years ago as a plausible theory, is now generally considered as involving too many hypotheses and subsequent changes. Earlier views of the transportation or migration of petroleum from the place of its origin to other strata are no longer generally accepted. Filtration was possible of the thinner varieties. That Ohio and Indiana petroleum was formed from the remains of shell fish coincident with the formation of its Trenton limestone habitat as ably maintained by Orton admits of no other explanation. The same may be said of Hunt's views as to the formation of petroleum in the Corniferous limestone.

Under the term bitumen is included natural gas, petroleum, natural asphalts, and coal—the "organoids" (Engler)—with a closer similarity between the members of the group than has been hitherto admitted, especially in their primal evolution. It seems evident that the formation from vegetation of Pennsylvania petroleum as well as of other similar oils which consist mainly of the hydrocarbons C_nH_{2n+2}, was accompanied by less chemical change than that of other varieties. The vegetable matter first gave paraffine as the principal product, which by natural agencies broke down into lower hydrocarbons. Then Pennsylvania petroleum was not subject to the action of sulfur which has been evidently an active agent in the formation of the heavier varieties.

Between the Pennsylvania type of petroleum and the asphalts and coals there are all stages of variation in composition resulting from the greater or less chemical changes in the primary series of hydrocarbons. Since sulfur is associated with all the heavier varieties of oil, asphalts, and coal, as well as a part of their composition, from what is known concerning its action on the hydrocarbons, it is difficult to escape the conviction that this element was largely instrumental in forming the series of hydrocarbons poorer in hydrogen that constitute the principal body of all these natural products. Only a moderate increase in temperature is necessary for its action, and such temperatures are quite sufficient to account for the loss of hydrogen even to carbonization as in the formation of coal. But since in the coals are still to be found petroleum hydrocarbons, the similar origin of coal and at least some varieties of petroleum is evident. Unquestionaby the vast deposits of oil in Texas were formed in a manner analogous to those in Pennsylvania, probably from vegetable matter and that through their association with extensive beds of sulfur, the series C_nH_{2n+2} disappeared completely by conversion into the series with less hydrogen including the asphaltic hydrocarbons.

In the immense fields of California of more recent origin where the oil contains large proportions of nitrogen and sulfur compounds, aromatic hydrocarbons, and an exceptionally large proportion of asphaltic bodies, there is good evidence of the action of sulfur. With reference to the large amount of nitrogen compounds contained in California petroleum, they could evidently have been formed from vegetation and their presence may be explained by their recent origin of which there is undoubted evidence in some of the California fields. That the older oil deposits in Pennsylvania and Texas contain only very small proportions of nitrogen compounds, may have resulted from the breaking up of these compounds and their disappearance in the longer periods of time. The swarming maggots that have been observed in some California petroleum are doubtless the result of bacterial action on the products of decayed vegetation. It, therefore, seems evident that the origin of California petroleum must also be looked for chiefly, if not entirely, in the decay of vegetation and that the hydrocarbons of which California oil now consists were formed primarily from the series C_nH_{2n+2} by loss of hydrogen.

At any rate, whatever conclusion is reached as to the source of the bitumens, it must be in accordance with the predominating characteristic of the hydrocarbons to lose hydrogen and to break down from those most highly hydrogenized through lower series to the asphalts and even to coal. It should also account for a closer relationship in origin between the deposits of coal, asphalts and petroleum than has hitherto been recognized.

While these views are evidently in some respects at variance with those formerly expressed, if as it seems plain, the origin of petroleum as well as of the other bitumens, is to be explained more directly on the basis of its composition, and the chemical changes to which it has been subjected in, and since, its evolution from organic matter, the question as to its history is divested of many complicating assumptions, and greatly simplified.

I should acknowledge my obligations to Mr. James Graham for assistance in the experimental work of this paper.

CASE SCHOOL OF APPLIED SCIENCE
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THE PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE[1]

By HERBERT T. KALMUS

In connection with the work on cobalt it has been necessary to prepare considerable quantities of the metal in as pure a state as possible. Nearly 1000 pounds of commercial black cobalt oxide have been given to this laboratory for these researches by the Deloro Mining and Reduction Co. of Deloro, Ontario, to whom we take this opportunity of expressing our thanks.

The writer wishes to acknowledge the work of Messrs. C. Harper, W. L. Savell, C. W. Day and R. Wilcox, who, in the capacity of research assistants at these laboratories, have done most of the actual experimenting. To Professor S. F. Kirkpatrick of the Department of Metallurgy, Queen's University, thanks are due for many valuable suggestions.

The process for the preparation of fairly pure cobalt oxide has been very completely worked out, and has been practised on a large scale at several Canadian smelters. For this reason the oxide was chosen as a raw material from which to prepare the metal. As the work progressed, it became more and more apparent that some of the uses for cobalt which were being demonstrated at these laboratories and elsewhere, would lead to the preparation of the metal in large quantities. Hence, it became of increasing importance that the metallurgy of the preparation of the metal from the oxide be studied, and this has been done with greater care than was necessary merely for the production of the quantities required for experimental purposes. There are four important reducing agents for obtaining metallic cobalt in reasonably pure form from commercial cobalt oxide. They are: I, Carbon; II, Hydrogen; III, Carbon Monoxide; IV, Aluminum.

The Co_3O_4 used[2] for these experiments was made from cobalt hydrate, precipitated by bleach from a cobalt chloride solution. This hydrate, in contact with the atmosphere, is greenish black in color. It was calcined at 750° C., yielding a black oxide of approximately the composition Co_3O_4. This is shown by the following analyses, made at widely different times, which are typical of a large number:

ANALYSES OF PURIFIED COBALT OXIDE (PERCENTAGES)

	June, 1912	November, 1912	April, 1913
Co	71.99	71.52	72.3
Fe	0.11	0.27	0.10
Ni	0.040	0.020	Trace
S	0.020	Trace	0.052
Ca	0.030	...	0.15
SiO_2	0.19	0.18	0.39

The oxides corresponding with the theoretical formulas would have cobalt content as follows:

Formula	Percentage, cobalt
Co_2O_3	71.1
Co_3O_4	73.4
Co_6O_7	76.0
CoO	78.8

It is obvious then, when we take into account the portion of the sample which is not cobalt oxide, that the oxide itself is largely Co_3O_4. It is not necessary for the purpose of our calculations to assume that this oxide alone is present, for we shall base our computations upon the actual analyses as we have found them. However, in writing the reactions throughout this paper, we shall, for simplicity, consider the oxide to be Co_3O_4.

PURIFICATION OF COBALT OXIDE

Cobalt oxide as we obtained it from the smelters, and as sold on the market, analyzed approximately as follows:

Barrel 1	Percentages	Barrels 3 and 4	Percentages
Co	70.36	Co	69.2
Ni	1.12	Ni	1.4
Fe	0.82	Fe	0.50
S	0.45	CaO	0.37
As	0.10	S	0.54
SiO	0.20	Insoluble	1.46
Ca	0.50	Ag	Trace

Analyses, of course, vary considerably from one shipment to another; the above samples are high in Fe, S and Ca, and would be considered by most smelters as No. 2 grade.

Metal produced from oxide analyzing as above, by the method to be described, is of sufficient purity for most purposes. This is especially true if lime be added to the melt to slag off the sulfur. However, for other purposes metal is required in which the impurities, nickel, iron, sulfur, arsenic and silica, are reduced to very small percentages. In this case it is best to remove these impurities from the oxide before reduction. Starting with a crude cobalt oxide, these impurities may be reduced as far as is desired by the following procedure:

SILICA—Dissolve the crude oxide in hydrochloric acid according to the reaction:

$$Co_3O_4 + 8HCl = 3CoCl_2 + 4H_2O + Cl_2$$

This may be done best by heating and agitating with steam. If silica is present, it will not dissolve, and may be removed by filtration or decantation. The same is true of silicates which are not decomposed by this treatment. Decomposable silicates would send a certain amount of silica into solution, which would be thrown out during the next step.

IRON AND ARSENIC—To the cobalt chloride solution formed by dissolving the oxide in hydrochloric acid,

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[1] Author's abstract of report under the above title to the Canadian Department of Mines. Published by permission of the Director of Mines, Ottawa, Canada. The general investigation of the metal cobalt and its alloys, with reference to finding increased commercial usages for them is being conducted at the School of Mining, Queen's University, Kingston, Ontario, for the Mines Branch, Canada Department of Mines.

[2] For a consideration of the various oxides of cobalt, including the proof that the black oxide used for these reductions was largely Co_3O_4, see the following article, page 115.

gradually add finely divided $CaCO_3$ or pure marble, until no further precipitate is formed. The heavy brown mud precipitated contains the iron and arsenic content of the original oxide.

NICKEL—For most purposes it will not be necessary to separate the small amount of nickel from the cobalt, but it may be done as follows: The cobalt chloride solution, containing a certain amount of nickel chloride, is of an intense red or claret color. Add a solution of bleach to the solution until it has almost completely lost its color. The bleach solution differentially precipitates hydrates of nickel and cobalt, so that the nickel is not appreciably brought down until the cobalt has been almost entirely precipitated.

The bleach will precipitate a black hydrated oxide of cobalt, and the diminishing redness of the solution will indicate the end point. If all of the steps above outlined have been applied to the original oxide, this final black precipitate may be calcined at about 750° C., to yield black Co_3O_4.

SULFUR—Any sulfur present in the original oxide and carried through to the final product, or introduced with the bleach, may be removed by boiling the final dried oxide with sodium carbonate and dilute hydrochloric acid. The reaction is:

$$CaSO_4 + Na_2CO_3 = Na_2SO_4 + CaCO_3$$

The soluble sodium sulfate formed is washed out with water. A further washing is given with dilute hydrochloric acid, which decomposes the calcium carbonate into soluble calcium chloride and CO_2 gas. The $CaCl_2$ is washed out with water. This method is, of course, applicable only for the removal of the small percentages of Ca and S found in the oxides in question.

A shipment of oxide from the smelter was analyzed before and after treatment by the above method, with the following results:

Percentages	Before	After
Co	70.36	71.99
Ni	1.12	0.041
Fe	0.82	0.11
S	0.45	0.020
Ca	0.50	0.021
As	0.10	None
SiO_2	0.20	None

There are other obvious methods of purifying the Co_3O_4. For example, the bleach solution may be freed of its SO_4 content with $BaCl_2$, and the Ca and excess Ba precipitated with Na_2CO_3, thus yielding a fairly pure solution of soda bleach. The SO_4 content of the $CoCl_2$ solution may be precipitated with $BaCl_2$ and the differential precipitation of cobalt and nickel accomplished with the purified solution of soda bleach.

I—REDUCTION OF COBALT OXIDE WITH CARBON

METHOD OF EXPERIMENT—These experiments all consisted in intimately mixing definite amounts of finely divided carbon in various forms with Co_3O_4, and heating the mixture to constant temperature for a measured time. The charges employed varied in size from a few grams to 10 lbs., and were heated in lined and unlined graphite crucibles, and in porcelain crucibles.

FURNACES—The reduction took place either in an oil-fired "Steele-Harvey" furnace of 60 pounds, metal capacity, No. 20 crucible, which could be controlled at any temperature up to 1550° C., or in a modified Hoskins electric resistor furnace. This latter has a heating chamber, 8 inches cube, which can be maintained constant to within about 10–20° C., at any temperature up to 1650° C. Some of the small charges were run in porcelain crucibles heated within an electric resistor furnace.

The reactions for the reduction of cobalt oxide with carbon are:

$$(1)\ Co_3O_4 + 4C = 3Co + 4CO,$$

$$\text{and } (2)\ Co_3O_4 + 4CO = 3Co + 4CO_2;$$

$$\text{or, combining } (3)\ 2Co_3O_4 + 4C = 6Co + 4CO_2.$$

If all the oxygen for the oxidation of the carbon be supplied by the cobalt oxide, and if all the carbon be burned to CO_2 then the reaction goes according to the last equation.

In practice, neither of these conditions is strictly obtained, but with proper design of furnace they may be closely approximated.

THE RUN—In each case the charge was made up by intimately mixing a weighed amount of finely divided oxide with a weighed amount of finely ground carbon. This mixture was placed in the crucible, which, with its charge, was placed either in the Steele-Harvey oil furnace or in the electric furnace. The mixture was frequently stirred with an iron rod during the reduction.

THE CARBON—The form of carbon chosen for the reduction, whether powdered charcoal, coke, coal, etc., depends somewhat upon the impurities from which it is desirable to keep the resulting metal free, but also this choice greatly influences the speed of the reduction.

Three sets of experiments were made with powdered anthracite coal, while further runs were made with lampblack or with powdered charcoal. The carbon was in all cases powdered to an extremely fine flour.

TEMPERATURE MEASUREMENTS—Temperature readings were made at frequent intervals with a platinum platinum-rhodium thermo-element, with a Wanner optical pyrometer, or with a Féry radiation pyrometer, and the furnace adjusted to keep the temperature constant to within about 20°.

The charge was put into the crucible which was within the furnace, both crucible and furnace being at a temperature somewhat higher than the intended temperature of the run. Some of the smallest charges were inserted with containing crucible. It was learned, by experience, for the different sizes of charge and qualities of crucible, at about what temperature to maintain the furnace prior to inserting the charge, in order that the charge might come to the desired equilibrium temperature, with proper furnace adjustment, in about ten minutes. There is, therefore, a period of about ten minutes, at the beginning of each run, during which the average temperature of the charge is not as high as that noted with the Wanner optical pyrometer, which observes the surface of the charge. We satisfied ourselves that the center of the charge was at the same temperature as the surface, within 20 or 30° C., after the first ten minutes, by exploring the center with a thermo-element, and noting simultaneously its readings and those of another thermo-element near the surface, and of the Wanner optical pyrometer.

In the following runs we have not attempted to make a correction for the lag in coming to temperature during these first ten minutes. This lag would be considerably less than ten minutes for the smallest crucibles used, about ten minutes for the four-pound charges, and possibly as long as twenty minutes in the worst cases, with the ten-pound charges.

The oxides used for the runs reported in Tables I and II analyzed as follows:

	Percentages		
Runs	A-H		RI-RVIII
Co	71.36		69.2
Ni	1.12		1.4
Fe	0.82		0.50
S	0.45		0.54
Ca	0.50	CaO	0.37
As	0.10	Insoluble	1.46
SiO_2	0.20	Ag	Trace

The anthracite coal used was very finely powdered. In the typical runs A–H, No. 12 unlined carbon crucibles were used, and the charge was stirred every ten minutes during reduction. In these runs no attempt was made to show the progress of the reduction, but at the close of the run the charge was raised as rapidly as possible to the melting point and the melt poured into an iron mould to be weighed. Considerable reduction must take place during the interval of melting the charge after the close of the run. The purpose of these particular runs was to study the yields under somewhat the same conditions which must necessarily obtain in practice. In the runs I–VIII, No. 20 unlined carbon crucibles were used; no attempt was made to obtain a yield. They are intended to show the progress of the reduction.

TABLE I—REDUCTION OF Co_3O_4 WITH POWDERED ANTHRACITE COAL (A)
RUNS A, C, H—HARVEY-STEEL OIL FURNACE
G, B, D, E, F—ELECTRIC CRUCIBLE FURNACE

No. of run	Charge Co_3O_4 Lbs.	Charge Coal Oz.	Average temperature ° C.	Time of reduction Min.	Yield of cobalt Lb.	Yield of cobalt Oz.	Yield of cobalt Per cent of theoretical	Per cent carbon in metal
A	5	8.3	1200	90	3	1.5	87	...
C	4	6.9	1200	30	2	12.5	98	0.18
H	10	16.0	1200	105	6	9	92	0.086
G	4	6.6	900	150	2	13	99	0.21
B	4	6.54	1200	60	2	13	99	0.29
D	4	6.9	1200	120	2	13.5	100	0.20
E	4	6.9	1500	60	2	11.75	96	0.22
F	4	6.6	1500	90	2	12.7	98	0.23

A—Considerable unreduced oxide slag. Carbon used is approximately the theoretical amount according to reaction (3).

C—Melt free from unreducible oxide slag. Carbon 10 per cent in excess of theoretical requirement.

H—3 oz. lime added shortly before pouring. Carbon, theoretical amount.

G—At end of 2.5 hours, charge not completely reduced, but completed during subsequent raising to melting point.

TABLE II—REDUCTION OF Co_3O_4 WITH POWDERED ANTHRACITE COAL (B)
HARVEY-STEELE OIL FURNACE

No. of run	Charge Co_3O_4 Lbs.	Charge Coal Oz.	Average temp. ° C.	Reduction time to removal of sample Minutes		Per cent Co in sample(*a*)	Reduction complete = 100
I	10	17.5	601	R2	82	73.6	Very slight
II	10	16.5	750	R3*b*	91	74.1	Very slight
III	10	16.5	888	R4*b*	90	73.8	Very slight
IV	10	16.5	1057	R5*b*	95	80.8	28
VI	10	16.5	1203	R6*a*	30	81.3	30
				R6*b*	49	93.0	74
VII	10	16.5	1283	R7*a*	31	91.1	70
				R7*b*	47	93.9	77
VIII	10	17.4	1502	1	11	76.7	12
				2	16	81.8	32
				3	21	91.0	66
				4	26	93.9	77
				5	31	93.9	Apparently some oxidation
				6	36	91.8	

(*a*)These analyses are for cobalt, nickel and iron combined, of which about 97 per cent was cobalt, as may be seen from the analysis of the original oxide. Carbon analyses were of course made, and the percentage of cobalt given in this column takes into account the residual carbon.

It will be noticed in the above runs with powdered anthracite coal that the reductions are extremely low. It was, therefore, thought advisable to check these runs with experiments on a very small scale in porcelain crucibles, in such a manner that there could be no doubt as to the time during which the charge was maintained at the temperature in question.

A number of such runs was made with a thermo-element near the center and at the outside of the charge. In the small furnace used, the crucible with its charge came to temperature in a very few minutes, so that the outside and inside thermo-element agreed to within 20° C. Approximately this condition was maintained throughout the run.

The results of the previous runs with powdered anthracite coal were confirmed by these small scale runs, and a satisfactory complete reduction could not be obtained at temperatures much below 1200° C.

REDUCTION OF Co_3O_4 WITH POWDERED CHARCOAL

Further experiments were tried on the reduction of Co_3O_4 with very finely powdered charcoal. A large number of these gave fairly concordant results, which showed a greater reduction at all temperatures than the corresponding powdered anthracite coal runs.

Without giving the details of about twenty-five runs, it may be said that complete reduction was obtained with from 20 to 30 per cent excess of powdered charcoal, at 900° C. or over, in less than an hour. At 1000–1100° C., the reduction with powdered charcoal was very much more rapid than at 900° C., often completing itself in less than 10 minutes. Of course, the time required depends, to some extent, upon the size of the furnace and charge.

REDUCTION OF Co_3O_4 WITH LAMPBLACK

Experiments on the reduction of Co_3O_4 with lampblack were tried with results identical with those on the reduction of Co_3O_4 with powdered charcoal.

BRIQUETS—Experiments on the reduction of Co_3O_4 with powdered charcoal were tried, forming the charge into briquets. A small[1] percentage of molasses was used as a binder. These experiments were made under the same furnace and temperature conditions as those on the reduction of Co_3O_4 with powdered charcoal in bulk. Seven such runs showed, throughout, that the reduction was not very different in its velocity from the corresponding runs with powdered charcoal, although the difference was uniformly in favor of the briquetted charges. A satisfactory reduction

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[1] The molasses would correspond to the addition of about 1 per cent carbon.

could probably not be made at temperatures below 800–850° C., even briquetting the charges, as compared with 900° C. for the charges in bulk.

The preparation of metallic cobalt by reduction in briquets or rondelles offers distinct commercial advantages in that the resulting metal is in a salable form without further melting and casting.

THE METAL—The metal produced by reduction of cobalt oxide with carbon is sufficiently pure for most purposes; it need not contain more than a few tenths of a per cent of carbon. The following characteristic analyses are taken at random from a large number to show the nature of the metal:

Analyses of Metallic Cobalt Produced by Reduction of Commercial Cobalt Oxide with Carbon (Percentages)

	7——12	8–15–12	10–10–12	10–11–12	6–11–13
Co	97.05	98.50	98.84	98.62	98.30
Ni	1.50	0.65	0.61	0.50	Trace
Fe	1.00	0.58	0.56	0.15	1.39
S	0.22	0.47	0.21	0.22	0.46
C	0.20	0.22	0.24	0.13	...
Ca	0.25	0.60	0.24	0.27	0.58
Mn	...	...	0.06	...	...
As	...	...	...	...	0.11
SiO_2	0.12	0.13	0.14	0.11	0.12

It is obvious that the oxides taken for reduction with carbon were those directly from the smelter, which had not been treated by the method outlined above to remove the impurities. The iron, nickel, sulfur and silica content could have been reduced to mere traces by purifying the oxide before reduction in accordance with the method given. We have done this repeatedly, where a pure metal was required for experimental purposes. It is, however, of importance to note that metal with very low carbon content may be made by direct reduction of the oxide with carbon.

CONCLUSIONS

I. Reduction of Co_3O_4 with powdered anthracite coal does not take place rapidly enough to make it commercially interesting, either in the oil-fired crucible type of furnace or in the electric crucible type of furnace, until a temperature in the neighborhood of 1200° C. is reached.

II. In either the oil-fired crucible type of furnace or in the electric crucible type of furnace, substantially complete yields of metallic cobalt may be obtained by reduction of Co_3O_4 with powdered anthracite coal, in the neighborhood of 1200° C., for not more than 1 hour, with subsequent rapid melting and pouring.

III. With the oil-fired crucible furnace, using unlined graphite crucibles, complete yields are obtained with powdered anthracite coal only when there is an excess of approximately 10 per cent of this latter.

IV. With the electric crucible type of furnace used by us, complete reduction may be obtained, using only the theoretical quantity of powdered anthracite coal. In this furnace there is a considerable reduction due to the carbon monoxide atmosphere caused by the carbon resistor plates.

V. Both in the oil-fired and in the electric crucible type of furnace, greater reductions of Co_3O_4 are obtained using powdered charcoal than with powdered anthracite coal, at corresponding temperatures.

VI. With the oil-fired or electric crucible type of furnace, complete reduction may be obtained with powdered charcoal at 900° C. or higher. For this reduction a considerable excess of charcoal was required: under our conditions from 20 to 30 per cent.

VII. Powdered lampblack shows results in accordance with those for powdered charcoal.

VIII. Briquetting the charges with an organic binder tends to increase the rate of reduction at all temperatures. A minimum of about 800° C. may be employed for the reduction of Co_3O_4 with charcoal in the form of briquets as against 900° C. for the same charge in bulk.

IX. With sufficient carbon to get a complete yield of metal, the final product need contain only about 0.2 per cent of carbon.

X. At this laboratory, in an electric furnace not especially designed for this work, we reduce enough oxide to make 56 pounds of the metal in an eight-hour day, with the furnace absorbing 12 kw. Thus, on a commercial basis, the power charge for this reduction would be small.

II—PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH HYDROGEN

METHOD AND APPARATUS.—These experiments consisted in placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of hydrogen gas was passed through the furnace. A schematic sketch of the apparatus is shown in Fig. 1.

After purification, the hydrogen entered the furnace at F and the excess was burned at B. During the run the exit for the gas was through the by-pass PB, the end Q being sealed.

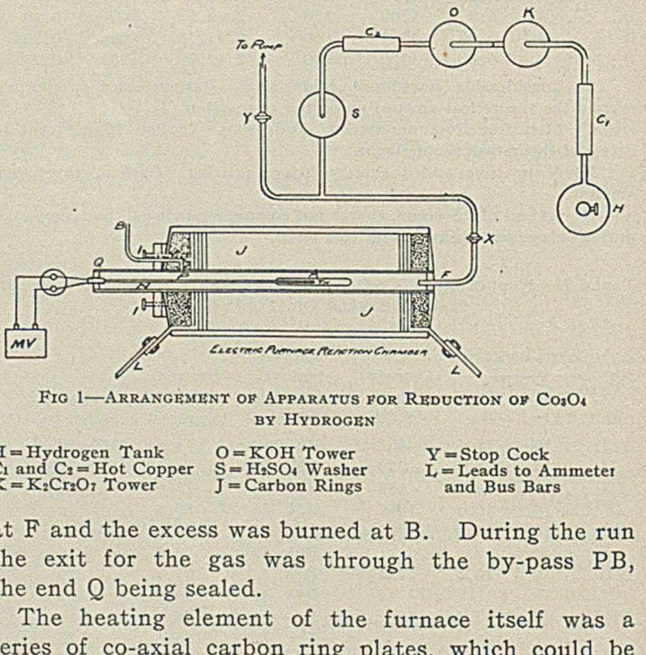

Fig 1—Arrangement of Apparatus for Reduction of Co_3O_4 by Hydrogen

H = Hydrogen Tank
C_1 and C_2 = Hot Copper
K = $K_2Cr_2O_7$ Tower
O = KOH Tower
S = H_2SO_4 Washer
J = Carbon Rings
Y = Stop Cock
L = Leads to Ammeter and Bus Bars

The heating element of the furnace itself was a series of co-axial carbon ring plates, which could be pressed together more or less tightly by suitable screws. The furnace was supplied with alternating current at 25 volts from a transformer, and could be controlled at any temperature up to 1350° C.

The details of the furnace are shown in Fig. 2. The temperature measurements were made by a platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter. In this way, the temperature was maintained substantially constant by hand regulation of the screws I. All temperature measurements were made with thermo-elements calibrated at frequent intervals, in the usual way, against known melting points.

CONDUCTING A RUN—After having heated the furnace to the desired temperature, by a suitable current through the carbon rings, runs were made as follows:

(*a*) After closing the cock X, which separates the purifying system from the furnace, the air was exhausted from the hydrogen system by opening cock Y, and operating a pump.

(*b*) Gas burners were lighted to heat copper filings in tubes C_1 and C_2.

(*c*) Solutions of potassium bichromate, potassium hydrate and sulfuric acid were started flowing through the purifying towers K, O and S, which were partially filled with glass beads.

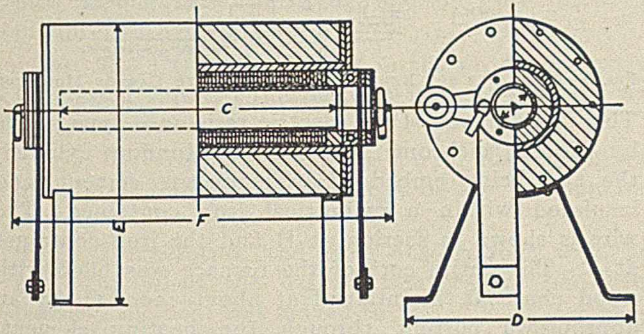

FIG. 2—DETAILS OF ELECTRIC FURNACE FOR REDUCTION OF Co_3O_4 WITH HYDROGEN

(*d*) Cock Y was closed and cock at outlet of hydrogen tank H was partially opened to allow a flow of hydrogen into the purifying system, until the pressure inside the system was a little greater than atmospheric pressure.

(*e*) Cock X was now opened to allow hydrogen to flow into the hot furnace.

(*f*) Flow of hydrogen was adjusted by cock at outlet of hydrogen tank H, until hydrogen burned freely at outlet end of furnace B. During the run the end Q was closed, and the gas escaped through the by-pass P-B.

(*g*) When adjustment (*f*) was satisfactory, assuring an excess of hydrogen within the furnace, the weighed dried alundum boat, containing the charge of cobalt oxide, was placed in the hot furnace at the position A, and the time noted.

(*h*) The run proper had now begun, during which observations of time, temperature, and power were made, and the furnace adjusted to keep the temperature constant.

(*i*) After a definite time, the boat, with its contents, was withdrawn from the centre of the furnace to the overhanging cool end of the furnace core N, in which it was allowed to cool, but through which, during the cooling, hydrogen was passed.

(*j*) When cool, the boat was removed to a desiccator and weighed.

II—COBALT OXIDE REDUCTION WITH HYDROGEN—COOLING IN AN ATMOSPHERE OF HYDROGEN

The cobalt oxide used for the following runs, I to IX, analyzed as follows in percentages:

Co..........	72.3	Ca.........	0.15
Ni..........	Trace	S...........	0.052
Fe..........	0.10	SiO_2.........	0.39

It will be noticed that this oxide contained 72.4

TABLE III—REDUCTION OF COBALT OXIDE WITH HYDROGEN

Number		Temperature ° C.		Time of reduction	Loss in weight	Reduction 100 =
Run	Boat	Mean	Average deviation	Minutes	Per cent	complete
I	I	585	1.3	5	25.5	94.2
				15	25.4	94.0
	II(*a*)			5	25.8	95.6
II(*b*)	I	584	1.0	15	26.0	96.2
				30	26.6	98.3
				60	26.2	97.0
	II			15	26.1	96.8
				30	26.2	97.0
				60	26.1	96.8
III		609	4.2	7	16.8	62.2
				15	22.1	81.8
				30	22.4	83.0
				60	25.2	93.0
IV	I	597	2.0	7	25.3	94.0
				15	25.4	94.2
				30	..	..
	II			7	25.4	94.2
				15	25.2	94.1
				70	..	..
V	IV(*c*)	598	1.7	15	25.5	94.3
				60	25.5	94.3
	I(*d*)			60	25.8	95.7
				120	25.7	95.3
VI	I	727	1.5	5	26.5	98.1
				10	26.5	98.1
				30	26.6	98.5
				60	26.6	98.5
	II			5	26.6	98.5
				10	26.5	98.1
				30	26.6	98.5
VII(*e*)	I	824	4.3	2.5	26.6	98.5
				5	26.6	98.5
				15	26.7	98.9
				30	26.75	98.8
				60	26.75	98.8
				150	26.8	99.0
	II			2.5	26.61	98.4
				5	26.71	98.7
				15	26.75	98.8
				30	26.75	98.8
				60	26.80	99.0
VIII	I	965	1.0	1	25.6	94.8
				5	26.9	99.7
				30	27.1	100.0
				60	27.1	100.0
	II			1	26.8	99.1
				5	26.9	99.4
				30	26.9	99.4
				60	27.0	99.7
IX	I	1073	2.1	2	26.28	96.8
				5	26.90	99.4
				30	27.00	99.7
				60	27.05	99.9
	II			1	24.38	90.0
				5	26.90	99.7
				30	27.00	99.8
				60	27.10	100.0

(*a*) It was noted at the close of this run that there was a slight oxidation at one point in the boat.

(*b*) All the reduced samples were steel-gray.

(*c*) Boat showed slight reoxidation at one end when removed from furnace.

(*d*) This final material analyzed 97.25 and 97.30 per cent cobalt on duplicates. The material resulting from this run contained 0.75 per cent of unreducible $CaSO_4$, CaO and SiO_2, and 1.4 per cent of oxygen presumably in the form of Co_3O_4 (the stable oxide at 598° C., see following article, page 115), and 0.10 per cent of nickel and iron. It should, therefore, contain 100 — 2.3 = 97.7 per cent of cobalt. This checks with the value determined by analyses, 97.3, to within the accumulative error in the analyses.

(*e*) The product from this run seemed to be of a slightly lighter gray shade than that from the runs at lower temperatures.

per cent of the metals cobalt, nickel and iron, in the form of oxides which may be computed without error to be cobalt oxide. Any sample contains, therefore, 0.75 per cent of unreducible calcium sulfate, calcium oxide and silica, 99.2 per cent of cobalt oxide running 72.4/99.2 = 72.9 per cent in cobalt. This oxide, therefore, corresponds very closely to Co_3O_4. The oxygen content of the substance which could be reduced by hydrogen, is equal to 27.1 per cent of 99.2 per cent = 27.0 per cent. This figure is accurate to within the experimental error of the runs, and is used as the basis of the following computations; that is to say, in the column headed "Percentage loss in weight," 27 per cent would represent complete reduction, and the last column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27 per cent actual reduction as total. The boats used ranged in weight from 5 to 6.5 grams and the charges of cobalt oxide from 2.0 to 2.1 grams.

The check between the composition of the oxide used for these hydrogen reduction experiments, as determined by analysis and as determined by the reduction experiments, is entirely satisfactory (see following article, p. 115).

A number of the early experiments to reduce Co_3O_4 with hydrogen were made allowing the reduced product to cool in the atmosphere. In every case reoxidation took place. These runs were made at various temperatures from 500° C. to 1000° C., and curiously enough the reoxidation at the higher temperatures was progressively less than at the lower temperatures.

CONCLUSIONS

I. The reduction of Co_3O_4 to metallic cobalt by hydrogen gas takes place very rapidly at all temperatures above 500° C.

II. At temperatures between 500° C. and 700° C., over 90 per cent of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction takes place very slowly, if at all.

III. Between 700° C. and 1100° C., the amount of reduction of Co_3O_4 to Co which takes place during the first few minutes increases very rapidly with rising temperature, and at the higher temperatures it is complete.

IV. The hydrogen reduction method is to be especially recommended for the production of moderate quantities of very pure carbon-free cobalt for special purposes, just as it has been used for the production of metallic tungsten.

V. For the production of cobalt from Co_3O_4 by hydrogen, the charge must be completely cooled in an atmosphere of hydrogen.

III—PREPARATION OF METALLIC COBALT BY REDUCTION OF THE OXIDE WITH CARBON MONOXIDE

METHOD AND APPARATUS—These experiments were performed by placing an alundum boat, containing a weighed amount of dried cobalt oxide, in a horizontal tube electric resistor furnace, maintaining its temperature therein constant for a definite length of time, during which a stream of carbon monoxide was passed through the furnace (see Figs. 3 and 4).

CARBON MONOXIDE GENERATOR—The carbon monoxide was supplied by passing carbon dioxide over hot wood charcoal, which reduced it according to the reaction, $CO_2 + C = 2CO$.

Carbon dioxide, after purification, entered the lower end of the carbon monoxide generating furnace at G.

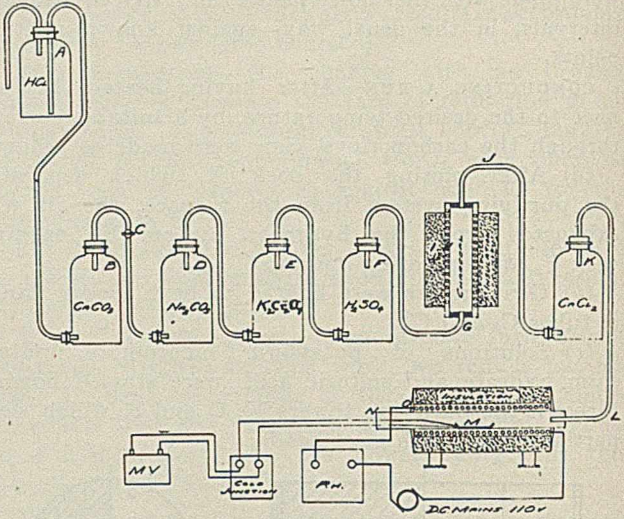

FIG. 3—APPARATUS FOR REDUCTION OF Co_3O_4 WITH CARBON MONOXIDE

This furnace was of the electric resistance type, made by winding nichrome wire over an alundum cylinder, the two being embedded in magnesite cement, and insulated within a cylindrical iron container. The wire is shown in section at H and the iron container at I. The entire core of the furnace was filled with wood charcoal, maintained at about 1000° C. by an appropriate current through the heating element. As a result, carbon monoxide gas left the generator at J, with a certain amount of moisture which was absorbed by passing through calcium chloride at K. Thus, substantially pure carbon monoxide entered the reaction furnace proper at L, passed over the alundum boat M, with its cobalt content, and the excess burned off at N.

THE REACTION FURNACE—The reaction furnace proper is shown in Fig. 3. It consisted of a central silica tube LN, 2 ft. in length, and 1 in. in internal diameter. This was wound with calorite or nichrome wire, of such resistance that it could be controlled by a suitable rheostat Rh on 110 volt direct current mains, to maintain a temperature constant to within less than 10° during a run, at any temperature up to 1000° C.

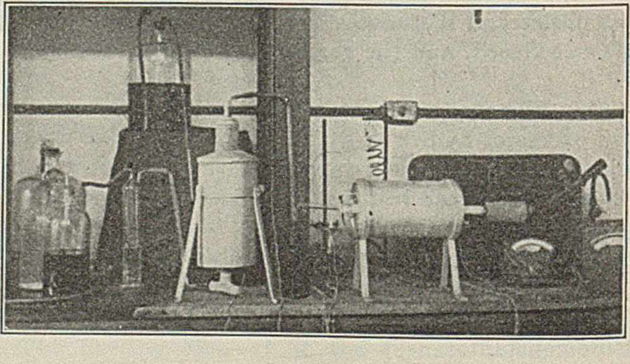

FIG. 4

TEMPERATURE MEASUREMENTS—The temperature measurements were made by a platinum platinum-rhodium thermo-element Th, and readings were taken at frequent intervals on a very sensitive millivoltmeter Mv. The thermo-elements used for the temperature measurements were calibrated at frequent intervals.

COOLING CHARGE IN CARBON MONOXIDE ATMOSPHERE—The silica tube NL extended beyond the end of the furnace proper from O to N. The portion O–N was 1 ft. in length and was kept cool by a circulation of water, so that at the close of a run the boat was removed from the centre of the furnace to O–N, where it cooled to room temperature in the stream of CO gas.

CONDUCTING A RUN—After having heated the reaction furnace, and the CO producer furnace, by suitable currents, to the desired temperature, runs were made as follows:

(*a*) The cock C was opened to allow CO_2 gas to pass through the purifying system DEF into the producer furnace at G.

(*b*) The CO gas generated in the producer furnace GJ passed through the reaction furnace LN and was lighted at N.

(*c*) The weighed dried boat with its charge was introduced into the exterior ON of the reaction furnace.

(*d*) Temperature and time observations were begun, and when the desired temperature had been reached, the boat was moved to M.

(*e*) The run proper had now begun, during which observations of time and temperature were made and the rheostat Rh adjusted to keep the temperature constant.

(*f*) After a definite time the boat, with its contents, was withdrawn from M to ON, where it was allowed to cool in a current of carbon monoxide gas.

(*g*) When the boat was cool, the current of carbon monoxide was gradually diminished by closing the cock C, until it was finally entirely cut off.

(*h*) When the boat was cooled to room temperature, it was removed to a desiccator and weighed.

COBALT OXIDE FOR CARBON MONOXIDE REDUCTION EXPERIMENTS

The cobalt oxide for the CO reduction experiments was identical with that used for the hydrogen reduction experiments so that the column headed "Reduction where 100 per cent is complete reduction" is computed in terms of 27.0 per cent actual reduction as total.

A number of the first runs were made, reducing Co_3O_4 with CO and allowing the reduced product to cool in the atmosphere before weighing. Under these conditions, reoxidation took place rapidly, so that but a single pair of typical runs are given. The boats used weighed 10.5+ and 13.3 grams and the charges of cobalt oxide, 2— grams.

The reoxidation of cobalt oxide after reduction with carbon monoxide takes place with great vigor. If the boat be withdrawn from the hot furnace directly into the atmosphere, it may be seen to glow with great brilliancy. If the content of the boat, while still warm, be snapped out on the floor, it will reoxidize with such vigor that a cracking sound, as of a mild explosion, attends the reaction, *i. e.*, the reoxidation taking place according to the reaction $6CoO + O_2 = 2Co_3O_4$ is extremely exothermic.

In the runs of Table IV, during the first part of the run, and up to the time that it began to gain in weight, the Co_3O_4 in both boats gradually became a gray color. This gray material is CoO. At the end of the run it was black again.

TABLE IV—REDUCTION OF Co_3O_4 WITH CO—COOLING IN AIR

Number		Temperature		Time of reduction Minutes	Per cent loss in weight	Reduction 100 = complete
Run	Boat	Mean	Average deviation			
I	I	602°	9	15	10.6	39.3
				30	11.1	41.1
				45	10.8	39.9
				60	12.9	47.8
				75	12.9	47.8
				82	11.8	43.6
				92	11.3	41.8
				107	7.8	39.6
	II	594	12	30	12.4	46.0
				45	11.7	43.3
				75	13.2	48.8
				97	12.3	45.5
				112	11.9	44.0
				142	10.3	38.2

On account of the irregularities of reoxidation, the furnace reaction chamber was lengthened by substituting a silica tube of length LN for the one of length LO as shown in Fig. 3. The overhanging tube ON, about 1 ft. in length, was cooled by water, and served as a cooling chamber for the boat while CO gas was still passed through it.

The following runs, representative of a large number, show the rate of the reduction of cobalt oxide by CO gas when the cooling was controlled so that no reoxidation could take place. The boats used weighed about 8 grams and the charges of oxide about 2 grams.

In Run III, Table V, the oxide became a greenish gray color at the end of the first five minutes, and a uniform steel-gray color at the end of fifteen minutes. From then on it began to gain in weight, due to a deposit of carbon. At the close of many runs at this temperature, there was an extremely heavy deposit of carbon in the boat.

This run was typical of a number, which showed a reduction from the original black oxide to the green, followed by a change from the green to the gray, and then a gain in weight, due to a deposit of carbon. The only possible source of carbon was from the carbon monoxide gas, so that the finely divided metallic cobalt, which was formed during the first stage of the reduction of the gray oxide, probably acted catalytically to decompose carbon monoxide gas at this temperature. This is an extremely interesting decomposition which might well be studied with considerable care.

Table V—Reduction of Cobalt Oxide by Carbon Monoxide Gas—Cooling in CO Gas

Number		Temperature ° C.		Time of reduction Minutes	Loss in weight Per cent	Reduction 100 = complete
Run	Boat	Mean	Average deviation			
III		347	3	5	18.2	67.3
				15	25.2	93.2
				45	Deposit of	....
				60	carbon	....
IV	I	451	3	5	22.1	81.8
				15	13.4	49.5
V	I	453	3—	5	21.4	79.2
				15	13.2	48.4
				45	Gain	....
				60	Gain	....
VI	I	583	5	5	16.2	60.0
				15	26.4	97.8
				35	26.8	98.0
				50	26.9	99.6
				65	27.0	100.0
VII	II	596	3	20	26.5	98.1
				30	26.6	98.4
VIII	I	600	5	10	21.0	77.9
IX	II	597	6	5	21.2	78.3
				15	24.7	91.0
X		611	6	49	26.3	97.7
				69	26.7	98.8
				86	27.2	100.0
				146	27.1	100.0
XI	I	594	6	5	25.7	95.0
				15	26.3	97.2
				45	26.7	99.0
				60	26.7	99.0
XII	II	601	1	5	25.6	94.9
				15	26.5	98.0
				45	26.5	98.0
				60	26.6	98.4
XIII		754	3	5	26.7	99.0
				15	26.8	99.3
				45	26.9	99.8
				60	26.9	99.8
XIV		752	4	5	26.8	99.6
				15	26.8	99.6
				45	26.9	99.8
				60	26.9	99.8
XV		749	3	5	24.9	92.3
				15	26.7	99.1
				45	26.8	99.6
				60	26.8	99.6
				150	26.8	99.6
XVI		751	3	5	26.0	96.2
				15	26.6	98.8
				45	26.7	99.1
				60	26.7	99.1
XVII		900	4	5	26.5	98.3
				15	26.9	99.8
				45	27.0	100.0
				60	27.0	100.0
XVIII		900	4	5	26.6	98.8
				15	26.8	99.7
				45	26.9	99.8
				60	26.9	99.8

A strong odor of hydrocyanic acid was noticed throughout run IV. After five minutes or so, a deposit of carbon began to form in the boat, due to the decomposition of carbon monoxide by finely divided cobalt, as in the runs at 350° C.

Throughout run V a strong odor of HCN was noticed. This is true of all the reductions of cobalt oxide with carbon monoxide in the neighborhood of 450° C.

These two runs are typical of a large number of similar ones. Our observations seem to show that the decomposition of CO by cobalt takes place only through a temperature interval in the neighborhood of from 300–450° C.

The check between composition of the oxide used for these CO reduction experiments, as determined by analysis and as determined by the reduction experiments themselves, is entirely satisfactory. (See following article, p. 115.)

CONCLUSIONS

I. The reduction of Co_3O_4 to metallic cobalt by carbon monoxide gas takes place very rapidly at all temperatures above 600° C.

II. Between 350° C. and 450° C., carbon monoxide at first reduces Co_3O_4 to cobalt, but after a time the finely divided cobalt decomposes the CO gas, depositing carbon.

III. At temperatures between 500° C. and 750° C., over 90 per cent of the reduction of Co_3O_4 to Co takes place in a few minutes, but a further reduction to completion takes place very slowly.

IV. Between 750° C. and 900° C., the amount of reduction of Co_3O_4 to Co, which takes place during the first few minutes increases very rapidly, and at the higher temperatures it is complete.

V. Where producer gas is available it should offer a cheap and efficient means of producing large quantities of pure metallic cobalt from the oxide.

VI. For the production of cobalt from Co_3O_4 by CO, the charge must be completely cooled in an atmosphere of CO.

IV—REDUCTION OF COBALT OXIDE WITH ALUMINUM

The heat of formation of a molecular weight in kilograms of aluminum oxide (Al_2O_3) is 392,600 kilogram-calories, and is greater than that of any other metallic oxide. The molecular heat of formation of ferric oxide (Fe_2O_3) is correspondingly 195,600 kilogram-calories. It is therefore obvious that if finely divided aluminum be intimately mixed with ferric oxide (Fe_2O_3), the latter, possibly in the form of rolling mill scale, that the reaction $Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$ will take place, provided the temperature be raised at some point in the mixture sufficient to start the reaction. This principle has been used by the Goldschmidt Thermit Co. to produce molten iron for welding purposes.

It is obvious that for every 160 kilograms of ferric oxide and 54 kilograms of metallic aluminum that are mixed together and fired in this way, there are developed 392,600 — 195,600 = 197,000 kilogram-calories of heat. This is sufficient to raise the entire mass to a white heat, so that the molten iron readily settles to the bottom from where it may be tapped.

In a similar manner, metallic cobalt may be prepared by reduction of cobalt oxide with aluminum according to the reaction:

$$3Co_3O_4 + 8Al = 4Al_2O_3 + 9Co$$

The molecular heat of formation of Co_3O_4 is 193,400 calories.[1]

It is therefore obvious that for every 723 kilograms Co_3O_4 and 216 kilograms of aluminum that are mixed together and fired, there are developed $4 \times 392{,}600 - 3 \times 193{,}400 = 990{,}200$ kilogram-calories of heat. We would, therefore, expect a reaction

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[1] *Tables Annuelles Internationales des Constantes*, **1**, 428 (1910).

quite as vigorous, if not more vigorous, than the corresponding one with ferric oxide.

Experiments were tried, October, 1912, using a standard Goldschmidt Thermit conical welding furnace. Into this was charged 5–10 lbs. of finely divided Co_3O_4 with the theoretical amount of aluminum, according to the equation $3Co_3O_4 + 8Al = 4Al_2O_3 + 9Co$. The reaction was started by lighting a fuse of finely divided aluminum and potassium chlorate, rolled in a piece of tissue paper. The furnace fired with extreme violence, in every case becoming an intense white heat. The vigor of the reaction was so great that the lining of the furnace, although the best alundum-magnesite-cement mixture, would stand up for only two or three charges.

THE METAL—The metal produced in this manner was readily tapped from the bottom of the furnace into iron or sand moulds. It frequently contained less than 0.1 per cent of aluminum, and, of course, was carbon-free.

The various metals, chromium, molybdenum, etc., made by the Goldschmidt Co. by this method, as they have come to us, run about 0.5 per cent in aluminum and are carbon-free.

CONCLUSIONS

This aluminum reduction method can obviously be used with considerable satisfaction where absolutely carbon-free metal is required, and where a somewhat increased cost is not prohibitive. Moreover, it affords a method of preparing cobalt-aluminum alloys at once by adding an excess of metallic aluminum.

The price of crude aluminum, such as might be used for this purpose, is in the neighborhood of 17 cts. per lb. One pound of aluminum will reduce and melt in this way a little over two pounds of metallic cobalt. Therefore, there is a charge of 17 cts. in the form of 1 lb. of metallic aluminum, for the power for reducing and melting two pounds of metallic cobalt. There might, of course, be some return for the fused aluminum oxide which resulted from the process, but even allowing liberally for this, the costs are high as compared with the carbon and carbon monoxide methods of reduction described elsewhere in this paper.

It is obvious that the heating costs must be high by the aluminum method, for heat is being supplied at a temperature greater than 2100° C., that is, at a temperature far in excess of what is required for the reduction of the oxide and the melting of the metal, and with consequent attendant increased losses, due to conduction and radiation.

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OXIDES OF COBALT[1]

By Herbert T. Kalmus

The following oxides of cobalt have been described in various places throughout the literature: Co_2O, CoO, Co_8O_9, Co_6O_7, Co_4O_5, Co_3O_4, Co_7O_{10}, Co_2O_3, $Co_{12}O_{19}$, Co_3O_5, CoO_2, and considerable disagreement is to be found among the statements concerning them.

The existence of many of these compounds is doubtful, and there are but three of them which particularly concern the commercial manufacturer of cobalt oxide: Co_3O_4, Co_6O_7 and CoO. These concern us in the production of metallic cobalt. We shall, therefore, describe these three oxides as we have observed them in the course of the experiments reported in our previous article, p. 107 of this issue of This Journal.

COBALTO-COBALTIC OXIDE, Co_3O_4

The ordinary black commercial cobalt oxide which has been prepared from the hydrate, by calcining in the neighborhood of 750° C., is a mixture of Co_3O_4 and Co_6O_7, but largely the former.

There is an abundance of proof throughout the previous paper that this black oxide is largely Co_3O_4, of which the following may be particularly noted:

(*a*) The purified cobalt oxide used for hydrogen reduction experiments, making allowance for the impurities according to the analyses, was computed to contain 72.9 per cent cobalt. The hydrogen reduction experiments, using this same oxide, showed, wherever the reduction was complete, a loss of oxygen amounting to 27.0 per cent. As was shown on p. 111, this checks with the 72.9 per cent of cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4, as may be seen from the following theoretical percentages:

	Per cent cobalt
Co_2O_3	71.1
Co_3O_4	73.4
Co_6O_7	75.9
CoO	78.8

(*b*) The purified cobalt oxide used for the carbon monoxide experiments, making allowance for the impurities according to the analysis, was computed to contain 72.9 per cent cobalt. The CO reduction experiments, using this same oxide, wherever reduction was complete, showed a loss of oxygen amounting to 27.0 per cent. As was shown on pp. 110 and 111, this checks with 72.9 per cent cobalt, with allowance made for the slight impurities. Hence, this black oxide must be largely Co_3O_4 according to the table under (*a*).

(*c*) As a further proof that the black oxide calcined at a good red heat is Co_3O_4, the following experiment was tried:

A pure black hydrate of cobalt was made from electrolytic cobalt by the potassium-cobalti-nitrite method. This was calcined to constant weight at 105° C., yielding a chocolate-brown powder, which was uniform under the microscope. Several samples of this brown powder were calcined to constant weight at 640° C., and in each instance showed a loss of water between 11.5 per cent and 11.8 per cent. Therefore, the brown powder corresponds very closely to $Co_2O_3.H_2O$.

The material resulting from these calcinations was a black powder identical in appearance under the microscope with the black cobalt oxide of commerce.

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[1] Published by permission of the Director of Mines, Ottawa, Canada. See footnote to previous article, page 107.

A sample of this previously calcined black oxide was calcined at a red heat to a constant weight of 0.8300 gram. The same sample was then completely reduced with a mixture of hydrogen and carbon monoxide gas at 900° C., which brought it to a constant weight of 0.6063 gram. Thus, the loss in weight was 27.2 per cent. Except for traces, this material was free from non-reducible substances, so that the oxide contained 72.8 per cent cobalt, against 73.4 per cent corresponding theoretically with Co_3O_4. This was checked several times, which substantiates the statement that black cobalt oxide is Co_3O_4.

(*d*) A further experiment was as follows: Black oxide was brought to constant weight at 640° C., and immediately thereafter brought to constant weight by heating to 1020° C. This experiment was tried several times and in every instance the percentage loss in weight was found to be very close to 7.1 per cent. The resulting gray oxide at 1020° C. analyzed 79.3 per cent Co, corresponding very well with CoO (78.8 per cent Co).

The theoretical loss in passing from Co_3O_4 to CoO is 6.6 per cent. As against this, the theoretical loss passing from Co_3O_4 to Co_6O_7 would be 3.3 per cent, and correspondingly, passing from Co_6O_7 to CoO the loss would be 3.3 per cent. Thus, there is very little doubt but that our reduction of the black oxide formed at red heat, to the gray at 1020° C., corresponds with the transition from Co_3O_4 to CoO.

(*e*) Two independent samples of brown $Co_2O_3.H_2O$, calcined to constant weight at 640° C., analyzed for cobalt,[1] respectively, 74.7 per cent and 73.8 per cent. This analysis is between Co_3O_4 = 73.4 per cent Co and Co_6O_7 = 75.9 per cent Co. This black oxide is therefore largely Co_3O_4 with some Co_6O_7.

The black hydrated cobalt oxide, as formed commercially by precipitation of a chloride or sulfate solution with bleach,[2] or the brown $Co_2O_3.H_2O$, may be calcined at any temperature between 385° C. and 910° C., to yield substantially the same product, but in practice it is better to calcine at a good red temperature, in order that the calcination may take place with reasonable speed.

That there is a range between 385° C. and 910° C., through which very little oxidation or reduction of the black Co_3O_4 takes place, is shown by the following figures:

Starting with Co_3O_4, heated to constant weight at 385° C. the loss in weight heating it to constant weight is

at 640° C.	0.7 per cent	at 860° C.	2.4 per cent
at 770° C.	1.2 per cent	at 910° C.	2.5 per cent

Just above 910° C., however, the reduction begins to take place very rapidly, and the black Co_3O_4 reacts to become gray CoO. Continuing the experiment for which the figures above are given, we have loss in weight heating it to constant weight

at 980° C. ......7.0 per cent

This oxide, Co_3O_4, shows no trace of being magnetic.

THE OXIDE Co_6O_7

Co_6O_7 is not to be distinguished from Co_3O_4 either in appearance or in method of preparation; in fact, we have not succeeded in forming a pure oxide of cobalt which analyzed very close to 75.9 per cent. On the other hand, as will be noticed in many places throughout this paper, the analyses of the material obtained by calcining at a red heat are frequently something in excess of 73.4 per cent after making allowance for impurities. We, therefore, assume that a certain amount of Co_6O_7 accompanies the Co_3O_4.

COBALT MONOXIDE, CoO

Cobalt monoxide is the stable oxide of cobalt when calcination takes place at a high temperature, that is, in the neighborhood of 1000° C. It is a gray powder and reacts to form the metal by heating with carbon monoxide gas at any temperature above 450° C., or with hydrogen gas at any temperature above 250° C.

Cobalt monoxide also exists in an allotropic form which is a yellow-green powder. Either the yellow-green or the gray cobalt monoxide oxidizes to Co_3O_4, or to a mixture of Co_3O_4 and Co_6O_7 when heated in the air to any temperature between 385° C. and 910° C. The yellow-green variety is readily formed by heating Co_3O_4 with 2 to 3% by weight of C at temperatures in the neighborhood of 900° C.

Numerous analyses of the purified gray oxide have been made, which range around the theoretical value 78.8 per cent. The following experiment was tried to prove that yellow-green oxide is an allotropic form of the gray CoO: Black Co_3O_4 calcined at 640° C. to constant weight was then calcined to constant weight at 1020° C. It lost, thereby, 7.1 per cent in weight, and the product was gray CoO. Yellow-green CoO, produced by the reduction of black Co_3O_4 with hydrogen at 300° C., was calcined to constant weight in air at 640° C., gaining, thereby, 6.5 per cent in weight and becoming black. This experiment, like the others, indicates that the gray and the yellow-green oxides are identical to within such limits that if the yellow-green be CoO, the gray cannot depart from it by more than the formula $Co_{19}O_{20}$. Such differences as there are, however, seem to show uniformly that the gray has slightly the greater oxygen content of the two.

A further experiment was performed with the yellow-green oxide as follows: Freshly prepared yellow-green oxide was reduced to metal with hydrogen and carbon monoxide gas, and brought to constant weight. During the reduction, the loss in weight was 21.5 per cent in one case and 21.3 per cent in another, corresponding very well with the reduction of CoO to metallic cobalt which would be 21.3 per cent.

Both the gray and the green CoO are nonmagnetic, and the samples of gray prepared by us, as well as those obtained from commercial sources, are homogeneous powders under 100 diameters magnification.

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[1] Including very small amounts of Ni and Fe.

[2] See page 107.

THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS

By Carleton Ellis

Received January 5, 1913

The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixtures, often heretofore a troublesome matter at best, now promises to become even more difficult.

The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

The specific gravity and melting point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearine, while the resultant melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by Normann and Hugel[1] to be 0.9999 at 15° C., while they note that tristearine has a specific gravity of 1.0101 at the same temperature.[2]

The index of refraction also is strongly modified. A sample of fish oil at 56° C., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36° C. at the same temperature. (Scale of the Zeiss butter refractometer.)

Observations made in the writer's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below:

Index of Refraction at 55° C.

(Abbe Refractometer)[3]

	Original Oil	Hydrogenated Oil
Corn	1.4615	1.4514 (M. P. 55.7° C.)
Whale (No. 1)	1.4603	1.4550 (M. P. 41.5° C.)
Soya bean	1.4617	1.4538 (M. P. 50.3° C.)
Cocoanut oil ("olein")	1.4429	1.4425 (M. P. 24.7° C.)
Linseed	1.4730	1.4610 (M. P. 42.3° C.)
Palm	1.4523	1.4517 (M. P. 38.7° C.)
Palm	1.4523	1.4494 (M. P. 44.8° C.)
Peanut (edible)	1.4567	1.4547 (M. P. 34.7° C.)

The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in the writer's laboratory.

Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one hour intervals.

It is of interest to note that while the addition of *hydrogen* to fatty oils reduces the index of refraction, the addition of *oxygen* increases the index as is shown in the case of blown or ozonized oils.

	Melting point	Index of refraction 55° C.
Original Oil	..	1.4588
1 hour	28.2° C.	1.4577
2 hours	31.3	1.4568
3 "	34.3	1.4557
4 "	37.9	1.4549
5 "	40.8	1.4540
6 "	43.8	1.4527
7 "	45.6	1.4518
8 "	47.3	1.4510
10 "	55.9	1.4496

The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening, showed a content of unsaponifiable bodies ranging from 0.45 per cent to 0.55 per cent; sesame oil with an unsaponifiable content of 0.70 per cent, after hardening contained 0.85 per cent unsaponifiable.

Cholesterol and phytosterol, according to Bomer, are not changed by treating oils with hydrogen, although this is somewhat contrary to the statement of Windaus,[1] according to whom cholesterol may be easily reduced by the catalytic process. Willstätter and Mayer[2] hydrogenated cholesterol in ether solution with a platinum catalyzer.

In the case of the acetyl number more noticeable changes take place according to Normann and Hugel. When hardening castor oil, for example, the hydroxyl number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

Acid number	3.5
Saponification number	183.5
Iodine number	4.8
Acetyl number	153.5
Acetyl number of the fatty acids	143.1
Acid number of the fatty acids	184.5
Saponification number of the fatty acids	187.9
Melting point of the fat	68° C.
Melting point of the fatty acids	70° C.
Melting point of the acetylated acids	47° C.

The properties of hardened castor oil have been noted by Garth,[3] whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. Hardened castor oil dissolves in alcohol only by heating and separates on cooling, but is soluble at ordinary temperature in chloroform. The constants of one sample of hardened castor oil examined by Garth are given in the above table.

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[1] *Chem. Ztg.*, **1913**, 815.

[2] The specific gravity of tristearine is given by the "Chemiker Kalender" as 1.0101 at 15° C., while Lewkowitsch reports the specific gravity of a specimen of not quite pure stearine in the melted state as 0.9235 at 65.5° C.

[3] Refraction values are given in terms of true refractive index and also according to the arbitrary scale of the butyro-refractometer, in order to follow the data available, as rendered.

[1] *Ber. d. chem. Ges.*, **1912**, 3051.

[2] *Ibid.*, **1908**, 41, 2199.

[3] *Seifen Ztg.*, **1912**, 1309.

These results obtained by Garth would indicate that the saponification and acetyl number do not change. The iodine number has fallen greatly and the melting point is much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

The effect of hydrogenation on color tests of oils is variable. Thus the Boudouin sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the Halphen test is not likely to give positive results even with oils which have been only slightly hardened.

The Becci test is operative with slightly hardened cottonseed oil, but is indistinct with highly hardened oil so that this test is significant only in event of a positive coloration.

Hardened fish oil loses all its essential characteristics such as the formation of well defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ($C_{20}H_{40}O_2$) and behenic acids ($C_{22}H_{44}O_2$), which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

As a test for hydrogenated peanut oil, Kreiss and Roth[1] have given a method which consists in saponifying 20 grams of the oil with 40 cc. of alcoholic potash; then adding 60 cc. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 cc. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand over night. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 cc. of 90 per cent alcohol with slight warming and the solution is placed in water at 15° for about one-half hour. The crystals which separate are recrystallized from 25 cc., then $12^{1}/_{2}$ cc. of 90 per cent alcohol and the melting point determined. The presence of at least 5 per cent arachidic acid causes the melting point of the third crystallization to be over 70° C.

Normann and Hugel[2] state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting point of the recrystallized fatty acids was at least 70°. Normann and Hugel state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the specified amount of alcohol is not sufficient to dissolve them. It is better to use 100–150 cc. of alcohol and heat on the water-bath until solution is affected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting point is constant.

In one case using hardened fish oil having a melting point of 44, three recrystallizations from alcohol gave a constant melting point of only 63°, while further recrystallization using acetone caused the melting point to advance to 76°. In doubtful cases one should try several solvent mediums. If the melting point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present. If one is certain of the unitary character of the oil then peanut and rape oil can be distinguished from fish oil by the cholesterol test, provided the statement of Bomer in regard to the unchangeability of cholesterol and phytosterol under ordinary conditions of oil hydrogenation is confirmed.

Data on hardened oils by Davidsohn[1] are tabulated below:

	M. P.	Acid No.	Saponification number	Moisture	Ash
Talgol	39.3	3.4	191.0	0.10	0.07
Talgol extra	46.5	3.5	191.3	0.13	0.05
Candelite	49.0	3.2	191.0	0.20	0.08
Candelite extra	51.9	3.9	190.8	0.15	0.04
Coryphol	79.3	3.3	189.9	0.18	0.05

These hardened fish oils or other hardened oils put out under the trade names indicated are manufactured by the Germania Oil Works of Emmerich.

Knapp[2] states that the attention of analysts should be directed to the fact that in the immediate future they will be called upon to analyze certain new artificial fats prepared by hydrogenation and, not improbably, to detect their presence as adulterants. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid magma, then a soft fat, and finally a hard fat, is obtained. Knapp observes "A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting point is naturally accompanied by a decrease in the iodine value and refractive index. Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting point raised to 60°–70° C. While it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly

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[1] *Chem. Ztg.*, **1913**, 58 and 369.

[2] *Ibid.*, **1913**, 815.

[1] *Org. f. d. Ol- und Fetthdl.*, **1913**, No. 14 and 15, and *Seifen. Ztg.*, **1913**, 529.

[2] *The Analyst*, **1913**, 102.

unsaturated acids as clupanodonic (in whale oils). Anyone who has seen a malodorous oil converted into a bland odorless tallow realizes the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation of a fat with any required analytical figures." In support of the foregoing, Knapp furnishes the following data:

	Original oil	Hardened oils		
Appearance	Clear liquid	Solid particles floating in oil	Soft greasy solid	Brittle solid
Butyro-refractometer (corrected to 40° C.)	57.7	..	..	47.7
Fatty acids				
Iodine value	110	94	55	22
Titer	34.7° C.	37.0° C.	42.5° C.	52.2° C.
Neutralization value (mg. KOH)	197	196	196	192

The analyst is chiefly interested in the question of how these fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. Knapp states that until the manufacturer accomplishes the difficult step of completely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils.[1] Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grams of the fat are heated in a flask with 20 cc. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate while hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water, and placed on a white tile. One drop of ammonium sulfide is added to this and also to a drop of water for comparison. Knapp however, tried this test only on a few hardened oils, and in some cases with negative results. Dimethylglyoxime is a much more delicate test, but unfortunately Prall has found[2] that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils—the bromide estimation—is quantitatively useless for these oils after hardening, as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur—*e. g.*, Halphen's reaction. Knapp believes Bomer's observation that phytosterol and cholesterol are not changed in this process is of great analytical value.

Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

Catalyst	Percentage of catalyst in oil	Character of product	Butyro-refraction (Corrected to 40° C.)	Melting point °C.
Nickel	1.00	Hard	45.7	49
Platinum	1.10	Hard	47.8	46
Palladium	0.06	Brittle	45.5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.

Bomer[1] is in substantial agreement with the foregoing, for he states that (1) the hardened oils, as a result of the more or less complete transformation of unsaturated fatty acids (oleic, linoleic, linolenic) into stearic acid, show an increase in the melting and solidifying points as well as a lowering of the refractometer number and iodine number while the saponification number is but little altered.

(2) Judging by the iodine numbers of the liquid fatty acids, these acids appear to be not uniformly transformed into stearic acid, but the transformation of oleic acid appears to progress more slowly than the less saturated linoleic and linolenic acids, etc.

(3) Among the hardened oils, the soft and medium hard products, in color, consistency and in part also in odor and taste, show a greater or less similarity to beef or mutton tallow, so that by external appearance one cannot distinguish these hardened oils from such animal fats; for example medium hard peanut oil is so completely like neutral lard, and hardened whale oil is so like mutton tallow, that one is not able to distinguish between these fats by appearance, consistency, odor nor taste.

(4) Not only in their outward properties are these hardened oils like hog fat and mutton tallow, but also the usual analytical constants are so similar that one cannot distinguish some samples of hardened peanut oils and hardened sesame oil from hog fat, nor whale oil, in some cases, from mutton or beef tallow. In the latter case even the Polenske numbers agree while in the case of sesame oil they are somewhat lower than hog fat.

Oil	Appearance	Melting point	Solidifying point	Refractometer at 40°	Acid No. (*a*)	Saponification No.	Iodine No.
Peanut oil untreated	Yellow liquid	..	..	56.8	1.1	191.1	84.4
Peanut oil hardened	White tallowy	51.2	36.5	50.1	1.0	188.7	47.4
Sesame oil hardened	White tallowy	62.1	45.3	38.4(*b*)	4.7	188.9	25.4
Cottonseed oil hardened	Yellowish lard like	38.5	25.4	53.8	0.6	195.7	69.7
Cocoanut oil untreated	White soft	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened	White lard like	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened	Yellowish tallowy	45.4	33.7	49.1	1.1	193.0	46.8

(*a*) Milligrams potassium hydroxide for 1 gram fat.
(*b*) Determined at 50° C.

Bomer examined a number of hydrogenated oils and tabulated the results of his investigations and from these the above condensed table has been compiled.

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[1] Too much reliance should not be placed on the nickel test as evidencing the presence or absence of hydrogenated oils. It is known to the writer that hardened oils which are free from nickel are on the market, these in some cases presumably having been prepared with the aid of palladium as a catalyzer.

[2] Bomer, *Zeitsch. Untersuch. Nahr. Genussm.*, **1912**, 24, 104; and *Analyst*, **1912**, 37, 452.

[1] *Chem. Rev. u. d. Fett und Harz Ind.*, **1912**, 220.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

	Solid fatty acids		Liquid fatty acids	
Oil	M. P.	Acid No.	Refraction at 40° C.	Iodine No.
Peanut oil untreated....	..	..	47.6	91.8
Peanut oil hardened.....	..	199.7	42.9	82.9
Sesame oil hardened.....	56.4	199.5	44.7	88.9
Cottonseed oil hardened..	45.0	206.8	48.3	115.6
Whale oil hardened......	..	199.5	44.4	96.0

Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.9 per cent, cottonseed oil 1.6 per cent, and whale oil 0.2 per cent of sterol, of which the three first hardened products mentioned exhibited the typical crystalline form of phytosterol. The melting point of these sterols ranged from 132 to 139° C., yielding acetates melting between about 126 and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

Bomer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated peanut oil obtained tristearine (amounting to about 2-3 per cent). Bomer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per cent of oleic acid into stearic acid, the melting point increased from 25.6° C. to 44.5° C., or thus 18.9° C., while the solidifying point advanced from 20.4° C. to 27.7° C., or only 7.3° C.

A species of hardened fish or whale oil known as "Talgit" has been examined by Müller,[1] who found the product to have an acid value of 12.8, an iodine number of 49 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids: 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz[2] thinks the low melting point to be due to the presence in the original fish or whale oil of hypogaeic and physetoleic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

Leimdorfer[3] regards the stearine produced by the hydrogenation of some oils to be perhaps an allotropic form of natural stearine.

An attempt is made by Grimme[4] to identify fish oils after they have been hardened. As stated, the ordinary constants give no clue to the original source of a hardened oil and hence Grimme resorts to color reactions. A list of tests is given for each of the four classes of fish oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of fish oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzine-xylene (1:1) and agitating 5 cc. of the solution with the reagent; after 5 minutes and 60 minutes the color was noted. Grimme finds the iodine-sulfuric acid reaction (1 cc. concentrated sulfuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

A draft of the Codex alimentarius Austriacus, which has been prepared by a board of prominent chemists and officials including Hefter, Wolfbauer, Fischer, Hartl and Pellischek,[1] embraces the subject of hydrogenated oils and it is stated that considered as a food product these oils will require further careful investigation before it is determined with certainty just what rank they will take as edible products. It is noted that the fats now offered for edible purposes are white to yellowish in color, almost odorless and tasteless. Usually the consistency lies between that of ordinary butter and hard tallow. Now and then samples are found which melt at about 60° C. and are as brittle as carnauba wax. These hard products, of course, are not intended by themselves to be used for edible purposes, but are employed to raise the melting point of soft fats. Samples of hardened peanut and sesame oil with iodine numbers reduced to 50 or lower, sometimes down to 20, have been examined. Cocoanut oil with an iodine number of 2 or even lower has been met with. The cholesterol of animal fats and the phytosterol of vegetable oils is not altered by the hydrogenation process. The hardened fats, it is stated, scarcely ever appear on the market in their true light but usually are put out under some trade name such as "Peanut-oleo," "Sesame-oleo," "Peanut-margarine," "Sesame-margarine," "Crisco," and the like.

Hardened oils examined by Aufrecht[2] in outward appearances resembled palm kernel oil. They were very hard and of granular fracture, were either pure white or yellowish in color. A distinct odor was perceptible on melting or heating. The taste recalled that of tallowy fats. The products were readily soluble in the usual fat solvent mediums, but the solubility in methyl and ethyl alcohol was very slight. The fats were easily saponifiable. The content of free fatty acid fluctuated between 0.51–0.83 per cent. The ash

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[1] *Seifen Ztg.*, **1913**, 1376.

[2] *Ibid.*, **1914**, 1445.

[3] *Ibid.*, **1913**, 1317.

[4] *Chem. Rev. u. d. Fett und Harz Ind.*, **1913**, 129 and 155.

[1] *Seifen. Ztg.*, **1913**, 1087.

[2] *Pharm. Ztg.*, **1912**, 876.

reacted alkaline and consisted of alkali carbonate and traces of iron oxide, but no nickel or other constituent could be detected. The following analytical results are given:

	1. Durotol (yellow)	2. Durotol (white)	3. Hydrogenated Tran.
Color	yellowish	white	white
Specific gravity at 15° C.	0.9252	0.9257	0.9268
Melting point °C.	46.5	46.	48.
Solidification point °C.	43.5	43.5	45.5
Viscosity at 50° C.	5.4	5.4	5.6
Acid No. (calculated as oleic acid)	0.51	0.57	0.83
Saponification No.	162.2	161.	173.5
Unsaponifiable matter (per cent)	1.92	2.1	2.4
Acetyl No.	1.2	1.2	0.95
Iodine No.	3.9	4.2	7.8
Hehner No.	95.8	95.8	96.4
Reichert-Meissl No.	0.38	0.36	0.52
Water	0.	0.	0.
Ash	0.037	0.03	0.05

The detection of traces of nickel by the usual analytical methods is often difficult. Dimethylglyoxime, proposed by Tchugaeff, is a reagent of great sensitiveness. Its application has been investigated by a number of chemists, and among these Bianchi and DiNola[1] report that the presence of copper and iron interferes with the test. They worked with an acid reagent and used the following procedure:

To the substance supposed to contain nickel one or two drops of concentrated hydrochloric or nitric acid are added and the acid solution so obtained is placed in a porcelain dish, or preferably on a strip of filter paper. A few drops of ammonia are added, or in case the strip of filter paper is used, this may simply be exposed to the vapors of ammonia. The liquid is acidified with acetic acid and a drop of concentrated alcoholic solution of dimethylglyoxime is added. The presence of nickel is shown by a red coloration which grows more pronounced in the course of time. This reaction is a very simple one and does not require any particular technical knowledge for carrying out.

Fortini[2] has simplified this reaction and uses an alkaline instead of an acid reagent which apparently gives more satisfactory results than the above procedure. Fortini mixes one-half gram of dimethylglyoxime, 5 cc. 98 per cent alcohol, and 5 cc. concentrated ammonium hydroxide in the order as given, yielding a clear, faintly yellowish liquid which in glass-stoppered bottles may be kept for a long time unchanged. The test is carried out as follows:

The sample to be examined is freed from fat by extraction with ether and to the residue a drop of the reagent is added. When nickel is present there will appear in a few seconds a rose colored flock caused by reaction with the nickel oxide present on the surface of the metallic nickel. Of course, if nickel is present in the form of a soap, the fat should be extracted with, for example, aqueous hydrochloric acid in the manner prescribed by Knapp in the foregoing. In order to make the reaction even more sensitive, the residue may be heated for a few moments in an oxidizing flame to produce nickel oxide.

The detection and determination of small quantities of nickel by α-benzildioxime is described by Atack[1] as follows:

An alcoholic solution of α-benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid, and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered.[2] Small quantities of nickel are determined as follows: 150 cc. of a hot saturated alcoholic solution of the oxime are added for every 0.01 gram of nickel, the mixture is heated for a few minutes on the water-bath, filtered, the precipitate washed with hot alcohol, and dried at 110°–112° C.; it has the formula $C_{28}H_{22}N_4O_4Ni$ and contains 10.93 per cent Ni. Nickel may be separated from cobalt in ammoniacal solution. α-Benzildioxime is prepared by boiling 10 grams of benzil, dissolved in 50 cc. of methyl alcohol, with a concentrated aqueous solution of 8 grams of hydroxylamine hydrochloride, for 6 hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

The hydrogen value is proposed by Fokin[3] as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs.

The "hydrogen value" of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0° and 760 mm.), which are absorbed by 1 gram of the compound. For the test, an apparatus is devised consisting of a distillation flask (50–150 cc.) having a small beaker fused inside on the bottom, and connected by means of the side-tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed about 0.1 gram of catalytic platinum, moistened with $^1/_2$ cc. of water, and in the flask the substance to be examined and 20–30 cc. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either the hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6–81.4 (78.8); oleic acid, 86.2–87.2 (86.2); fatty acids from sunflower oil, 119.6–120.8 (122.9); fatty acids from linseed oil, 164.9–166.3 (166.0); castor oil, 73.7 (75.5); Croton oil, 260.9 (theoretical, 258.4); undecoic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colophony does not absorb hydrogen under the conditions of the test. The "hydrogen value" of course is not a determination as yet of use in the identification of hardened oils, but is noted here because of its incidental interest.

The foregoing embraces most of the information available from published sources on the analytical side of hydrogenated or hardened oils and it is hoped that the very meagreness of the data may serve as a stimulus

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[1] *Boll. Chim. Farm.*, **1910**, 517.

[2] *Chem. Ztg.*, **1912**, 1461.

[1] *Chem. Ztg.*, **1913**, 37, 773.

[2] Compare Ibbotson; *J. S. C. I.*, **1911**, 1317.

[3] *J. Russ. Phys. Chem. Soc.*, **40** (1908), 700; *J. Chem. Soc. Abstr.*, **94** (1908), II, 637.

for abundant investigations tending to clarify the subject and enabling fairly definite procedures to be adopted for the qualitative and quantitative examination of these products.

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THE CHEMISTRY AND PROPERTIES OF GLYCEROPHOSPHATES (GLYCERINOPHOSPHATES)

By Gaston DuBois

Received October 16, 1913

In an article on "Calcium Glycerophosphate," which appeared in two numbers of the *Journal de Pharmacie et de Chimie* of May 1 and 16, 1913, the authors, E. François and E. Boismenu, start their critical review of the literature on glycerophosphates by pointing to the great number of publications on the subject.

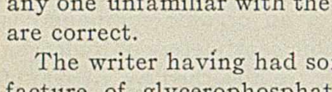
They believe that in spite of the comparatively voluminous literature few of those interested in this subject can draw exact conclusions from those publications as to the nature or composition of synthetic glycerophosphates and of the products found on the market.

In the literature including the leading authoritative publications on organic chemistry we find such contradictory statements as to make it impossible for any one unfamiliar with the subject to recognize which are correct.

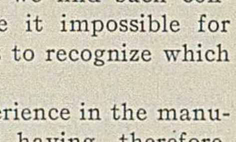
The writer having had some experience in the manufacture of glycerophosphates, and having, therefore, spent some time studying the chemistry of these products, deemed it advisable to collect the most important known facts on the subject and to endeavor to draw conclusions by adding his experience to that gathered from the research work of others, and also to point out a few of the erroneous statements and inconsistencies found in some publications.

Before going into the details of the chemistry and properties of glycerophosphates, and the findings of the various chemists who have developed this field, let us briefly examine what compounds are theoretically possible as a result of the action of phosphoric acid or its salts, on glycerine.

By the interaction of 1 molecule phosphoric acid with one molecule glycerine, two isomeric monoglycerophosphoric acids are possible.



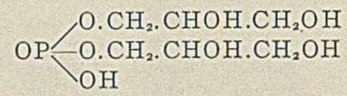
1. α-monoglycerophosphoric acid



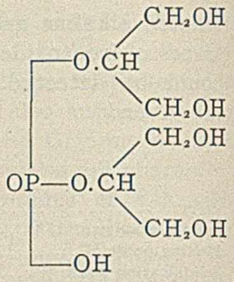
2. β monoglycerophosphoric acid

These acids can form mono- and dibasic salts. The dibasic calcium salts of above acids are the main components of calcium glycerophosphate of the market.

If one molecule phosphoric acid interacts with two molecules glycerine, again two isomeric diglycerophosphoric acids are possible:

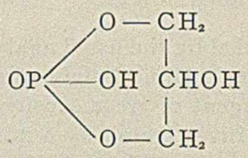


3. α diglycerophosphoric acid

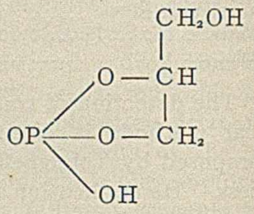


4. β diglycerophosphoric acid

Some authors claim diglycerophosphoric acids to have the following constitution:[1]



5. α diglycerophosphoric acid



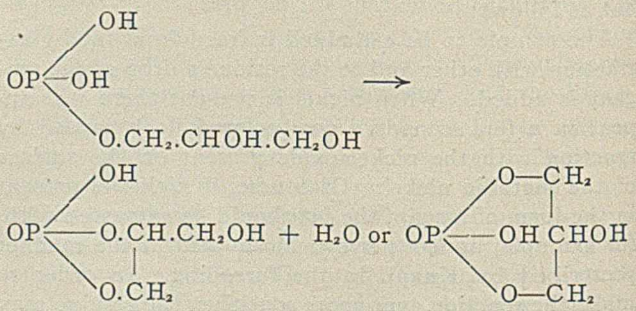
6. β diglycerophosphoric acid

The diglycerophosphoric acids, whatever their constitution may be, can form only monobasic salts. The salts of these acids are readily partly saponified by the action of alkali hydroxides yielding mainly monoglycerophosphates.

Diglycerophosphoric acids are formed when phosphoric acid is mixed with glycerine, preferably an excess of the latter, and the mixture heated to above 110° under reduced or atmospheric pressure. The formation of diglycerides at temperatures above 110° was demonstrated very conclusively by Adrian and Trillat,[2] by Power and Tutin,[3] and also by Carré.[4]

The question, which are the correct formulas for the α and β diglycerophosphoric acids, formulas 3 and 4 or 5 and 6 is not settled yet. Adrian and Trillat analyzed diglycerophosphoric acid and obtained figures for C and H corresponding about with the amount contained in formulas 3 and 4.

It is possible that both are correct as it is reasonable to expect that monoglycerophosphoric acid when heated could, by the elimination of water, form diglycerophosphoric acid:



We now come to the last class of esters formed

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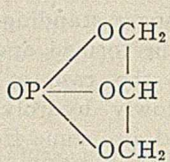
[1] Carré, *C. r. de l'Acad. des Sciences*, **137**, 1070–73, also **138**, 47–49.

[2] *J. Phar. et Ch.*, [6] **7**, 226–30.

[3] Power and Tutin, *J. Chem. Soc.*, **87**, 240–57.

[4] Carré, *C. r. de l'Acad. des Sciences*, **137**, 1070–73.

by the action of phosphoric acid on glycerine, the triglycerophosphoric ester. This compound has the following formula:



It is, according to Carré, insoluble in water, alcohol and acetone, and forms a hard, spongy mass which can be powdered.

It is interesting to note from the following example the relative amounts of mono, di and tri esters formed under various conditions, which is shown in the following table taken from G. Prunier's investigations.

Equal amounts of 60 per cent phosphoric acid and glycerine 28° B. were heated together under atmospheric pressure.

Temp.	Hours heated	Monoether	Diether	Triether	Total
110°	72	39.3	37.4	0.6	77.3
110°	84	43.9	33.5	0.6	78.0
130°	12	36.8	29.0	0.6	66.4
130°	24	36.1	27.1	1.9	65.1

Equally interesting is the result of investigations by G. Prunier[1] on the rate and limit of esterification of phosphoric acid by glycerine under varying conditions of concentration, temperature and pressure.

The investigation shows that the best results are obtained if the water formed during the reaction is eliminated, which can best be attained, either by heating the reaction mixture under reduced pressure or by exposing a comparatively large evaporating surface. The limit of esterification under reduced pressure appears to be reached when 80 per cent of the acid is esterified and this point is arrived at more quickly at higher temperatures, 24 hours being required at 110°, 12 hours at 130° and 8 hours at 150°. Under atmospheric pressure the speed of esterification also increases with higher temperatures, but the limit of esterification decreases. For example with 85 per cent acid and glycerine 30° B. at 110° the limit of esterification is 75.8 per cent but drops to 60.9 per cent at 130° and to 49.4 per cent at 150°. Under atmospheric pressure the best results for the esterification are obtained at 110° and by using 60 per cent phosphoric acid and glycerine 30° B. whereby 78 per cent of the acid is esterified.

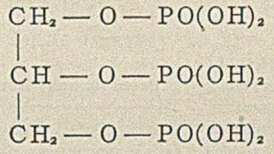
At higher temperatures and under reduced pressure the chief product is the diester, this being replaced, in part by the monoester when esterification is slow (namely, at higher pressures and lower temperatures) and by the triester when the operation is conducted at a still higher temperature.

Regarding the stability of glycerophosphoric acid or in other words its velocity of hydrolysis, F. Malengreau and G. Prigent[2] found that the decomposition of glycerophosphoric acid is a case of autocatalysis, caused by the action of the uncombined acid groups of the phosphoric acid, as when these are neutralized the decomposition at 100° is practically reduced to zero. With rising temperature the hydrolysis is notably accelerated. There is a certain acidity or concentration of H ions above and below which the stability of the compound increases. This explains why strong acids, such as HCl, H_2SO_4, acetic acid, etc., retard the decomposition owing to the increase in the concentration of the H ions in the solution. On the other hand weak acids such as oxalic and citric acids and their salts accelerate the hydrolysis of glycerophosphoric acid. The degree of acidity at which the hydrolysis is the greatest is represented by acid salts of glycerophosphoric acid.

The potassium salt decomposes more rapidly than the calcium and sodium salts. The salts of strong acids have mostly but a slightly accelerating effect but the salts of weak acids accelerate the hydrolysis reaction considerably.

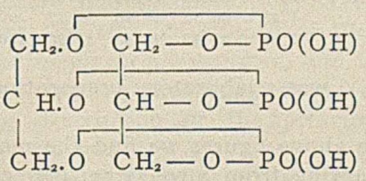
Before leaving the subject of the possible compounds resulting from the esterification of phosphoric acid by glycerine, the investigations by A. Contardi, recently published should be briefly mentioned.[1]

By heating at 120–130° three molecules crystallized phosphoric acid under reduced pressure with one molecule glycerine, *glycerotriphosphoric* acid is obtained:

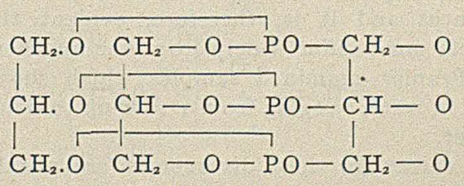


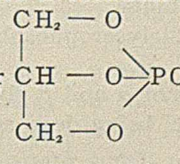
$$\begin{array}{l} CH_2 - O - PO(OH)_2 \\ | \\ CH - O - PO(OH)_2 \\ | \\ CH_2 - O - PO(OH)_2 \end{array}$$

This triphosphoric ester heated with one molecule glycerine yields *diglycerotriphosphoric* ester:



which compound yields when again heated with one more molecule glycerine the neutral triglycerotriphosphoric ester:



This compound is identical with Carré's triglycerophosphoric ester  the latter being just one-third of the formula proposed by Contardi.

The correctness of Contardi's formula for triglycerophosphoric ester has not yet been proved owing to

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[1] *Bull. de la Soc. Chim. de France*, **1907**, [4] 1, 1046–48.

[2] *Z. physiol. Chem.*, **1911**, 73, 68–84.

[1] *Gazz. Chim. Ital.*, **42**, II, 270–82.

the insolubility of this compound, which makes it impossible to determine the molecular weight.

P. Carré does not agree with Contardi's findings;[1] the question of the existence of above compounds is, therefore, not definitely settled.

In contrast to the methods used by all of the above mentioned authors for synthesizing glycerophosphoric esters, I find that the present manufacturing methods, judging from the patent literature, start not from phosphoric acid, but mostly from mono- and dibasic salts of ortho- or metaphosphoric acids. One patent describes the use of a mixture of metaphosphoric acid, disodium phosphate and glycerine; another patent covers the use of monosodium phosphate and glycerine, etc.

The purpose of deviating from the original method of Pelouze (phosphoric acid and glycerine) is partly in order to prevent the formation of triglyceroesters, by protecting one of the acid groups by a base, and partly for other practical reasons which do not enter into the subject of this paper.

We now come to the examination of the principal salts of glycerophosphoric acid found on the market, the calcium, sodium and potassium glycerophosphates.

CALCIUM GLYCEROPHOSPHATE.—An examination of various market products which I carried out in our laboratories showed how widely these products differ in composition.

Sample	H_2O of crysts. and moisture	Based on anhydrous product				Added org. acid fig. as citric acid
		Ash	CaO	P_2O_5	Titration	
1	10.03	55.32	19.23	32.03	56.1%	–
2	9.43	50.93	22.70	28.15	80.7%	7%
3	8.79	54.66	24.45	29.58	85.3%	5%
4	10.39	56.35	22.2	33.68	71.0%	–
5	12.73	59.02	26.56	31.9	....	–
L. P. 6	1.25	60.32	26.96	33.77	99.29	–
Theory	7.89	60.47	26.68	33.80	100.0%	–

Sample No. 6 was a laboratory preparation almost free of water.

From the above figures we find the moisture in the products varying from 8.79–12.73 per cent, the ash from 50.93–59.02 per cent, CaO from 19.23–26.56 per cent, P_2O_5 from 28.15–33.68 per cent. All of the figures for ash, CaO, P_2O_5 being based on dry substance.

If we compare their solubilities we find still greater differences and it is, therefore, evident that these products must differ widely from one another.

G. Prunier examined samples which showed solubilities in water ranging from 1 : 11 up to 1 : 60 parts of water.

The causes for these divergences are mainly:

1. The presence of organic acids (citric acid, etc.) which increase the solubility.
2. The presence of diglycerophosphates which also increase the solubility.
3. Different mixtures of α and β glycerophosphates the β glycerophosphate being less soluble than the α isomeride.

The two first causes will not be discussed in this paper as organic acids or diglycerides are impurities added for the purpose of apparently increasing the solubility. That the solubility is mostly only apparently increased is explained by the fact that although such products will at first readily dissolve in 25–40 parts of water, on longer standing, however, calcium citrate will gradually be formed and precipitate out of the solution and in the case of diglycerides being present, they will slowly hydrolyze forming monoglycerophosphates and also some free phosphoric acid. Furthermore, as is shown in this paper, the presence of organic acids (weak acids) or their salts will increase the hydrolysis of monoglycerophosphates, thereby causing $CaHPO_4$ to be formed.

The mistake has been repeatedly made by various authors in determining the solubility of pure calcium glycerophosphate, not to take into consideration the fact that the products examined may have contained one or the other of the two possible isomerides or even a mixture of both of these, and the result, naturally, has been that very widely differing statements were made concerning the solubility of these products.

Tutin and Hann in an endeavor to finally ascertain the nature of the natural and synthetical[1] glycerophosphoric acids, have prepared these products and their barium salts and also the α and β monoglycerophosphoric acids separately and their barium salts under such conditions as they hoped would exclude the formation of other products.

As the determination of the properties of the α and β isomerides is of the utmost importance as a basis for a thorough knowledge of the composition of commercial products and of the requirements to be established for such products, the writer will briefly discuss a part of Tutin and Hann's work and results. This appears all the more necessary in view of the importance of their researches and because their findings regarding the solubility of α barium glycerophosphate as well as that of the synthetical product do not coincide with the results of more recent investigations.

Tutin and Hann prepared α barium glycerophosphate by chlorinating dry allyl alcohol and thereby producing β dichlorhydrin, which was heated with one and a half molecules of crystallized phosphoric acid at a temperatue of 150–155°. The product obtained was boiled with milk of lime and the α-calcium glycerophosphate thereby obtained, converted into the barium salt.

It should be noted that the yield in the esterification of β dichlorhydrin with phosphoric acid is small and that furthermore, the heating of the mixture at 155° for several hours does not exclude the possibility of HCl being driven off, whereby phosphoric acid would combine with glycerine allowing the formation of β glycero- or diglycerophosphates, or even glycerodiphosphoric esters.

In connection with the above method of preparing α calcium glycerophosphate, it is interesting to compare the Eng. Pat. 2883, whereby monochlorhydrin or monoacetin is heated with syrupy phosphoric acid until *no more hydrochloric acid* or *acetic acid is evolved.*

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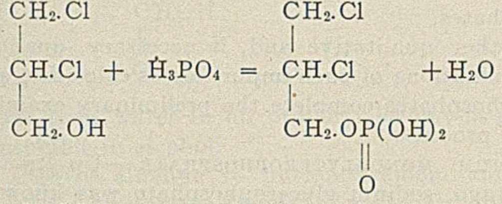
[1] *Compt. rend.*, **1912**, 155, 1520–21.

[1] By synthetical glycerophosphoric acid is meant the product obtained by heating glycerine and phosphoric acid for 24 hours at 105–110° C.

We find here an attempt to produce the esterification by introducing phosphoric acid in the position occupied by the chlorine in monochlorhydrin whereas Tutin and Hann did just the opposite; they intended to introduce phosphoric acid in the only remaining hydroxyl group of β dichlorhydrin leaving the chlorine groups intact.

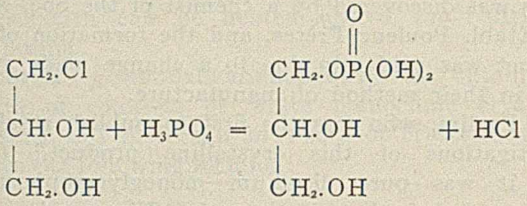
Tutin and Hann



$$\begin{array}{lcccl} CH_2.Cl & & & CH_2.Cl & \\ | & & & | & \\ CH.Cl & + H_3PO_4 & = & CH.Cl & + H_2O \\ | & & & | & \\ CH_2.OH & & & CH_2.OP(OH)_2 & \\ & & & \quad\quad\quad\| & \\ & & & \quad\quad\quad O & \end{array}$$

β dichlorhydrin

Eng. Pat. 2883



$$\begin{array}{lcccl} & & & \quad\quad\quad O & \\ & & & \quad\quad\quad\| & \\ CH_2.Cl & & & CH_2.OP(OH)_2 & \\ | & & & | & \\ CH.OH & + H_3PO_4 & = & CH.OH & + HCl \\ | & & & | & \\ CH_2.OH & & & CH_2.OH & \end{array}$$

α monochlorhydrin

In view of the above, I am of the opinion that the figure obtained by Tutin and Hann for α barium glycerophosphate, soluble 1 : 26.6/17°, cannot be accepted as final. This figure does not correspond with the solubility determined quite recently by Langheld, Oppmann and Meyer,[1] which they found to be 1 : 11.9.

The solubility 1 : 53.7, found by Tutin and Hann for the synthetical barium glycerophosphate, obtained by heating glycerine and phosphoric acid for 24 hours at 105–110°, is also so far off from the solubility of α barium glycerophosphate that their result would apparently require confirmation.

I compare in the preceding paragraph the synthetical barium glycerophosphate, obtained by Tutin and Hann, with the α barium glycerophosphate obtained by Langheld, Oppmann and Meyer. This comparison is justifiable as the two products should be almost identical. The main product of esterification of glycerine by phosphoric acid under the conditions as carried out by Tutin and Hann, is the α-isomeride. This corresponds to the fact that when glycerine is treated with an equivalent amount of hydrochloric acid, α chlorhydrin is the chief product obtained, only a small amount of β chlorhydrin being formed.

We find that in all cases in which mono esters of glycerine are formed at low temperatures, by the interaction of acids or their salts on glycerine, the α isomeride is the chief product of the reaction.

If the solubility of synthetical barium glycerophosphate of 1 : 53.7 found by Tutin and Hann were correct, this barium compound would then be less soluble than the corresponding synthetical calcium glycerophosphate, the solubility of which was determined by Power and Tutin and also by Adrian and Trillat.

Synthetic		
Ca glycerophosphate......	1 : 22.4/16°	Power and Tutin[1]
Ca glycerophosphate......	1 : 22.0/25°	Adrian and Trillat

I find, however, that the barium glycerophosphates are more soluble than their corresponding calcium salts. Let us for instance compare the solubilities of the barium and calcium salts prepared from crystallized sodium glycerophosphate, which latter product was prepared for the first time about seven years ago and has since been examined very carefully by various authors and recognized as pure β sodium monoglycerophosphate.

β Ca glycerophosphate.....	1 : 59.5/18°	Rogier and Fiore
β Ca glycerophosphate......	1 : 77 /15°	Paolini
β Ba glycerophosphate.....	1 : 22.2/21°	Rogier and Fiore
β Ba glycerophosphate.....	1 : 36.8/17°	Tutin and Hann

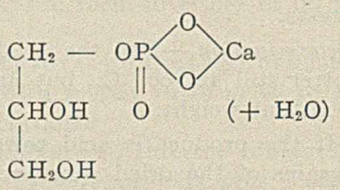
If we admit that the synthetical calcium glycerophosphate prepared as above described, contains mostly the α isomeride, we can conclude that the solubility of α calcium glycerophosphate in water must be about 1 : 22/16°, and that the solubility of the α barium glycerophosphate is greater than that of the calcium salt or as found by Langheld, Oppmann and Meyer, 1 : 11.9/22°, which, as these authors remark, corresponds very closely to the figure obtained by Tutin and Hann for barium glycerophosphate produced from lecithin, the solubility of which they found to be 1 : 13.9.

The foregoing leads forcibly to the conclusion that the synthetical glycerophosphates produced at low temperatures (100–110°), and the natural glycerophosphates obtained from lecithin are almost identical, and in all probability, a mixture of the α and β isomerides, in which the α isomeride predominates.

By eliminating the statements, which by their contradictory nature and inconsistency have tended so far to obscure the true knowledge of the chemistry and properties of glycerophosphates, and by condensing from the foregoing the actual facts, we come to the following description of the principal salts of glycerophosphoric acid:

CALCIUM MONOGLYCEROPHOSPHATE.—Both the α and β isomerides are known.

α CALCIUM GLYCEROPHOSPHATE is a white amorphous or crystalline powder of the following formula:



When precipitated from a cold, saturated, aqueous solution, by prolonged heating on the water bath, it separates as a fine crystalline powder, which after drying at 70° C. is practically anhydrous.

When precipitated out of a cold aqueous solution by the addition of alcohol, it forms an apparently amorphous precipitate which on drying below 70° C. retains one molecule of water; when, however, it is precipitated from the solution of its corresponding sodium salt, by the addition of $CaCl_2$, it forms a crys-

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[1] *Ber. d. chem. Ges.*, **45**, 3757 (1912).

[1] *J. Chem. Soc. Transactions*, **89**, 249–57.

talline precipitate, containing one molecule of water of crystallization, which is not driven off when the product is dried below 70° C. Both products are hygroscopic.

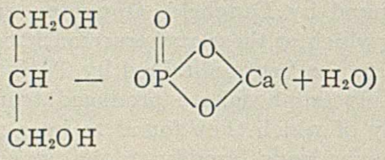
Anhydrous α calcium glycerophosphate is soluble in about 22 parts of water at 20° C., and precipitates out on heating, being soluble only in 108 parts of water at 100°.

It is insoluble in alcohol.

It is neutral or very slightly alkaline towards phenolphthalein; on addition of one equivalent of acid, the acid salt is obtained which is neutral towards methyl orange.

The dry salt contains 26.68 per cent CaO and 33.80 per cent P_2O_5 and yields on incineration 60.47 per cent ash.

β CALCIUM GLYCEROPHOSPHATE is much less soluble than the α isomeride; it dissolves in about 60 parts of water at 20° C. It is obtainable as a crystalline or amorphous precipitate under the same conditions as were enumerated for the α isomeride. It has the following formula:



COMMERCIAL CALCIUM GLYCEROPHOSPHATE is a mixture of the two above described isomerides; therefore, no specific solubility can be given for this mixture. It is evident that very different results will be obtained if the solubility of such a mixture is determined by shaking an excess of the product with water and determining the amount of substance dissolved in a weighed amount of water, or whether the solubility is determined by adding to a weighed amount of the product barely as much water as is required to produce a clear solution. The first method is naturally worthless in this case, whereas the second method gives us the actual solubility.

Commercial products should dissolve in 40 to 50 parts of water at 20° C. For the rapid estimation and comparison of market products I would recommend the following tests:

Moisture Determination.—Dry the product at 120–130° C. or better still at 100° C., but under reduced pressure, to constant weight.

Titration.—If the product is acid towards phenolphthalein, 2 grams of the dried substance in 100 cc. of water are titrated with *N*/2 NaOH (determination of organic acids).

If the product is neutral or very slightly alkaline towards phenolphthalein, 2 grams in 100 cc. of water are titrated with *N*/2 HCl using methyl orange as indicator; 1 cc. *N*/2 HCl equals 0.105 gram calcium glycerophosphate. Although the titration is not an exact determination, still it is a convenient method for the rough estimation of calcium monoglycerophosphate.

If diglycerides are present, the titration will yield low results indicating, in some cases, the presence of 10 per.cent or more diglycerides.

Ash Determination is made by very slow and careful incineration of 0.5 gram dried substance, until a white ash is obtained.

A low ash percentage indicates the presence of organic acids and other organic impurities including diglycerides. A high ash percentage indicates the presence of inorganic salts, such as chlorides, sulfates, phosphates.

Further qualitative and, if necessary, quantitative determinations of such impurities as chlorides, sulfates and phosphates complete the preliminary examination of the product.

SODIUM MONOGLYCEROPHOSPHATE.—Up to a few years ago, sodium glycerophosphate was known only in form of a syrupy liquid, or as a very hygroscopic white powder. The crystalline sodium glycerophosphate was discovered by a chemist of the Soc. Anon. des Etabl. Poulenc Frères, and the formation of this product was evidently due to a change made at the time in their method of manufacture.

V. Paolini, who was the first to publish results of investigations of this crystalline product,[1] found that it was pure disodium monoglycerophosphate and concluded that it was the β isomeride. This explains why it could be obtained in a crystalline form, whereas the products obtained by the interaction of glycerine and phosphoric acid at temperatures below 110° C., after conversion into the sodium salt, had never been known to crystallize, which can be explained by the fact that in this case, principally the α isomeride is formed.

In the early part of 1912, I analyzed sodium glycerophosphate, which, for purposes of purification, I recrystallized several times, and found

	Per cent
Water	31.2
Sod. monoglycerophosphate	68.9 by titration
Sod. monoglycerophosphate	68.5 by gravimetric P_2O_5 determination

Conflicting statements are found throughout the literature concerning the water of crystallization in sodium glycerophosphate; some authors give it as 1, some as 3, and again others as 7 molecules.

I found that the crystalline product contained $5^1/_2$ molecules of water, for which the following theoretical figures would correspond:

H_2O	31.41%
Sod. glycerophosphate	68.59%

these correspond very closely to our analysis figures (given above).

My views in this matter were confirmed by a publication by V. Paolini,[2] which appeared a few months later, in which the author having examined samples of four different sources, found them also to contain $5^1/_2$ molecules of water of crystallization.

α SODIUM MONOGLYCEROPHOSPHATE is obtainable as a colorless or slightly yellow syrupy liquid which,

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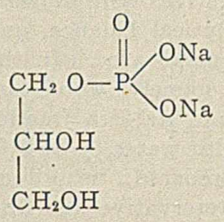
[1] V. Paolini, *Atti R. Accad. dei Lincei, Roma*, **1911**, 20, I, 807–12 and also from same publication, **1912**, 21, II, 330–52.

[2] *Atti R. Accad. dei Lincei, Roma*, **1912**, 21, II, 350–52.

when dried completely under reduced pressure, forms a white porous mass which can be powdered but is very hygroscopic.

It has the following formula:



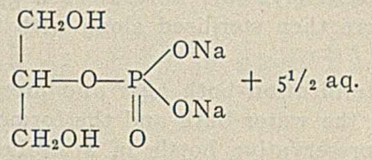
It mixes with water in all proportions but is practically insoluble in alcohol.

It is slightly alkaline to phenolphthalein and on addition of one equivalent amount of acid to its aqueous solution, the acid salt is obtained which is neutral to methyl orange.

Its solution can be heated up to 120° without decomposing.

β SODIUM MONOGLYCEROPHOSPHATE is obtainable in form of colorless or white monoclinic crystals, containing $5^1/_2$ molecules of water of crystallization.

It has the following formula:



It is easily soluble in water; a saturated water solution at 20° C. contains about 40 per cent of the salt.

In the form of large crystals, this salt is, at 15°, stable when exposed to the air, whereas when finely powdered and exposed to the air it effloresces. This explains why the fine sodium glycerophosphate crystals found on the market contain usually more anhydrous sodium glycerophosphate than corresponds to a salt containing $5^1/_2$ molecules of water.

COMMERCIAL SODIUM GLYCEROPHOSPHATE.—The products that have been sold under the name of "sodium glycerophosphate 50 per cent" or "75 per cent" and also "about 100 per cent" which I have had the opportunity to examine, showed a surprising lack of uniformity in strength as well as purity.

Most of these products were in form of a syrupy liquid. It is of course impossible to produce a 75 per cent or even 50 per cent solution of β sodium glycerophosphate, as we have just seen that a saturated solution contains only about 40 per cent β sodium glycerophosphate crystals.

The liquid market products are composed of mixtures in which therefore mostly the α sodium glycerophosphate predominates.

Some manufacturers in determining the strength of their products have been guided merely by the specific gravity, others evidently have determined the strength on the basis of a variable amount of water of crystallization which, of course, accounts partly for the lack of uniformity in strength.

A 75 per cent solution, containing 75 per cent sodium glycerophosphate + $5^1/_2$ aq. is a syrupy liquid, which mixes readily with water and is, therefore, quite convenient for use.

A preparation containing 75 per cent *anhydrous* sodium glycerophosphate, however, although it mixes in all proportions with water, has the great inconvenience of dissolving very slowly in cold water, and requiring many hours' stirring before complete solution is obtained. Even when heated the product does not dissolve readily.

I am, therefore, of the opinion that, for the sake of uniformity and convenience in handling, it should be required that the strength of the product be figured on the basis of its contents in sodium glycerophosphate + $5^1/_2$ aq. and this basis being admitted, a 75 per cent solution would unquestionably be the most desirable form for the consumer, if he must have a liquid preparation.

The last but not least interesting form in which sodium glycerophosphate is found on the market is the crystal form, which in itself is the best guarantee of its purity and, therefore, is preferable to all other forms wherever purity is of paramount importance.

The strength of the various sodium glycerophosphates can readily be determined by titration. This method yields for pure products checking results with the gravimetric method (P_2O_5 determination). It is carried out as follows:

Titration.—2–4 grams of the product accurately weighed are dissolved in 100 cc. of water and titrated with $N/2$ HCl, using methyl orange as indicator.

One cc. $N/2$ HCl equals 0.1576 gram monosodium glycerophosphate + $5^1/_2$ aq.

The product should also be tested for sulfates, chlorides and carbonates, which are almost invariably present in the liquid preparations but should not be present in the crystals.

The products should not contain any phosphates.

POTASSIUM GLYCEROPHOSPHATE.—Both α and β isomerides are obtainable as a colorless or slightly yellow syrupy liquid. When dried completely under reduced pressure a porous and very hygroscopic mass is obtained.

Potassium glycerophosphate mixes readily in all proportions with water. The product has never been obtained in crystal form in either of its modifications (α and β).

COMMERCIAL POTASSIUM GLYCEROPHOSPHATE.—This product is known mostly in form of 50 per cent and 75 per cent solutions.

Some manufacturers figure the contents on the basis of potassium glycerophosphate plus a certain amount of water of crystallization. I can see no reason for doing this as the product has never been obtained in crystal form. The only logical way of figuring the contents is on the basis of anhydrous potassium glycerophosphate.

These market products are best tested exactly as described for the sodium salts, whereby in the titration, 1 cc. $N/2$ HCl equals 0.124 gram potassium glycerophosphate.

Concluding, I wish to emphasize that while I believe the above data embodies the most important investigations on the chemistry of glycerophosphates, and resulting conclusions, yet I fully realize that much remains to be done in order to define, without a doubt, the characteristics of the various isomeric glycerophosphoric esters, which naturally can be achieved only after the various compounds shall have been synthesized in such a way as to exclude the possibility of other compounds being formed.

Until such time the figures given for the solubilities, for instance, must be regarded only as tentative.

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TOXICITY OF VARIOUS WOOD PRESERVATIVES[1]

By C. J. Humphrey and Ruth M. Fleming

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During the past three years the writers have been conducting toxicity tests at the Forest Products Laboratory, Madison, Wisconsin, on various wood preservatives. These tests have been limited to substances in actual use in the industry or to those compounds submitted by coöperators as having a possible preservative value.

The toxicity of a given substance is not necessarily an ultimate criterion of its service value, but when correlated with other suitable properties, such as cost, ease of injection, permanence, non-corrosive action on metals and wood, fire resistance, and ease and safety in handling it assumes high importance in influencing our judgment as to what may normally be expected from the substance.

The writers have confined their attention to toxicity only, and with the view of bringing the essential data to the attention of the industry the more important results of our investigations to date are here presented.

While we are attacking the problem from two angles, namely, by the quick method of mixing the preservative with agar culture media and inoculating with fungi, and by the slower and probably more conclusive method of testing small injected wood blocks, the present paper will consider only the former, as the latter work is not yet far enough along to report upon.

Our method is essentially this: Agar culture media of the following formula is prepared:

Extract of 1 lb. lean beef in 1000 cc. distilled water.
25 grams Löflund's malt extract.
20 grams agar-agar.
(Carefully filtered but reaction not adjusted; slightly acid.)

Seventeen cc. of this medium are measured out into 50 cc. glass-stoppered bottles, using a specially graduated 17 cc. pipette, the bottles then being placed in clamp-frames and sterilized with steam at 100° C. for 25, 20 and 20 minutes, respectively, on three successive days.

The handling of the preservatives involved slight modifications for individual cases, but in all instances the concentrations reported are based on the actual weight of preservative in 20 cc. agar-preservative mixture. The character of the substance determined the method of introducing it into the agar medium.

With inorganic salts soluble in water, from 3 to 10 per cent solutions (grams per 100 cc. solution) were prepared and *measured* out into 50 cc. glass-stoppered bottles from either a 10 or 25 cc. standardized burette graduated in $^1/_{20}$ or $^1/_{10}$ cc., respectively. To each bottle sufficient distilled water was added to make 3 cc.

All other preservatives were *weighed* out into similar bottles on an analytical balance, and distilled water likewise added to make 3 cc. In the case of certain thick viscous oils, namely, wood tar, wood creosote, coal tar creosote and its fifth fraction, which do not readily emulsify with water, 5 to $33^1/_3$ per cent stock emulsions were prepared, using equal amounts of gum arabic and preservative and diluting with water to the desired concentration; these emulsions were then used in place of the crude preservative.

In a few instances where the preservatives were very low in toxic properties, more than the specified 3 cc. were necessary in order to secure the higher concentrations, and in these cases it became necessary to take into consideration the excess of preservative and to reduce the amount of agar by just this amount in order that the combined volume might not exceed 20 cc.

After the preservative had been introduced into the bottles as indicated, the stoppers were sealed in with a rubber-glycerine burette cock grease and the bottles were then sterilized along with the agar containers.

After sterilization both agar and preservative were heated on the water bath and the former was poured into the preservative bottle in a sterile culture box, thoroughly shaken, and then poured into sterile petri dishes 100 mm. in diameter and 10 mm. deep. After cooling, the surface of the medium was inoculated at the center with a weft of fungus mycelium 5 to 6 mm. square cut from a petri dish culture 2 to 3 weeks old. The test dishes thus prepared were then placed in an incubator and held at approximately 25° C. for from 4 to 10 weeks, usually 4 to 6. For each set of concentrations a check culture, using 17 cc. agar media plus 3 cc. of distilled water, was prepared.

The method as above outlined is not, by any means, intended to furnish the last word on the toxicity of a preservative, but it has the advantage of being quickly and easily applied and gives us at least valuable indications. The principal objection is the possibility in some instances that the preservative may combine with certain constituents of the culture media, thus rendering part of it inert. This is known to be the case with such compounds as zinc chloride, copper sulfate and mercuric chloride. With the oils this objection probably does not enter so seriously, but even here it would be difficult to say what might occur in such heterogeneous compounds as the various tar distillates and similar substances of highly complex constitution.

Another variable which only a large number of tests can correlate is the difference in susceptibility among different fungi. Since molds are, as a rule, much more resistant to toxic agents than true wood-destroyers, the writers have avoided their use, as well as that of bacteria and yeasts. Even among the true wood-destroying fungi considerable variation exists,

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

Table I—List of Preservatives Tested Showing Essential Properties and Killing Point (a)

Preservative	Specific gravity 60° C.	Per cent distills below 180° C.	215° C.	245° C.	275° C.	305° C.	320° C.	360° C.	Killing point (per cent) *Fomes annosus*	*Fomes pinicola*	Description	Coöperator
Wood tar (hardwood), No. 1561	1.195	About 27	About 31	51	..	..	..	..	1.25	0.75	Black viscous liquid with pyroligneous odor; 24 per cent water	Marden, Orth and Hastings, Chicago, Ill.
Wood creosote (Douglas fir), No. 1099	1.052	About 16	About 31	54.7	..	..	..	..	0.65*	0.20*	Black liquid with strong pyroligneous odor	Logged-Off Land Utilization Co., Seattle, Wash.
Spirittine wood preserver, No. 1932	1.006	14.2	23.2	35.2	36.7	..	..	..	Between 1 and 2	...	Reddish brown liquid; 0.47 per cent acid; a softwood creosote	Spirittine Chemical Co., Wilmington, S. C.
Water gas tar creosote, No. 1101	1.058	About 7	About 10	..	16.3	About 22	About 27	56.4	40+	40+	Mobile oily liquid with kerosene odor	United Gas Improvement Co., Philadelphia, Pa.
Water gas tar creosote, No. 2233	1.042	3	6.7	21.2	35.3	48.5	53.7	77.6	Between 3 and 4	...	Dark brown liquid	United Gas Improvement Co., Philadelphia, Pa.
Water gas tar creosote, No. 2235	0.995	3.3	12.8	37.7	61.7	75.3	80.3	..	Around 0.45	...	Greenish brown liquid	United Gas Improvement Co., Philadelphia, Pa.
Coal tar creosote, No. 1074	1.048	4.8	17.8	44.4	54.1	67.2	74.1	..	0.55	0.225	Liquid; 8.4 per cent water	Creosote Supply Co., Chalmette, La.
Coal tar creosote, Fraction I, No. 1094	0.934	35.1	78.3	..	..	..	..	..	0.30	0.225	Light liquid at room temperature	Semet-Solvay Co., Ensley, Ala.
Coal tar creosote, Fraction II, No. 1106	1.003	About 2 to 3	30	About 80	About 92	..	..	..	0.225	0.15	Naphthalene odor; nearly solid at room temperature	Semet-Solvay Co., Ensley, Ala.
Coal tar creosote, Fraction III, No. 1107	1.045	..	0.9	16.2	49.2	77.7	85	..	0.325*	0.125	Liquid at room temperature	Semet-Solvay Co., Ensley, Ala.
Coal tar creosote, Fraction IV, No. 1108	1.088	..	..	0.9	4.7	38.5	54.3	..	3.30*	0.125*	Liquid at room temperature	Semet-Solvay Co., Ensley, Ala.
Coal tar creosote, Fraction V, No. 1109	1.150	..	..	..	..	4.1	10.1	48.7	33*	7.80*	Heavy tarry liquid	Semet-Solvay Co., Ensley, Ala.
Avenarius Carbolineum, No. 1843	(16.5°) 1.126	..	1.1	2.6	6.1	16.4	About 29	..	5.25	0.30	Thick liquid at room temperature; 1.91 per cent tar acids	Carbolineum Wood Preserving Co., Milwaukee, Wis.
S. P. F. Carbolineum, No. 1844	(16°) 1.127	..	..	Below 9	..	..	About 30	..	2.25	...	Thick dark brown liquid; 2.42 per cent tar acids	Bruno-Grosche and Co., New York City
C. A. Wood preserver, No. 1931	1.120	0.5	2	4	8.2	20.6	28.9	70.1	Between 1 and 1.5	...	Brown liquid; probably high boiling fractions of coal tar creosote	C. A. Wood Preserver Co., St. Louis, Mo.
Holzhelfer, No. 2097	1.113	7.3	7.8	9.9	12.8	23.8	29.6	58.9	Above 2.5	...	Thick greenish brown liquid; partial emulsion $ZnCl_2$ and creosote oil with small amount of copper	Vaughan Paint Co., Cleveland, Ohio
Copperized oil, No. 1095	(25°) 0.937	..	Below 0.2	About 3	About 10	About 22	30.2	About 80	35*	40	Probably a crude petroleum with a little copper and vegetable oil to make a homogeneous solution	Ellis Foster Co., New York City
Fuel oil, No. 1103	0.871	..	About 3	About 9	About 20	40.6	About 51	About 75	Above 6	...	Light liquid; odor of crude oil	E. W. Peters, Picatinny Arsenal, Dover, N. J.
Kerosene, No. 1847	0.798	25.1	65.5	89.7	..	..	..	..	Above 34	...	Refined petroleum oil	Standard Oil Co.
Cresol-calcium, No. 2086	...	..	..	..	..	..	..	..	Between 0.14–0.28	...		Blagden, Waugh and Co., London, Eng.
None Such Special, No. 2696	...	..	..	..	..	..	..	..	Above 40	Above 50	Yellow oily liquid with strong varnish or paint odor; chemical composition not known	George M. Saums, Trenton, N. J.
Sapwood antiseptic, No. 1611	1.027	..	..	..	..	..	..	..	Above 75	...	NaCl, 2.92 per cent; $CuSO_4 + 5H_2O$, 0.182 per cent; $CaSO_4$, 0.246 per cent; $FeSO_4 + 4H_2O$, 0.0605 per cent; $ZnSO_4 + 7H_2O$, 0.246 per cent (by weight)	J. W. Long, Chicago, Ill.
Sodium fluoride, No. 1929	...	..	..	..	..	..	..	..	0.25	0.15	About 60 per cent pure	
Zinc chloride, No. 2239	...	..	..	..	..	..	..	..	0.50	0.75	Commercial salt meeting specifications American Railway Engineering and Maintenance of Way Association	Grasselli Chemical Co., Cleveland, Ohio
Zinc sulfate, No. 1711	...	..	..	..	..	..	..	..	Above 0.50	...	Commercial salt	

(a) In using these tables it should be noted that the figures given are checked to within an accuracy of 10 per cent, or less, except as follows: In the figures marked with an asterisk (*) the killing point has not yet been checked in duplicate; in certain cases the killing point is given as between certain limits, and further work will define these more accurately; those toxicities ndicated as "around" a certain concentration are close to the true value but may fluctuate slightly on either side; where indicated as "above" a certain concentration, the result merely indicates that this is the highest concentration yet tested, and the ultimate killing point may be considerably higher.

as will be seen in the tables following, but this is usually within narrower limits.

Both the fungi used by the writers grow well on the media employed, *Fomes annosus* Fr. covering the surface of the petri dish in about 20 days and *Fomes pinicola* (Sw.) Fr. in about 15.

Table I shows a list of the preservatives tested, together with salient properties, and the concentration necessary to prevent growth of the organisms. In this table the preservatives have been grouped according to their nature, such as coal tar, water gas tar, and wood tar distillation products, petroleum oils and water-soluble inorganic salts, in order to give an easy direct comparison.

In general the table shows that the two fungi react, in most cases, quite differently to the same substance, *Fomes pinicola*, as a rule, being a far less resistant organism than *Fomes annosus*. With *Fomes annosus* the first three fractions of coal tar creosote are considerably more toxic, and the last two fractions much less toxic, than the oil itself; with *Fomes pinicola* only the last fraction is less toxic. This indicates the advantage, from a toxicity standpoint, of removing at least a part of the heavier tar oils.

TABLE II—PRESERVATIVES ARRANGED IN ORDER OF TOXICITY AND SHOWING RATIO TO COAL TAR CREOSOTE

	Killing point					
	Fomes annosus				*Fomes pinicola*	
			Ratio to coal tar creosote No. 1074			
Preservative	Per cent	Lbs. cu. ft.			Lbs. cu. ft.	Per cent
Coal tar creosote, Fraction II, No. 1106	0.225	0.140	2.5	1.5	0.094	0.15
Sodium fluoride, No. 1929	0.25	0.156	2.2	1.5	0.094	0.15
Cresol-calcium, No. 2098	0.14–0.28	0.087–0.174	3.9–2.0	..	..	...
Coal tar creosote, Fraction I, No. 1094	0.30	0.187	1.8	1.0	0.140	0.225
Coal tar creosote, Fraction III, No. 1107	0.325*	0.203	1.7	1.8	0.078	0.125
Water gas tar creosote, sp. gr. 0.995, No. 2235	Around 0.45	...	.....	..	..	...
Zinc chloride, No. 2239	0.50	0.312	1.1	0.3	0.468	0.75
Zinc sulfate, No. 1711	Around 0.50	...	.....	..	..	...
Coal tar creosote, No. 1074	0.55	0.343	.....	..	0.140	0.225
Wood creosote, No. 1099	0.65*	0.405	0.84	1.12	0.125	0.20 *
Wood tar, No. 1561	1.25	0.78	0.44	0.3	0.468	0.75
C. A. Wood preserver, No. 1931	1–1.5	0.6–0.9	0.55–0.37	..	..	...
Spirittine wood preserver, No. 1932	1–2	0.6–1.2	0.55–0.27	..	..	...
S. P. F. Carbolineum, No. 1844	2.25	1.404	0.24	..	..	...
Holzhelfer, No. 2097	Above 2.5	......	.....	..	..	...
Coal tar creosote, Fraction IV, No. 1108	3.3*	2.059	0.16	1.8	0.078	0.125*
Water gas tar creosote, sp. gr. 1.042, No. 2233	3–4	1.9–2.5	0.18–0.14	..	..	...
Avenarius Carbolineum, No. 1843	5.25	3.27	0.104	0.75	0.187	0.30
Fuel oil, No. 1103	Above 6	...	.....	..	..	...
Kerosene, No. 1847	Above 34	...	.....	..	..	...
Coal tar creosote, Fraction V, No. 1109	33*	20.59	0.017	0.029	4.867	7.80*
Copperized oil, No. 1095	40	24.96	0.015	0.0056	25+	Above 40
N. S. Special, No. 2696	Above 45	28+	0.014—	0.0045	31.2+	Above 50
Water gas tar creosote, sp. gr. 1.058, No. 1101	Above 40	25+	0.016—	0.0056	25+	Above 40
Sapwood antiseptic, No. 1611	Above 75	46.8+	0.007—	..	..	...

The carbolineums and similar products which consist, in the main, of the higher boiling constituents of creosote in all cases proved much less toxic than coal tar creosote.

Wood creosote from Douglas fir appears to compare very favorably with coal tar creosote, but the softwood creosote, under the trade name of Spirittine Wood Preserver, which has a much lower specific gravity, appears to be much less effective.

In the case of water gas tar creosotes the toxicity increased rapidly with decreasing specific gravity, the heavier 1.058 oil possessing very low antiseptic properties and the 0.995 oil proving at least, or more, toxic than coal tar creosote.

Petroleum oils, according to the three samples tested, have low antiseptic value.

Cresol-calcium in these tests shows a high toxicity and the poor results reported against it in practice are apparently due to a change in chemical constitution which did not take place under our method of testing.

Zinc chloride, in the commercial form, is slightly more toxic to *Fomes annosus*, and far less toxic to *Fomes pinicola*, than coal tar creosote.

Sodium fluoride is over twice as toxic to *Fomes annosus*, and about one and one-half times as toxic to *Fomes pinicola*, as coal tar creosote.

While the work has not progressed far enough with zinc sulfate to give conclusive results, the indications are that it compares very favorably with both zinc chloride and coal tar creosote.

None Such Special, which is claimed by the manufacturers to water-proof and give a hard finish to timber, as well as to prevent or stop decay, proved very low in toxic properties, and even stimulated growth in high concentrations; however, the physical properties, when injected into wood, may be such as to exclude fungus growth and thus substantiate the claims made for it.

In Table II the preservatives are arranged in the order of their toxicity to *Fomes annosus*, the concentrations are reduced to pounds per cubic foot and the ratios of their efficiency as compared with coal tar creosote are presented. Had the preservatives been listed in their order of toxicity to *Fomes pinicola* the arrangement would have been somewhat different and Avenarius Carbolineum and creosote Fraction IV would have appeared higher in the scale, and creosote Fraction I and zinc chloride considerably lower.

It is seen that ten of the twenty-five preservatives tested fall below 1 per cent, or more accurately 0.65 per cent, for their killing point for *Fomes annosus; Fomes pinicola* was used with only fourteen of them but of these ten fell below 1 per cent, or more accurately, 0.75 per cent.

It is interesting to note that sodium fluoride and Fraction II of coal tar creosote head the list with nearly equal toxicities. Just what constituents of the naphthalene fraction are the effective ones is not known at present, but the work of other investigators indicates that pure naphthalene has low toxic properties. The very favorable results from sodium fluoride would place this in the first rank of water-soluble preservatives. This, together with several other fluorine compounds, has come into considerable use abroad, particularly in Austria, and it is the opinion of the writers that we have in these substances very efficient wood preservatives which can be adapted to use in many situations. The industry particularly needs some substance which can safely be recommended for building timbers.

In comparing the two carbolineums with coal tar creosote it is seen that approximately 30 per cent of the former distils below 320° C., while 74 per cent of the creosote comes over. This indicates the greater toxicity of the lower boiling constituents. As to what causes the greater toxicity of S. P. F. Carbolineum over Avenarius Carbolineum we are not prepared to say, but the fact that the former is higher in tar acids is very suggestive.

The poor showing made by copperized oil against both fungi indicates that adding copper in this form to low-toxic petroleum or vegetable oils is of very doubtful value.

In conclusion, the writers are prone to take a very conservative position when it comes to analysis of the data presented and generalizations drawn therefrom. We wish to strongly emphasize again the fact that toxicity alone does not necessarily give a direct comparison of the service value of preservatives, and that all the statements made comparing different substances refer to the toxic properties only. However, we do feel that the results here set forth will prove of considerable value in outlining further tests which will serve to bring out actual service values.

We wish to record our acknowledgments to Dr. Haven Metcalf, Pathologist in Charge, Laboratory of Forest Pathology, Bureau of Plant Industry, Washington, D. C.; to Mr. Howard F. Weiss, Director of the Forest Products Laboratory, U. S. Forest Service, Madison, Wisconsin, for facilities and material placed at our disposal; also to Mr. Ernest Bateman, Chemist in Forest Products, Forest Products Laboratory, who has supplied all the data on the physical and chemical properties of the preservatives examined.

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A RAPID METHOD FOR DETERMINING THE PERCENTAGE OF CASEIN IN MILK

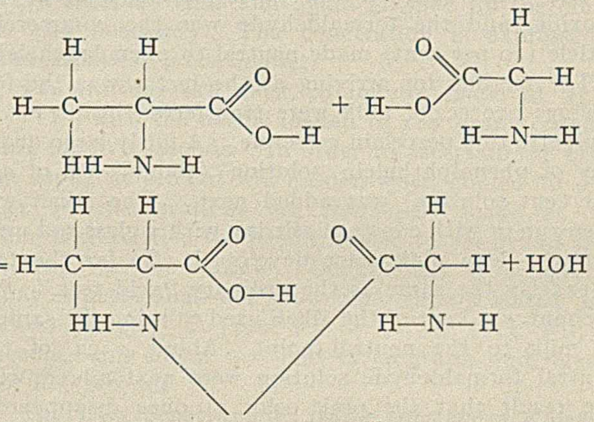
By W. O. WALKER

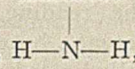
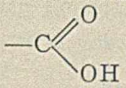
Received February 14, 1913

During the past few years dairymen have been giving a good deal of attention to the advisability of taking into account the percentage of casein when paying patrons for milk to be used in cheese-making. Some advocate paying on a fat basis only, others on the fat and casein basis. It is not the object of this article to discuss the merits of either of these methods, but to outline a process which has been tried out in the author's laboratory for quickly and simply arriving at the amount of casein in milk.

It is well known that several methods have been suggested of late, the most promising probably being the centrifugal method of Hart. This has, apparently, yielded satisfactory results in many cases, but has been found to give varying results with preserved samples, and with fresh milk, under different conditions of temperature, etc.

Research into the constitution of the protein molecule has revealed the probability of its consisting of a complex linkage of a large number of amino acids. To illustrate this linking up of amino acids we may use the following equation, which shows how one molecule of a simple amino acid, such as amino-propionic acid, may become bound to a molecule of another amino acid such as amino-acetic acid:



Both the molecules of amino-propionic acid and amino-acetic acid, as indicated above, possess an alkaline (amino) group,  H—N—H, as well as an acidic group,  $-C{\overset{O}{\underset{OH}{}}}$, and when they combine we may have the union taking place in the manner indicated, in which the alkaline (amino) group of one molecule interacts with the acidic group of the other molecule, thus leaving an alkaline group and an acidic group still existing in the product, which may be looked upon, for our purpose, as a very simple representative of the proteins.

It has further been observed that when formaldehyde is added to proteins, the neutral character of the molecule disappears, with the result that the acidic property predominates strongly. It is thought that the formaldehyde reacts with the alkaline groups forming methylene derivatives, thus leaving the acidic groups free to act. These acidic groups may now be neutralized with standard alkali, and if the value of the alkali in terms of protein be known, the percentage of protein present may be estimated.

Hugo Schiff[1] was the first to point out the importance of the reaction between formaldehyde and amino acids. S. P. L. Sorensen worked out most of the details for the quantitative application of the reaction for estimating amino acids. H. Droop Richmond adapted the reaction to the estimation of total proteins in milk.

The author decided to apply the reaction to the estimation of casein in milk, with the use of the alkali commonly used for the 'acid test' now in general use in cheese factories in Ontario.

In hoping to apply the reaction to estimate casein only, the problem is, of course, to obtain the proper factor, which, when multiplied by the quantity of alkali necessary to neutralize the acidity developed after treatment with formaldehyde, will give the quantity of casein in the sample. Since the formaldehyde reacts with both casein and albumin, and, since the amounts of these two in milk do not bear a constant ratio to one another, it was not to be expected that a factor holding good in all cases could be obtained. However, a factor has been obtained that is giving unexpectedly good results.

The alkali solution was ninth normal sodium hydroxide, and the formaldehyde was the commercial article (40 per cent) made neutral to phenolphthalein.

The method for arriving at the factor was the following: 10 cc. of milk were transferred by means of a pipette to a porcelain casserole. A fairly large quantity of phenolphthalein solution (about 1 cc. of a 1 per cent solution) was added next. The alkali was then run in with constant stirring with a glass rod until a fairly deep pink color developed. So far the test is exactly the same as the ordinary "acid test." No account was kept of the alkali used to bring the sample of milk to the neutral point. About 2 cc. of the neutral formaldehyde solution were next added, with the result that the pink color at once disappeared. The reading of the burette was then taken, and alkali again added with stirring until the same degree of color developed. The reading of the burette was again taken, the difference between the two readings being the amount of alkali used in the second titration.

Sample	Kjeldahl method	New method	Difference
1	2.45	2.53	+0.08
2	2.45	2.45	0.00
3	2.61	2.63	+0.02
4	2.51	2.52	+0.01
5	2.77	2.69	—0.08
6	2.53	2.61	+0.08
7	2.32	2.36	+0.04
8	2.96	2.96	0.00
9	2.69	2.66	—0.03
10	2.45	2.36	—0.09
11	2.32	2.30	—0.02
12	2.52	2.56	+0.04
13	2.31	2.27	—0.04

Another 10 cc. of milk was next treated by the official Kjeldahl method for casein, and from this result the value of 1 cc. of $N/9$ alkali in terms of casein was determined. From a large number of samples the value: 1 cc. $N/9$ alkali = 1.63 per cent casein was arrived at. Above is a comparison of some results obtained by the official Kjeldahl method and the new method, using the factor 1.63.

In determining the percentage of casein in a given sample of milk the procedure is exactly as outlined for determining the factor, omitting the Kjeldahl determination. The test occupies only a few moments. It has, of course, the disadvantage that only one sample can be handled at a time, but as a number of samples can be run in a few minutes, this may not prove to be of very great consequence.

From the fact that the chemicals and apparatus required are exactly the same as are in common use in cheese factories, with the exception of the formaldehyde which is very inexpensive, it is thought that the method should commend itself to the serious consideration of dairymen. It is, of course, important that the formaldehyde solution be kept neutral. This may be accomplished by adding a few drops of the indicator solution (phenolphthalein) to the formaldehyde in the bottle, and then adding the alkali until a pink color develops. This fades in the course of time, and the formaldehyde must then be treated again with the alkali.

The proper amounts of indicator (1 per cent solution) and formaldehyde solutions to be used have been found to be about 1 cc. of the former and 2 cc. of the latter. An excess of either, however, occasions no error. In the manipulation of the test it is well to add sufficient of the alkali during the first titration to bring the color to a decidedly deep pink, and at the second titration to bring the color to the same shade. The titrations are best carried out in a white cup or porcelain casserole.

If it is desired to estimate the acidity also, the reading of the burette may be taken after the first titration.

The casein is then estimated from the difference between the first and second titrations. Thus both the acidity and the casein are estimated in the one operation. Those dairymen who use $N/10$ alkali and 9 cc. of milk as the sample will, of course, employ the same factor. The test is at present recommended for unpreserved milk only, although the author expects to be able to announce a suitable preservative at an early date.

The following table is given for the use of those not wishing to take the time to multiply the amount of alkali used by the factor 1.63.

Cc. $N/9$ alkali used	Per cent casein
1.00	1.63
1.05	1.71
1.10	1.79
1.15	1.87
1.20	1.95
1.25	2.04
1.30	2.12
1.35	2.20
1.40	2.28
1.45	2.36
1.50	2.44
1.55	2.53
1.60	2.61
1.65	2.69
1.70	2.77
1.75	2.85
1.80	2.93
1.85	3.01
1.90	3.10
1.95	3.18
2.00	3.26

Instead of using a 10 cc. pipette for taking the

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[1] *Annalen*, **310**, 25 (1900); **319**, 59 (1901); **325**, 348 (1902).

samples and consequently having to multiply the amount of alkali used by 1.63, it is advisable to use a 16.3 cc. pipette, in which case, the reading on the burette denotes directly the percentage of casein.

A very convenient and simple form of acidimeter has been lately put on the market by the author which may be used for both the "acid test" and the "casein test."

A series of comparative tests, using both the new method and the centrifugal method, has been carried on at the Eastern Dairy School, Kingston. The tests were made independently on the same milks by Messrs. Echlin and Cameron. Mr. Echlin did the work with the new test, and Mr. Cameron that with the centrifugal method. The resulting figures, as can be seen from the following table, are in surprisingly close agreement.

Centrifugal method	New method	Centrifugal method	New method	Centrifugal method	New method
2.6	2.64	2.25	2.35	2.2	2.27
2.7	2.69	2.3	2.35	2.4	2.43
2.5	2.44	2.35	2.43	2.4	2.43
2.55	2.61	2.6	2.59	2.4	2.43
2.55	2.61	2.5	2.51	2.5	2.59
2.55	2.61	2.5	2.51	2.45	2.51
2.3	2.36	2.25	2.27	2.4	2.43
2.3	2.36	2.25	2.27	2.4	2.43
2.6	2.61	2.2	2.19	2.45	2.49
2.5	2.53	2.35	2.35	2.5	2.55
2.5	2.53	2.35	2.35	2.3	2.27
2.25	2.28	2.35	2.35	2 35	2.35
2.25	2.28	2 4	2.43	2.4	2.43
2.2	2.20	2.4	2.43	..	..
2.5	2.56	2.35	2.35	..	..
2.6	2.63	2 35	2.35	..	..
2.7	2.67	2.35	2.35	..	..
2.3	2.43	2.3	2.27	..	..
2.3	2.43	2.3	2.27	..	..
2.5	2.43	2.4	2.43	..	..
2.45	2.35	2.4	2.43	..	..
2.56	2.67	2.4	2.43	..	..
2.56	2.67	.3	2.27	..	..
2.55	2.59	2.25	2.27	..	..
2.55	2.59	..	..	..	..
2.55	2.59	..	..	..	..

The average difference for the above sixty-three determinations is 0.03+.

Gordon Hall of Chemistry
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I. A NEW ELECTRICALLY CONTROLLED AND TIMED ASPHALT PENETROMETER

II. THE EFFECT ON PENETRATIONS OF VARIATIONS IN STANDARD NEEDLES

By Hermann W. Mahr

Received July 14, 1913

I

Success in the laying of asphalt pavements is probably more dependent on the proper consistency of the asphalt cement used to bind the mineral aggregate than on any other feature. The varied origins of modern bituminous cements have made the determination of their consistency the most important test applied to these materials. Formerly a few varieties of standard solid bitumens, quite uniform in character, fluxed with definite proportions of petroleum residuums of standard and specified composition, yielding cements of a desired consistency, formed the bulk of the asphaltic cements; but recently many paving bitumens obtained by distilling asphaltic petroleums to the consistency of cements have come on the market. Proximate chemical analysis is of little value in fixing their origin, and the highway chemist is obliged to rely almost solely on determinations of consistency to ascertain their suitability.

There are several rough methods for determining the consistency of asphaltic cements, but the most generally used scientific determination is by means of penetrometers. The first of these instruments was devised by Bowen, and has been followed by machines working on the same principle by Kenyon, Dow and the New York Testing Laboratory. The two latter are those generally used at present. The penetrometer has made it possible to control the consistency or as usually expressed, the penetration, within narrow limits.

The penetrometers consist essentially of a needle of specified size (Roberts, No. 2) fixed in a rod, the rod and needle being of, or loaded to, definite weights. A clamp of some nature holds the rod with the needle, allowing the latter to penetrate as nearly as possible without friction. A device for measuring the amount the needle has penetrated after it has been released for a specified time and again grasped by the clutch, is also necessary. The penetration is expressed in hundredths of a centimeter.

Penetrations are most commonly made at 25° C. (77° F.) with the needle loaded to 100 grams penetrating for five seconds. In order to ascertain the extent an asphaltic cement will harden when chilled to 0° C. (32° F.), penetrations are frequently made at this temperature with the needle loaded to 200 grams penetrating for one minute. Occasionally it is specified that cements shall not show more than a stated penetration at 37.7° C. (100° F). or 46° C. (115° F.), the needle being under a weight of 50 grams and released for five seconds.

The Dow penetrometer frame consists of a base to which is fastened a broad upright support with two shelves at different distances from the base. The needle is held in an aluminum rod weighted by a rectangular frame of the same metal. The latter is fixed to the rod at about one-third the distance from its lower end. Weights are placed on the lower part of the frame to load the needle. The above-mentioned framework encloses the lower shelf on which is placed the sample. The rod passes through a hole in the upper shelf and is here grasped by the clamp which is closed on the rod by a spring when not penetrating. The rod and needle are released from the clamp by pressing the spring together with a button-ended rod.

The device for measuring the amount penetrated is fixed above the end of the rod. This consists of a rack, set vertically, the end of which can be brought down to meet the top of the rod. This rack is in gear with a pinion on a horizontal shaft. The latter passes through a graduated dial and an adjustable hand is fastened to it there. A counterweight which hangs from a cord winding up on a small pulley on the pinion shaft allows the rack to be raised or lowered. The divisions on the dial correspond to a movement of 1/100 cm. by the rack.

The Dow instrument has many features which make its use time-consuming. It also requires considerable skill and attention to obtain results checking within three or four degrees. The shelf, on which rests the water bath containing the sample, is fixed in position. This limits the height of the sample container and the bath. The weighted frame limits the width of the vessel used for a water bath, and is an inconvenience in placing the sample on the shelf and setting the needle. When the clamp is opened the space within is quite large. This allows the rod to deviate from a vertical position while penetrating. The weight of the large frame also tends to bring the needle out of the vertical. To avoid this action requires extreme care in setting, and even then it takes place to a small extent. When the rod is again clasped by the clamp, it is moved horizontally, thus bringing a force on the needle other than its weight. On bringing the rack down on the rod, after the needle has been set or penetrated, its weight is liable to drive the rod and needle down into the asphalt. The operator is inclined to avoid this by stopping the rack just above the top of the rod, thus introducing inaccuracies in the determination. The counterweight and its cord often become tangled in the shaft and shelves and are in the way.

These objectionable features of the Dow penetrometer led the New York Testing Laboratory to modify it. This instrument is described by Clifford Richardson in his work on asphalt paving.[1] The fixed shelf of the Dow machine is replaced by one on a screw. This allows the sample to be brought up to the needle very slowly, and the setting can be made with greater accuracy. The weighted frame is dispensed with and replaced by a weight on the lower part of the rod just above the needle. The rod slides in a collar of considerable height and is thus maintained in a vertical position. The clamp holding the rod is fixed in this collar and grasps it more firmly than that of the Dow penetrometer. Instead of a counterweight, the rack is kept in position by a spring pressing against it.

The wide collar, forming part of the clamp of the New York Testing Laboratory instrument, gives rise to considerable friction on the rod. This violates the basic requirement of the ideal penetrometer. The clamp requires the exertion of considerable force to release the rod. This tends to cause the operator to allow the clamp to shut before the expiration of the standard penetrating period. The force required to open the clasp is also liable to disturb the setting of the instrument and thus introduce inaccuracies.

The errors due to the construction of the present machines and to the personal equation of the operator often require a long series of determinations in order to obtain three results which lie within a limit of three or four degrees. Some specifications for asphaltic cement require its consistency to lie within limits ten degrees apart on the penetrometer. It is therefore difficult to interpret the specifications strictly with the results obtained on the present penetrometers. This has given rise to a demand for an instrument which eliminates some of the constructional errors of the present ones, and also some of the personal errors.

The errors in penetrating, apart from those of the instrument, are quite numerous. The sample, usually contained in a small tin box, must be firmly set in the water bath. This can be very satisfactorily accomplished by means of a glass vessel with a deep layer of fairly hard asphaltic cement.[1] The sample must have been at the standard temperature long enough to have attained it throughout. In this connection, laboratories working with a large number of asphaltic cements will find a good thermostat a great convenience. After a sample has been maintained thirty minutes at constant temperature it can be placed in the penetrometer water bath, filled with water from the thermostat at the same time.

A personal error of considerable magnitude has already been indicated, that of setting the rack on the rod before and after penetrating. In the timing of the penetration period lies probably the greatest error of the determination. The timing is done by either a stop-watch or a metronome. The use of the former is more open to inaccuracies than the latter.

The variation in the size of the standard needles has often been pointed out as a source of variation in results obtained by different chemists or by the same operator from time to time. The personal errors have been so large that no definite conclusions could be drawn as to the extent of this source of difference.

The importance of eliminating the time error and shock, due to the manual control of penetrometers, has long been recognized. With this object in view, Dow and Griffith devised and patented[2] an electrical limiting-time-interval clamp, to be applied to the then generally used Bowen penetrometer. This clamp clasped the thread supporting the weighted bar which held the needle, and released it for the desired intervals. This electrical limiting-time-interval clamp was cumbersome and complicated in its working and regulation. When Dow devised the penetrometer which bears his name, and which superseded the Bowen instrument, he omitted from it his time-interval clamp.

The advent of the simple, compact, Sieman's intermediate relay with time limits has made it possible to electrically time and control penetrometers of the present type. The penetrating device of the instrument can be directly controlled by the electrically timed magnet, instead of through the intermediary of a clamp, as in the Bowen-Dow-Griffiths electrical penetrometer. This simplifies the operating mechanism and reduces the chances of trouble from its derangement.

A new form of penetrometer, electrically controlled and timed, used for over a year in this Laboratory, is shown in Figure 1. Figure 2 is a sketch of the electromagnetic clutch for holding the rod with its needle. The clutch is on a bracket sliding on the upright rod of the instrument, to which it may be secured by means of a set screw. The weighted rod A, which holds the needle, is of steel, brass-clad. It slides through the openings in the thin German silver plates, C C, and is partly enclosed by the concave poles, B_1 B_2, of the electromagnet. The plates are set so the rod does not come into contact with the poles of the magnet, and are

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[1] "The Modern Asphalt Pavement," John Wiley & Sons.

[1] *Bull.* **38**, Office of Public Roads, U. S. Dept. of Agriculture.

[2] U. S. Patent 512,687 (1894).

rounded where they touch the rod, thus eliminating all friction. The rod and needle weigh 50 grams and are weighted to 100 and 200 grams by weights of 50 and 150 grams, respectively, slipped over the rod above the needle, and there fastened by set screws.

The penetration is measured, as in other machines, by means of a rack and pinion, the latter being fastened to an adjustable hand on a dial. The counterweight and spring, used in the previous types of instruments for holding the rack in place, are dispensed with. The pinion shaft has an additional gear wheel. This gear is in mesh with a worm on a shaft at right angles to the first, the worm shaft being driven by means of a milled head at one side of the dial. By turning the milled head the rack may be raised or lowered and accurately set on top of the rod. In setting the needle on the surface of the sample, the latter is first raised to within less than a millimeter of the former. The rod is then forced down by the rack until the needle touches the surface of the asphaltic cement. During the setting the rod is held by the magnet, the electromagnetic force being overcome by that exerted by the rack. This device and method of procedure enable very accurate settings of the needle and rack to be made.

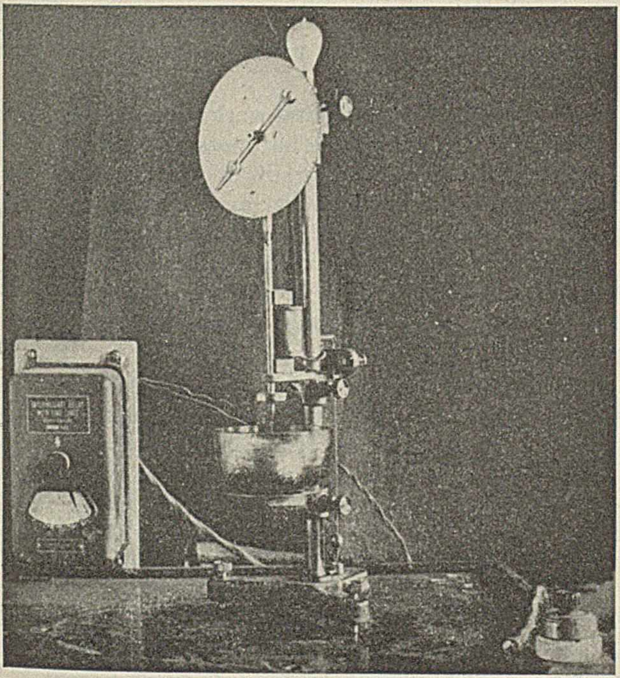

FIG. 1

The sample is placed on a movable shelf which can be rapidly lowered to allow cleaning of the needle. In order to set the machine in a vertical position, a plumb bob and adjusting screws are attached to the penetrometer. A small electric lamp, fastened to the top of the standard and in series with the electro-magnet, indicates when the current is on. The instrument is wound to be connected to a 110 volt direct current circuit.

The use of the electro-magnet clutch precludes the shock or displacement of the machine, due to a clamp operated by hand. The circuit is broken by pressing a button. To eliminate the time error of the observer, a Sieman's intermediate relay with time-limit is used. The penetrometer is placed in the circuit with one side of this device, and the lighting circuit passed through a switch and the relay electro-magnet. On breaking the current through the latter, the penetrometer circuit is broken and automatically made at the end of five seconds.

The accuracy of the penetrometer was tested by determining the penetration of three asphaltic cements, using the same needle. The penetrations were made at 77° F., with the needle loaded with 100 grams, penetrating for 5 seconds. After each observation the needle was cleaned with chloroform, dried, and brought to 77° F.

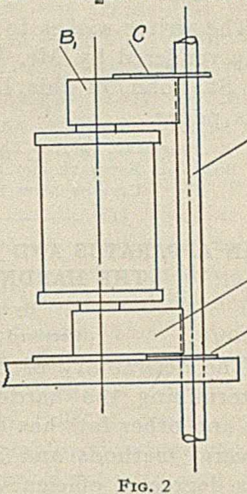

FIG. 2

The results are given in the following table:

PENETRATION OF ASPHALTIC CEMENTS. (77° F., 100 g., 5 sec.)

	Oil asphalt cement No. 1	Oil asphalt cement No. 2	Trinidad asphalt cement
Determination No. 1.....	55	53	85
Determination No. 2.....	55	53	84
Determination No. 3.....	55	53	84

II

Richardson[1] has stated that variations in the size of the needles give rise to uncontrollable variations in penetrations determined with them.

Since all errors are eliminated in the machine described, it was possible to ascertain the extent of this variation. Three needles were selected from each of three packages of standard needles. Oil asphalt cement No. 1 was then penetrated, using these needles, taking the precautions outlined above.

PENETRATION OF OIL ASPHALT CEMENT NO. 1, BY DIFFERENT NEEDLES (770 F., 100 g., 5 sec.)

Needle	Package	Penetration	Needle	Package	Penetration
1	1	55	6	2	55
2	1	55	7	3	55
3	1	54	8	3	54
4	2	54	9	3	54
5	2	54			
				Average,	54.6

The greatest deviation from the mean is 0.6 of a unit.

CONCLUSIONS.—A new form of penetrometer, which eliminates the errors due to the construction of previous instruments and permits rapid accurate determinations, has been described.

The personal error in timing penetrations has been eliminated through the use of this penetrometer in connection with an intermediate relay with time-limit.

The variations in determinations of penetration due

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[1] *Loc. cit.*

to variations in the standard needles has been investigated and found to be negligible.

The writer wishes to express his appreciation of the help rendered by Mr. Walter Erlenkotter and Mr. A. D. St. John, of this Laboratory, in connection with this paper.

STANDARD TESTING LABORATORY
BOARD OF ESTIMATE AND APPORTIONMENT
CITY OF NEW YORK

AN APPARATUS AND METHOD FOR DETERMINING THE HARDNESS OF BUTTERFAT

By A. E. PERKINS

Received September 22, 1913

The desirability of having an accurate method for determining the hardness or consistency of butterfat and other fats has been felt for a number of years. Several methods and apparatus having a greater or less degree of efficiency have been devised from time to time.

The first methods were proposed for the examination of olive oil. Of these earlier methods the most practical was devised by Serra Carpi.[1] His method was to cool the olive oil down to 20° C., for three hours, and by means of a suitable arrangement, he placed on the solidified fat a cylindrical iron rod, 2 mm. in diameter and 1 cm. long and conical at the bottom. Weights were then put on to the rod until it sank completely into the fat. Thus, for pure olive oil 1700 grams and for cottonseed oil 25 grams were required.

Woods and Parsons[2] report satisfactory results in determining the hardness of butter by the use of a method which consists essentially of dropping a weighted glass rod through a glass tube 1 meter long, held vertically above the surface of the butter to be tested, and noting the depth of penetration on a scale attached to the glass tubing. The determinations were performed at 15.5° C. after the butter had stood in a cool room for several days. The results were expressed in mm. of penetration.

R. Brulle[3] measured the hardness of butter with an apparatus which he called an "oleogrammeter." This is an instrument consisting of a vertical rod on the top of which is fixed a large plate. The rod is allowed to slide in a ring fastened to a stand. The end of the rod is placed on the surface of the solidified fat, and then weights are put on the dish until the rod sinks briskly into the fat. The weights required represent the resistance of the butter to the "oleogrammeter." The butter samples were kept at 21° C. for an hour before testing. This method is essentially the same as that used by Serra Carpi[4] for olive oil.

Sohn[5] proposes three forms of apparatus and lays down the following rules, strict adherence to which are necessary:

1. The rod must descend in an absolutely perpendicular direction.
2. It must slide in its bearing with the least possible friction.
3. Conditions of temperature must be constant.
4. Vessels of one diameter must be used for the material under examination.
5. The rod must enter the center of the vessel or at a fixed distance from the circumference.
6. The same depth of material must always be used.
7. The material must be allowed to rest a certain fixed time before testing.

J. B. Lindsey[1] and his associates determined the hardness of butter with an apparatus analogous to that used by Woods and Parsons,[2] the only real difference being that they dispensed with the large glass tube and the depth of penetration was measured on the plunger. Their determinations were performed on butter which had been in cold storage for some time and then allowed to stand at room temperature for several hours.

Hunziger, Mills and Spitzer[3] report results in measuring the hardness or "mechanical firmness" of butter with an apparatus which measured the crushing effect of a plunger, size and weight not stated, on briquettes of manufactured butter. No mention is made of the conditions of temperature under which the tests were conducted.

In some of our experimental work here, we considered it desirable to measure the hardness of butter fat with a reasonable degree of accuracy, and in such a way that results obtained throughout experiments extending over long periods of time would be entirely comparable. After trying several of the above-mentioned methods, none of which proved delicate enough for our purpose, the following apparatus and method were devised.

The apparatus used, as shown in the accompanying cut, comprises a firm support (A) and a separate light frame (B) carrying the penetrating needles and the weights. The support consists of a heavy iron base (*c*) into which are inserted 2 upright rods (*d* and *e*) about 1 meter long, one of which is hollow and contains wires connecting the electro-magnet (*g*) with (*h*). These uprights are about 25 cm. apart and are joined together at the top by a piece of hollow iron rod (*f*): (*h*) and (*h*) are binding posts for attaching the batteries to operate the magnet. A key (*j*) attached to the base serves for making and breaking the current through the magnet: (*k*) and (*l*) are millimeter scales reading downward. Attached to the upright rods is an adjustable platform (*m*) for carrying the sample whose hardness is to be tested. The coarser adjustment of the height of the platform is secured by means of the clamps (*n*) and (*o*). This adjustment does not need to be regulated except at rare intervals. A finer adjustment is secured by simply turning (*m*) which is supported from (*n-o*) by a $^3/_4$ inch nut and screw. The frame is of hollow brass tubing to get it as light as possible, while still retain-

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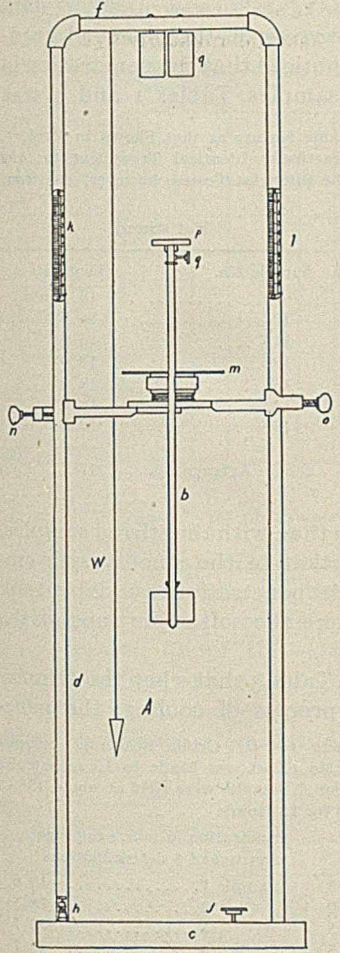
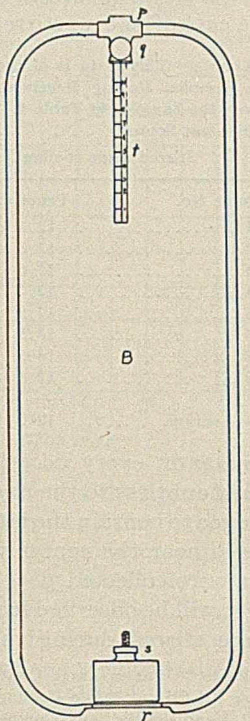
[1] Serra Carpi, *Z. anal. Chem.*, 1884, **23**, 566.
[2] Woods and Parsons, *Bull.* **13**, New Hampshire Exp. Sta.
[3] R. Brulle, *Compt. rend.*, 1893, **116**, 1255.
[4] *Loc. cit.*
[5] Sohn, *Analyst*, **1893**, p. 218.

[1] Lindsey and Associates, *13th Ann. Rept. Hatch Exp. Sta.*, p. 28; *14th Ann. Rpt. Hatch Exp. Sta.*, p. 167; *16th Ann. Rpt. Hatch Exp. Sta.*, p. 59; *21st Ann. Rpt. Hatch Exp. Sta.*, p. 99.
[2] Woods and Parsons, *loc. cit.*
[3] *Bull.* **159**, Purdue University, Indiana Agr. Exp. Sta.

ing the necessary degree of strength. It is about 40 cm. long and 15 cm. wide: (*p*) is a piece of soft Swedish iron to be acted on by the magnet. Directly beneath this inside the frame is a socket and a set-screw (*q*) to hold the needle (*t*) in place. At the opposite end of the frame is a small platform (*r*) for carrying the weights, which are made with a hole drilled through the center so that they can be placed over the screw projecting above the platform and held firmly in place by the nut (*s*). The frame (B) when carrying any one of the set of needles weighs 200 grams. Additional weights are provided, making possible any combination of exact multiples of 100 grams up to 1400. A set of needles is provided having cross-sectional areas of 5, 10, 15, 25, 50 and 100 sq. mm. They are cylindrical in shape and slightly more than 10 cm. long, being marked at a distance of 10 cm. from the end. The larger sizes are of hollow tubing plugged at the ends, and the smaller made with heavy shanks to secure uniformity of weight. The scales (*k* and *l*) attached to the upright rods which were previously referred to, are so placed that when the frame with needles and weights is held in place by the electro-magnet, preparatory to making the test, the point of the needle is at zero on the scales. The height of the adjustable platform (*m*) is then so regulated that the surface of the sample to be tested is at 100 mm. on the scale. A small plumb bob (W) or a wooden rod of proper length measuring downward from (*g*) is made use of in this connection. The distance of fall before reaching the surface of the butter is, then, always 10 cm.





In making the determination, the frame (B) with a suitable needle and weights is suspended from the electro-magnet, and the beaker of fat placed in position beneath the needle, the height being regulated as described above. The frame is then released by means of the key. The depth of penetration is ascertained by stretching a very fine wire in line with the mark on the needle, and noting its position on either scale. The average of the two readings is taken as the depth of penetration. Since the cross-sectional area of the penetrating needle is known, and the depth of penetration has been ascertained, their product indicates the volume of butterfat displaced. The amount of weight acting on the needle is known, and the distance through which it falls is constant; if then, the amount of weight employed, expressed in grams, is divided by the volume of fat displaced, expressed as cu. mm., the quotient will represent the weight in grams required to displace 1 cu. mm. of the fat, or the number of kilos required to displace 1 cc. at the stated temperature. This is the basis employed to express the proportionate hardness of the fat. A sample of fat is said to have a hardness of 1 at a given temperature when 1 kilo will displace 1 cc. of fat; or of 1.2 or 0.85 when 1200 or 850 grams, respectively, are required to displace 1 cc. of fat. When all other conditions are constant, it is evident that the hardness is in inverse proportion to the depth of penetration, and direct comparisons can be made.

The amount of weight employed and the size of the needle used will depend, of course, on the character of the fat, and the temperature at which the hardness is determined. With a proper combination of needles and weights, the needle will remain practically stationary in the fat after the initial plunge. If, however, too much weight or too small a needle is employed, the needle continues to sink slowly, making an accurate reading of the depth of penetration impossible. In the reverse case with too large a needle or too little weight, the penetration is of course much less, and the percentage experimental error proportionately greater.

The suspension of the weights far below the needle brings the center of gravity of the falling portion of the apparatus below the point of the needle, causing the latter to invariably assume a vertical position, making it much easier to ascertain the true depth of penetration than would be the case if the point of the needle (*t*) were at or below the center of gravity. After its release by the electro-magnet, the apparatus meets with no resistance whatever in its fall, except that offered by the air until the point of the needle reaches the surface of the butter.

It might be argued that gravity was acting through a greater distance in the case of a sample which was penetrated 30 mm. than in the case of one which was penetrated, say only 15 mm.; or again, it might be argued that the amount of friction on the sides of a small needle would be proportionately greater than that on a larger needle, on account of the greater area in proportion to its volume. These objections, if they are applicable, would tend to counteract each other; and at any rate, their influence is not perceptible in the results; for, duplicate determinations carried out with varying sizes of needles and weights, where the depth of penetration is necessarily greater in some cases than in others, show no greater variations than occur when the same sizes of needles and weights are used throughout, provided combinations which render readings difficult to make be avoided.

In practice we endeavor to secure a combination of needles and weights which will give a penetration of about 25 or 30 mm. and with our wide range of weights, 200 to 1400 grams, have ordinarily found it necessary to make use only of the needles having sectional areas of 25 and 50 sq. mm., when working at ordinary temperatures.

While the agreement of duplicate readings is not as close as is ordinarily expected in quantitative chemical work, it is, considering the nature of the determination, reasonably satisfactory when the samples have been properly prepared. The extreme variations rarely exceed 2 or 3 millimeters with a penetration of 25 to 30, and in the majority of cases, the readings have a closer agreement than that mentioned above. In practice we have taken the average of five or six readings as the final result. After the samples are prepared, we have been able to make and record from 40 to 50 readings per hour.

Since the end to be attained in this work was knowledge regarding the properties of the fat itself as distinguished from those properties which may have been introduced in the process of manufacturing the fat into butter, the hardness, like the other physical and chemical constants, has been determined on the rendered fat. Data have been introduced in Table 8 showing the hardness of several samples of butter prepared in different ways; also the hardness of the rendered fat from the same butter.

The method of procedure adopted in working with rendered butterfat is as follows: About 200 cc. of the mixed melted fat are placed in a 250 cc. Griffin shape aluminum beaker which is set in cold water, 10 to 20° C. in a pan having a smooth level bottom. The fat is frequently stirred with a glass rod until the rod can just be removed without leaving an impression in the fat. The sample is allowed to stand in the water a few minutes longer until it is well solidified. The stirring is done to prevent the separation of the fat into zones of different hardness, a condition which occurs when the melted fat is left to solidify without stirring. Tables 1, 2, 3 and 4 show data illustrating the effect of stirring on the observed hardness of the fat. It will be noticed that the penetration in the case of the unstirred samples, Tables 1 and 2, was greater on every occasion than with the stirred samples, due doubtless to the fact that in the small vessels employed to contain the fat, the penetration invariably took place near the center where the softer portions of the fat were collected.

Table 1—All the Samples Shown in Table 1 were Taken from the Same Large Dish of Melted Butterfat which had been Thoroughly Mixed, and were Identical in Composition. After Being Poured into the Small Jars in which the Hardness was Measured the Samples Received the Same Treatment in Every Respect, Except that the Samples so Designated were Stirred with a Glass Rod as Described Elsewhere in this Paper, while they were Being Cooled in a Pan of Running Water. The Samples Designated as Unstirred were not Disturbed Until they were Solid. The Samples were All Removed at the Same Time to the Constant Temperature Bath and Kept at Almost Exactly 15° C. for 18 Hours.

Stirred while cooling		Not stirred	
Sample No.	Penetration	Sample No.	Penetration
1	21.0 mm.	8	28.0 mm.
2	22.0 "	9	24.0 "
3	22.5 "	10	29.0 "
4	22.5 "	11	25.0 "
5	22.0 "	12	25.0 "
6	23.0 "	13	27.0 "
7	22.0 "	14	24.0 "
		15	25.0 "
Average	22.1 "	Average	25.8 "

Table 2—This Data is of the Same Nature as that Shown in Table 1, the Samples Having Received Practically Identical Treatment to that Given the Samples in Table 1. The Butterfat Tested, however, was from a Different Source.

Stirred while cooling		Not stirred	
Sample No.	Penetration	Sample No.	Penetration
1	12.5 mm.	9	18.5 mm.
2	12.5 "	10	16.0 "
3	12.5 "	11	16.0 "
4	12.0 "	12	18.0 "
5	12.5 "	13	19.5 "
6	13.5 "	14	18.5 "
7	13.5 "	15	17.5 "
8	12.5 "		
Average	12.7 "	Average	17.7 "

It will be observed from Table 3 that when the samples were stirred during the process of cooling, the penetration was practically the same regardless of which portion of fat was penetrated. In the case of the unstirred samples, Table 4, the penetration was much greater when measured at the center than when measured near the edges of the receptacle. The penetration measured midway between the center and edge was just about the average of that obtained at the center and that obtained at the edge. Stirring the fat in this way while it is cooling makes unnecessary a strict observance of rules 4, 5, and 6 as laid down by Sohn and quoted above.

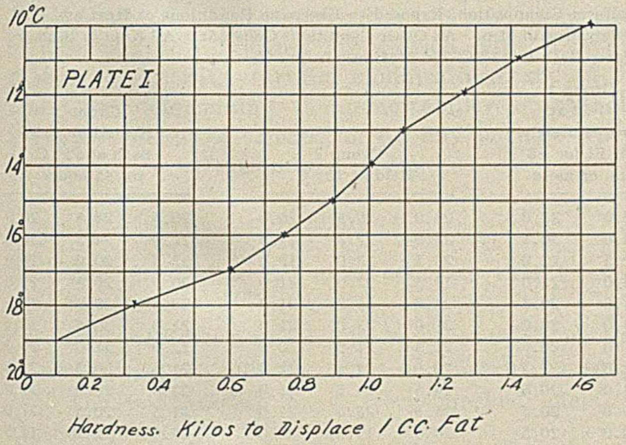
Table 3—Fat in Large Containers (600 Cc. Griffin Beakers). Samples were All Stirred While Cooling. No Effort was Made to Have Samples 1, 2, 3 and 4 of the Same Composition. Samples were Held at about 15° C. in the Constant Temperature Bath for 18 Hours.

Penetration in mm. at center 1 determination only		Penetration in mm. near edge Average of 4 determinations	
Sample 1	20.5	Sample 1	18.6
2	27.0	2	25.5
3	30.5	3	30.7
4	30.5	4	29.7

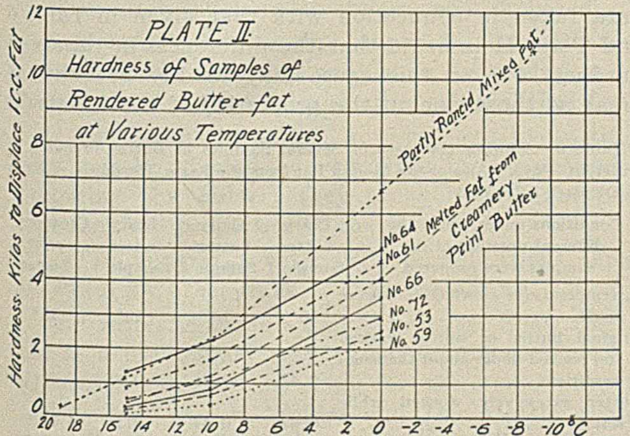
Table 4—The Same Conditions Obtained Here as Described for the Samples in Table 3, Except that None of the Samples were Stirred during the Cooling Process.

Penetration in mm. at center 1 determination only		Penetration in mm. near edge Average of 4 determinations	
Sample 1	30.5	Sample 1	22.1
2	30.5	2	22.0
3	29.5	3	21.8
4	29.0	4	20.8

The samples prepared in this way are transferred to a covered water bath tightly packed with heat insulating material inside a double walled wooden box. They are held here for 12 hours (over night) or longer at a temperature not more than 1° C. from that at which the tests are to be made. The temperature is then adjusted to exactly the proper point and not allowed to vary more than 0.1° C. from that temperature for 6 hours before the tests are made. Samples held under these conditions gave much more uniform and satisfactory results than we were able to secure on recently solidified samples. The method of procedure in making the determination itself has already been given as a part of the description of the apparatus.



Sohn in the article quoted above emphasized the importance of a close temperature control, and we have likewise found this absolutely essential, if results of any value are to be expected. The necessity of such a close control over the temperature can be better understood after a study of the results recorded in Tables 5 and 6 and Plates I and II showing the hardness of several samples of fat at different temperatures. These results show clearly that a difference in temperature of even 0.1° is a very important matter when attempting to measure the hardness of fat.



It will also be noticed that the rate of increase in hardness, due to temperature, is considerably greater at lower temperatures than it is near the freezing point of the fat, which in the case of butterfat, is in the vicinity of 20° C. These results also serve to illustrate the well-known fact that there is a marked difference in hardness due to the individuality of the animal producing the fat. The numbers in Table 6 and Plate II correspond to the herd number of the animal producing the sample. These were selected at random from cows in the dairy herd at the Ohio Experiment Station and by no means represent extremes.

Table 5—Showing the Hardness of the Same Samples of Butterfat at Temperatures Ranging from 10° C. to 19° C. Each Value as Stated was Calculated from the Average of Several Determinations Carried Out According to Our Regular Method of Procedure as Given Elsewhere. Hardness in Terms of Kilos Required to Displace 1 Cc. of Fat at Stated Temperatures.

Temperature	Hardness	Temperature	Hardness
10°	1.630	15°	0.890
11°	1.420	16°	0.750
12°	1.270	17°	0.603
13°	1.092	18°	0.337
14°	1.012	19°	0.113

Other factors such as breed, the advance of the period of lactation, and the character and amount of food, are supposed to have considerable influence on the hardness of the fat. The available data on certain of these points is well summed up by Hunziger, Mills, and Spitzer.[1] As already stated this method and apparatus were devised as a means of studying certain of these factors.

For general work with this method the most satisfactory temperature to be used in making determinations of the hardness of butterfat is probably that temperature between 15° and 0° C., which can be maintained with the greatest ease and constancy under available conditions. Any temperature above 15° C. will probably be too warm to permit an accurate determination of the hardness of soft samples of butterfat. In some ways the results secured at 10° C. or 0° C. are more satisfactory than those to be obtained at higher temperatures, because in working with the greater values the chances for error are lessened.

Table 6—Showing the Hardness of Several Samples of Butterfat at Different Temperatures. The Numbers Correspond to the Herd Number of the Animal Producing the Sample.

Temperatures	19° C.	15° C.	10° C.	0° C.	—7° C.	—9° C.	—10° C.
53	..	0.20	0.65	2.53	..	..	..
59	..	0.12	0.38	2.33	..	..	..
61	..	0.84	1.65	4.60	..	..	..
64	..	1.27	2.25	5.00	..	..	..
66	..	0.26	0.82	3.54	..	..	..
72	..	0.56	1.02	2.93	..	..	..
Melted fat from Creamery print butter	..	0.43	1.18	4.11	7.08	..	..
Sample of mixed fat. Partly rancid	0.21	1.11	2.41 (9.5° C.)	6.66	..	10.8	12.0

The relative hardness of the samples at these temperatures may not, however, always represent their relative hardness at higher temperatures as shown by the data in Plate II and Table 6; and the fact must not be lost sight of, that from a practical standpoint the hardness of butter at 0° C. or even 10° C. is of little significance; while the hardness of butter at temperatures above 15° C. is a very important matter, for a butter which will stand up well and retain its hardness under summer conditions is greatly to be desired; such butter is especially demanded for export to tropical countries. Hunziger, Mills, and Spitzer[1] present evidence to show that the hardness of the fat is a very important matter which must be taken into account in regulating the water content of butter.

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[1] *Bull.* **159**, Purdue University, Agricultural Experiment Station.

In our work with rendered butterfat below 10° C. we have found it necessary to melt and remove a thin layer of fat from the outer edges of the container to prevent the formation of cracks throughout the sample, due to the contraction of the fat on cooling, since these interfered seriously with the determination. This was accomplished by wrapping the sides of the container of well solidified fat for a few seconds with a towel wrung out of hot water, and pouring out the melted fat. This gave a solid block of fat which did not crack when cooled. At —10° C., or below, the fat samples are inclined to split, when penetrated by the needle, like a block of free grained wood struck with an ax, and we were unable to secure satisfactory results at lower temperatures.

Most of our work has been done either at 10° or 15° C. During the greater part of the year it has been found practicable to maintain the latter temperature quite satisfactorily in an unheated basement room with the equipment which has already been described. This can be done whenever the room temperature is reasonably constant and is not more than 2° C. in either direction from the temperature to be maintained. A constant temperature room or apparatus is very desirable when either can be had. We have used with great satisfaction rooms in the cold storage plant at the Ohio Experiment Station in securing part of the data contained in this paper. A temperature of 0° C. can be maintained quite satisfactorily in a room several degrees above that temperature by keeping the insulated water bath well supplied with crushed ice.

Statements made by certain of the investigators named above suggested that previous exposure to heat or cold might permanently affect the hardness of the butterfat. To determine whether such was the case, a large number of samples of mixed fat were prepared and treated under much more rigorous conditions of both heat and cold than those which need ever be met with in carrying out determinations by this method. Part of these samples were held at different times for from 48 to 96 hours at a temperature approximating 10° F. Others were heated at 95° C. on a steam bath for periods of 48 hours; others were held at 15° C., the temperature at which all were tested. At the conclusion of the special treatment, all were treated according to the usual method described elsewhere in this paper. These results are given in Table 7. They seem to show that neither heat nor cold within the limits encountered in operating this test have any marked permanent effect on the hardness of butterfat. Likewise samples which we have repeatedly heated and cooled in obtaining other data contained in this paper have shown no change of hardness in the process.

In working with manufactured butter, results can be obtained which duplicate each other more closely than the results secured on the rendered fat; also less care is required in the preparation of the samples. The butter under examination was either in the form of 1 pound prints or was well packed in the 250 cc. aluminum beakers already referred to, and immersed in the constant temperature bath in the same manner as described for samples of rendered fat. At first thought, it would seem that data regarding the hardness of fat could be obtained to better advantage on the manufactured butter than on the rendered fat itself. Some of the investigators referred to above have followed this method. While we have not extended our investigation to include all of the details of the manner in which the hardness of manufactured butter may be affected by the methods employed during its manufacture, the results given in Table 8 clearly show that the hardness of the fat as determined in this way will probably be very greatly influenced by differences of method in preparing the butter. This data taken in connection with that given in Table 6 and Plate II indicate that the differences in observed hardness due to this cause may readily be fully as great as those due to the properties of the fat itself.

Table 7—Showing the Hardness of Several Samples of Butterfat of Uniform Composition, Exposed to Excessive Conditions of Heat and Cold. Penetration in Mm. All Other Conditions Constant. All Kept in Insulated Water Bath at 15° C. for 24 Hours before Testing.

Group 1 Held at approximately 10° F. for 48 hrs. or more		Group 2 Held at 15° C.			Group 3 Heated on steam bath at 95° C. for 48 hours		
22.0	23.0	24.0	20.5	20.0	20.5	24.5	20.5
23.0	20.5	23.0	22.5	19.0	21.0	24.5	20.5
22.5	22.0	23.5	23.0	19.0	23.5	20.0	24.0
23.0	21.0	19.5	23.0	21.0	20.5	20.5	21.0
24.0	20.5	23.0	22.5	21.0	22.5	20.5	20.0
23.0	20.0	21.0	25.0	21.0	21.0	20.5	20.5
21.0	20.5	21.5	21.5	20.0	22.0	21.0	21.0
21.0	22.5	20.0	22.5	21.0	21.5	20.5	21.0
24.0	20.0	24.5	24.5	21.0	22.0	20.0	21.5
23.0	20.5	25.5	25.0	21.0	21.5	20.5	21.0
20.0	20.5	20.0	19.0	20.0	23.0	22.5	21.5
19.0	21.5	23.5	19.0	20.0	20.0	20.5	..
22.5	..	..	..	..	..	..	..
Average, 21.6		Average, 21.6			Average, 21.4		

Table 8—Showing Hardness of Several Samples of Butter Prepared in Different Ways. Also of the Melted Fat from the Same, Hardness = Kilos to Displace 1 Cc. Fat.

Conditions under which the different portions of the samples were prepared	Dairy butter Sample 1	Dairy butter Sample 2	Dairy butter Sample 3	Creamery print butter
C. temperatures at which tests were made	10°	10°	10°	15°
Original butter or butter worked and packed under about the usual conditions	0.42	0.35	0.55	0.11
Butter excessively worked while soft	0.63	0.44	0.56	0.19
Butter excessively worked while hard	0.16	0.14	0.28	0.07
Rendered fat from the same butter	1.15	0.76	0.84	0.44

It occurs as a probable explanation of the above described phenomena that the crystalline structure of the soft worked butter is developed by this treatment, while that of the butter worked excessively while hard is broken up thereby. The soft worked butter possessed a high luster while the hard worked butter had a dull lusterless appearance, which may be regarded as further evidence in support of the above view.

Under the microscope the solidified rendered fat presented a well defined crystalline structure. The butter worked somewhat excessively while hard showed no evidence of crystal formation but appeared in masses of varying size all rounded. The butter worked excessively while in a soft condition seemed to have a structure intermediate between that of the hard worked butter and that of the solidified rendered fat, both rounded masses and crystals being in evidence.

This method should be of service to the butter-judge under certain conditions where an accurate judgment regarding the body of butter is especially desired. It should be particularly useful in laboratories where detailed examinations of the properties of fats, oils or lubricants are carried out. The apparatus itself with certain modifications should be useful for determining the penetrability of asphalt, the setting point of cement, or for any purpose where an accurate penetration test is desired.

CONCLUSIONS

1. This method is the most accurate that has yet been described.

2. It is necessary to stir the samples while cooling to prevent separation into zones of different hardness.

3. The temperature has a very marked effect on the hardness of the butterfat.

4. The sample should be kept at a constant temperature for 6 hours or more before testing.

5. The temperature to which the fat had previously been subjected seemed to make no difference in the hardness provided the samples were treated as described.

6. The determinations can be made with great rapidity after the samples are properly prepared.

7. More closely agreeing duplicate determinations are procurable with this method in examining manufactured butter than in examining the rendered fat.

8. The results obtained, however, are likely to be very greatly affected by variations in the method of preparing the butter; they probably will not truly represent the properties of the fat itself.

9. The apparatus with slight modifications should be useful for other work of a similar nature.

The writer is indebted to Mr. R. H. Shaw for the use in a preliminary way of an unpublished piece of apparatus designed by him for the same purpose; and to Prof. C. H. Eckles and Dr. Matthew Steel for valuable advice and suggestions. The apparatus was designed and part of the work done while the writer was employed in the laboratory maintained jointly by the Dairy Division, United States Department of Agriculture, and The Missouri Agricultural Experiment Station, at Columbia, Mo. Additional work has been done in the laboratory of the Dairy Department of the Ohio Agricultural Experiment Station, Wooster, Ohio.

NOTE.—The original apparatus still in use at the Missouri Station was constructed for the writer by Mr. Emil Klinkerfuss, mechanician at the University of Missouri. A duplicate apparatus for use at the Ohio Experiment Station has been constructed by Eimer and Amend.

INFLUENCE OF SMALL AMOUNTS OF ETHYL ALCOHOL ON FERMENTATION IN CANE SUGAR SYRUP

By C. B. COCHRAN[1] AND J. H. PERKINS[2]

Received October 17, 1913

Preparatory to determining the preservative values of a variety of compounds, we made them up into standard alcoholic solutions. The volume of the solution containing the amount of the compound desired was mixed with a definite amount of simple syrup, which then contained, in addition to the added compound, a small amount of alcohol. In several instances, we noted that yeast did not act on these syrups exactly as they did on similar syrups containing no alcohol. We then carried on the following experiments in order to determine just what influence a small amount of alcohol has on fermentation in cane sugar syrup.

Simple syrups, ranging in specific gravity from 1.2112 to 1.26 at 20° C., were made by dissolving granulated cane sugar in warm—not hot—water. Sufficient alcohol to make the percentage desired was then added to each syrup, some of the syrup, however, being kept for blank or control tests.

These syrups were then tested as follows: one thirty-second of a Fleischmann's yeast cake was thoroughly mixed with one fluid ounce of syrup, with the exception of the 1.245 syrups, to 50 cc. of which one-sixteenth of a yeast cake was added. Portions of the syrup were then put in two fermentation tubes and kept in an incubator at between 31 and 32° C. The percentage of gas was noted daily. When the two tubes contained the same amount of gas, the result is not stated in duplicate.
The percentage of absolute alcohol is given by volume.

Per cent alcohol by vol.	Sp. gr. syrup 20° C.	Time Days	Per cent of gas	Per cent alcohol by vol.	Sp. gr. syrup 20° C.	Time Days	Per cent of gas
0.033	1.259	1	100	None	1.2558	1	70
None	1.259	1	55 & 78			2	100
		2	100	1.633	1.25544	1	45 & 42
0.658	1.2572	1	100			2	80 & 83
None	1.2572	1	22			4(a)	100
		4(a)	100	1.88	1.2514	1	65 & 80
0.77	1.2112	1	20 & 30			2	100
		2	80 & 100	None	1.2514	1	70 & 80
None	1.2112	1	15			2	100
		2	100	1.88	1.26	1	15 & 35
1.0	1.2563	1	65 & 70			2	80 & 100
		2	100	None	1.26	1	45 & 55
None	1.2563	1	20			2	100
		2	53	2.0	1.245	3	75
		4(a)	100	None	1.245	2	100
1.25	1.2558	1	60 & 70	3.0	1.245	3	30
		2	100	5.0	1.245	4	3

(a) The third day being Sunday, no reading was made.

CONCLUSIONS.—1. One per cent or less of alcohol markedly accelerates fermentation in syrup of above densities.

2. 1.25 per cent of alcohol has very little influence.

3. Beginning with 1.25 per cent the presence of alcohol retards fermentation in these syrups, the amount of retardation increasing with the increase in the percentage of alcohol.

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LABORATORY AND PLANT

FILTER PRESSES[1]

By E. J. Sweetland

That there is great room for improvement in the methods of filtration commonly employed cannot be doubted. The plate and frame filter press ordinarily used comprises anywhere from 40 to 100 filter chambers, each of which must be cleaned individually by hand every time the filter is filled.

It was to eliminate the excessive amount of hand labor in cleaning filter presses that the filter under discussion was primarily designed, but as the construction was developed many incidental advantages of importance developed with it, as will be pointed out further on.

The single advantage in plate and frame filter presses that has kept them in favor is the fact that their peculiar construction affords a very large filter area in a comparatively small space. Filtration cannot be forced beyond a certain reasonable limit; when this limit is reached, it is necessary to increase filter area to increase capacity. To endeavor to increase capacity by increasing pressure instead of filter area is futile, for excessive pressure merely presses the cake to a compact, almost impervious layer and the object is defeated at once.

With this in view, the modern filter must not depart from a construction that permits of ample filter surface. Other things being equal, the capacity, and consequently the value, of a filter is proportional to the filter area.

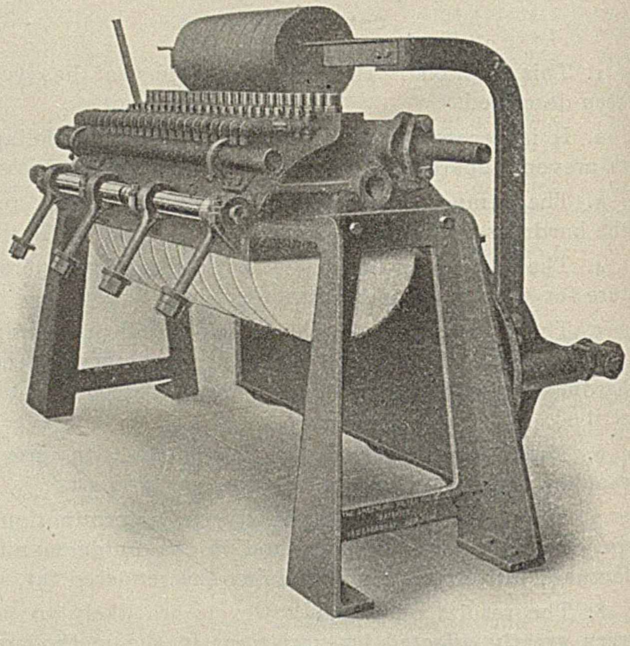
The sluicing type of filter press is one example of a filter press construction that eliminates hand labor in cleaning. In this type the cake is disintegrated by a stream of water forced into each chamber. The cake thus liquefied flows to the waste reservoir, or dump. The usefulness of this method is limited for obvious reasons, chief of which is the need of recovering the cake as dry as possible in most processes.

The uses of filter presses are so varied that great flexibility is required. One process will demand a filter capable of handling a thick sludge containing twenty or thirty per cent solids, forming cakes probably four inches in thickness, which have to be thoroughly washed; the next problem may consist of clarifying a viscous fluid containing but traces of solids, so finely divided as to make a thick cake an impossibility. One problem calls for recovery of the solids only, the filtrate being of no value, while another rejects the solids as refuse after recovering the liquid content; still another requires recovery of both liquid and solid. Some plants make certain products at certain seasons only and must use the same filter press for an entirely different product at other seasons. To be a commercial success it would seem that the modern filter press should lend itself to these various requirements and the construction be made adjustable as far as possible.

As will be seen from the following description, the filter under discussion is a radical departure from the plate and frame filter press and is even more simple in construction.

CONSTRUCTION

This filter has become known as the "clam-shell" type due to the shell being in two parts hinged together to open and close somewhat after the manner of the clam-shell bucket used on steam shovels.



Counter-weighted Press Open

The filter body comprises two semi-cylindrical members hinged together, one member being provided with an inserted gasket which seals the joint between the two to form a water-tight cylinder when closed.

A plurality of openings is provided along the top to receive the stem or outlet nipple of the filter leaves. These outlets are spaced quite close together so that the leaves may be closely spaced if desired, as is the case when thin cakes are to be formed; but the leaf spacing may be increased to any degree by taking out part of the leaves and stopping off the intermediate outlets.

Variable spacing is quite essential, for it is not always possible to ascertain in advance exactly what spacing will be best suited to the material; and further, there is always the possibility of the process being modified to change the filtering properties of the material and make a change in leaf spacing desirable.

The filter leaves are usually made of wire screen, well crimped to provide ample drainage. The screen is bound at the edges to stiffen the construction and protect the cloth. An outlet nipple with a side open-

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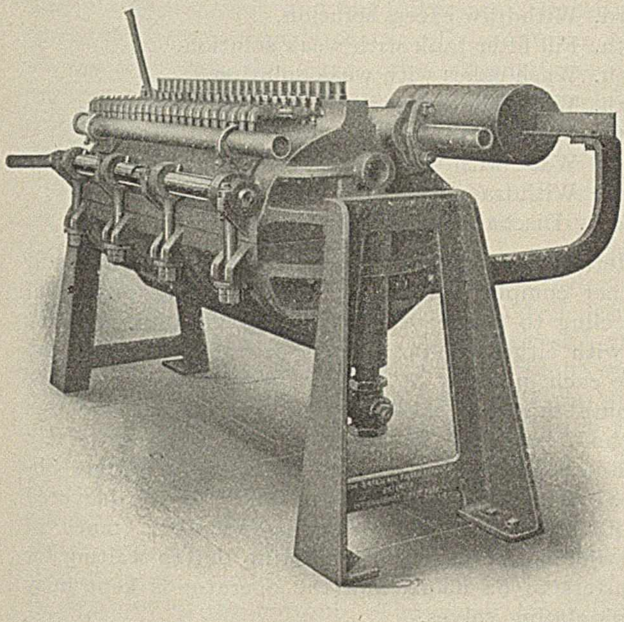
[1] Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10–13, 1913.

ing furnishes an exit for the filtrate and means of holding the leaf in the filter body. The filter cloth covers the entire metal construction of the leaf except the outlet nipple and is held on either with metal clips or by being stitched around the edges.

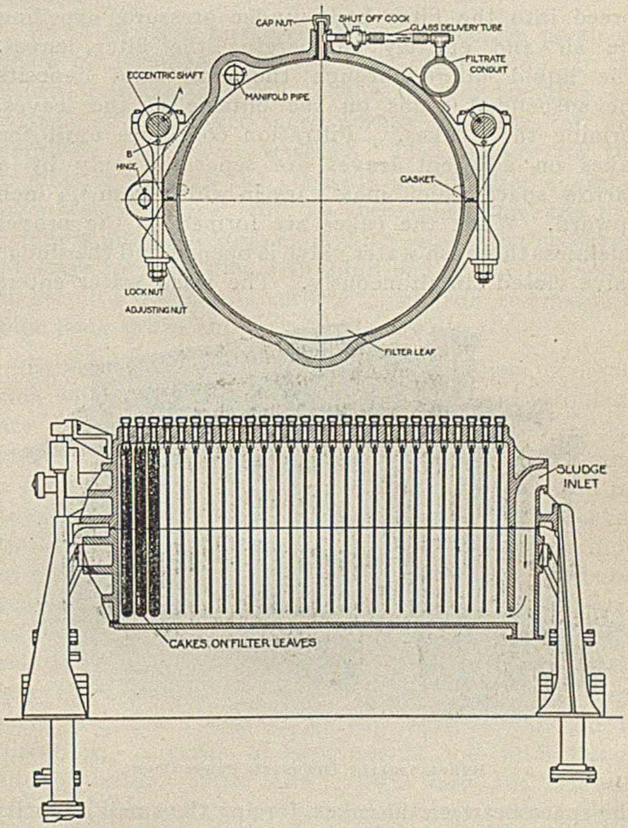
The leaves are held in place in the filter by a cap nut which engages the top of the nipple and draws the shoulder of the leaf tightly against the rubber washer which fits in a recess inside the filter body. The side outlet of the nipple aligns with the filtrate delivery fittings on the outside of the press.

The accompanying cross-sections of the filter body clearly show how the filter leaves are held in place by the nipple at the top. Each leaf has separate outlet fittings comprising shutoff cock, glass delivery tube, etc. These fittings allow the operative to see the filtrate from each individual leaf as it flows through the glass, and any leaf that might become injured or require renewal of cloth is indicated at once by a turbid filtrate in the glass. In this event the shutoff cock governing the defective leaf is closed until the filter is opened and the leaf replaced. To remove a leaf only the cap nut has to be removed—the outlet fittings are not disturbed.



Counter-weighted Press Closed

In the earlier designs of this filter the two halves of the shell were held in closed position by hand-operated swing bolts. These were fairly quick and convenient to operate but still left room for improvement. It was desired to modify the construction to an extent that would reduce the time to unlock and open the filter from a few minutes to a few seconds, if possible. This was accomplished by a very simple change in the construction. The hinges, which formerly took no strain while the filter was in locked position, were increased in strength and number and made to take the strain formerly taken by the swing bolts on the back of the filter body. To eliminate any possibility of breakage, the hinges are made of steel, which can be fully depended upon for strength. What seemed the great problem in working out this improvement was the need of accurate hinge adjustment to take up wear in the gasket. This problem like many mechanical problems proved to be simpler than was anticipated, for it was solved by simply making the hinge pins into one continuous shaft reaching from end to end of the press, and turning the bearing which received all of the hinges on the upper member eccentric to the normal axis of the shaft. This construction not only affords adjustment, but makes adjustment of all hinges simultaneous by merely turning the hinge shaft slightly when adjustment is necessary to draw the upper and lower halves of the shell closer together as the gasket gradually flattens out from continued use. The shaft is held from turning by set screws, which are loosened when adjustment is made.



Cross and Longitudinal Sections of Sweetland Filter Press

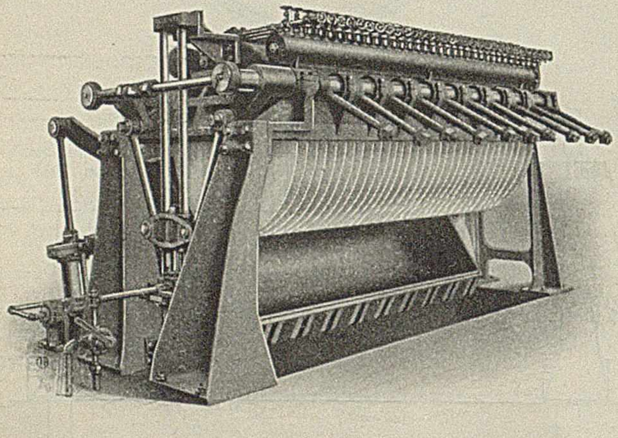
An eccentric shaft with swing bolts rests in babbitted bearings along the front of the upper half. Each bolt has an adjusting nut and lock nut for initial adjustment and for taking up wear. The swing bolts are tightened or loosened simultaneously, due to the eccentricity of the shaft, when the latter is turned through an arc of 180°, and means is provided for swinging the bolts clear of the lugs on the lower half just at the point when they have loosened sufficiently to disengage themselves.

This arrangement makes it possible to open or close a filter press of moderate size in a few seconds. The lower half of the shell is poised with counterweights to facilitate opening and closing.

In large machines an eccentric shaft is used on both front and back, and a hydraulic cylinder operates the two simultaneously by means of a crosshead and connecting rods. The lower member in this case is swung open and shut by a hydraulic cylinder at either end which is so arranged that the shell is opened so wide as to invert it and thus clean itself of any cake that might have fallen before it was fully opened.

OPERATION

In operating the filter the liquid to be filtered is forced into the filter body under pressure, expelling the air and entirely submerging the filter leaves. The liquid filters through the cloth and deposits the suspended solids on the outside of the leaves, forming the "cakes." Filtration continues until the cakes on adjacent leaves are separated only by a narrow space which may vary in width from $^1/_8$ inch upward. When the cakes are formed to the proper thickness the wash water valve is opened and the sludge valve closed simultaneously. The wash water enters the space between the cakes, forcing the small quantity of unfiltered sludge to deposit its solid component upon the cake surface. The space between adjacent cakes is now occupied by water which, being under pressure, percolates through the cakes, driving the strong liquor ahead and effectively displacing it until the cakes are washed to the desired degree, which is indicated by frequent tests of the effluent.



Hydraulically Operated Press Open

I feel justified in enlarging somewhat upon the subject of washing the cakes, for therein lies a great difference between this and other leaf filters. It should be noted that there are no chambers or containers to be packed solidly full of cake. The spaces between the leaves are not packed solidly full, but a cake is deposited on the surface of each leaf and these cakes are allowed to build up until only a narrow space remains between them, and in this space lies the secret of successful automatic discharging of the filter, and efficient washing. The cakes have been formed under equal conditions, the sludge being evenly distributed and the pressure equal throughout the filter chamber; therefore, the cakes must be of even thickness and density and must wash evenly. That this actually occurs has often been demonstrated by testing samples of the washed cake from various parts of the press.

All filters of the leaf type wash by "direct contact" methods; that is, the wash water is in direct contact with the cake; but the methods of washing that have heretofore been practiced with leaf filters whether vacuum or pressure are indeed anything but direct.

The usual method of forming and washing the cakes on filter leaves is as follows, assuming that the cake has to be washed first with weak liquor and then with water:

1st. Fill filter tank.
2nd. Deposit cake on leaves.
3rd. Withdraw excess solution.
4th. Fill filter tank with weak solution.
5th. Wash cakes with weak solution.
6th. Withdraw excess weak solution.
7th. Fill filter tank with water.
8th. Wash with water.
9th. Withdraw excess water.
10th. Discharge cakes from leaves.

Here are ten distinct operations, which are still further complicated by the fact that the cakes will not cling to the leaves unassisted, but must be held on with either compressed air or vacuum during the time each quantity of excess is withdrawn. I do not dispute that the cakes can be washed well by this method, but raise the point that it is an extremely round-about method of accomplishing a simple object. Most of the power consumed is not devoted to filtration but to transferring solutions, much of the time is not devoted to filtering but to waiting for transfers to be made, and the operator is kept busy manipulating valves.

The delay in filtering necessitated by the many transfers materially cuts down the duty of the filter, and the process becomes a complicated one, requiring many tanks and much accessory apparatus to take care of excess solutions.

Nor is this all. The transfers of excess solutions referred to introduce other complications. The cakes must be supported upon the leaves at all times by pressure. Air pressure (whether produced by suction or otherwise) must be used during the transfers. If too much pressure is used, the cake will be cracked (due to the shrinkage of partial drying) and the wash water will "short-circuit," that is, pass through the channels formed by cracking. If too little pressure is used, all or part of the cakes may fall from the leaves, which would preclude the possibility of efficient washing. Lastly, if the cakes are of a slimy character, the partial drying during the transfer packs the particles of slime, and makes it less pervious than ever to the passage of wash water.

The origin of the many complications cited above is traced directly to void or "dead" space in the filter tank or chamber which contains the filter leaves. If there were no dead space, there would be no excess solutions, and consequently none of the complications which attend them.

The "clam-shell" construction of filter body has no void spaces. It contains nothing but the filter leaves and manifold pipe. When the filter leaves are loaded with cake, the entire filter chamber is full except the feed channel for distribution along the bottom, and the narrow space between the cakes for the entrance of wash water. There is, therefore, no excess solution to handle. Filtration is continuous from the time cake-forming is commenced until washing is finished, and the process of filtering and washing is reduced to the simplest possible form.

When washing is finished, the cakes are partially dried with compressed air, the lower half of the filter body is swung open and the cakes are dumped into a car or conveyor underneath. To assist the cakes to dislodge from the leaves, the current is reversed by turning steam or compressed air inside of the leaves, which not only causes the cakes to drop off, but benefits the cloth by keeping the pores open.

For the benefit of those who insist that better washing can be obtained by draining the filter body before introducing wash solutions or water, I would point out that the filter construction here described offers every facility for carrying out this method, if desired; but after installing many of them, large and small and under widely varying conditions, and seeing trials made both ways, I strongly advocate the direct method without withdrawing solutions.

If the material is very slow-filtering and the space between the cakes wide, then it is better to introduce the wash water through the manifold pipe and let the water entering the top fill the chamber by downward displacement, forcing the excess solution out of the drain valve at the bottom. The water, being lighter than the sludge, does not mix with it, but floats on top during displacement. In this case filtration is continuous, pressure is maintained in the chamber, no time is lost, and the cakes are constantly submerged.

It is so frequently asked why the body of this filter was designed cylindrical instead of square that I shall take this opportunity to point out the reason. Obviously the principle could be carried out in a filter body of square or rectanglar section. The reasons for cylindrical construction are:

1. The cylindrical construction affords great strength whereas any shape with straight sides would require so much reinforcement to give it the necessary strength as to make it cumbersome and awkward.

2. The leaves are exposed to view by simply swinging the body open.

3. A circular leaf is conveniently supported from one point and is very strong and light.

4. If the chamber were square, the leaves would be inaccessible, or else would have to be lifted out with the cover to discharge, and this would involve mechanical difficulties.

The circular form of leaf does not involve as much waste in filter cloth as might be imagined. There is to be sure a slight waste of cloth cut from the corners but most of this has an important use in reinforcing the cloth at the edges of the leaf; on the other hand, a large percentage of the cloth used in plate and frame presses is not used for filtering, but to form a joint between the frames. If we figure it out in any case, we find the percentage of cloth purchased that is utilized as filter medium, is about the same for either shape. In fact, the cost of cloth per unit of work done is much less in the case of the leaf construction, because the capacity per square foot is greater, and the cloth is not injured by being squeezed between the frames.

As to filtering mixtures containing coarse particles, these offer difficulty in any type of filter, due to the coarse particles settling to the bottom, making the bottom of the cakes more porous than the top and resulting in uneven washing. The remedy for this trouble is to keep the contents of the filter chamber in a state of agitation. To accomplish this, the feed pump is provided large enough to supply the necessary pressure for filtration with additional capacity enough to permit a restricted overflow to run from the manifold pipe back to the supply tank during filtration.

New light is being thrown on the subject of filtration with almost every new installation, and problems are being successfully solved that appeared at the start to be impossible of solution. To cite an instance: a sample of a heavy viscous liquid was submitted for test. It contained a gummy residue that blocked the filter cloth from the start, the rate of flow of filtrate per square foot of cloth was but a few cubic centimeters per hour, and the cloth became so coated as to defy cleaning by any practical method. As the solution only was required, and the residue was worthless, there seemed to be no objection to adding some inert granular substance to the liquid as an aid to filtration. A series of experiments was undertaken, adding various "filter aids" to the fluid, and the outcome of this work was that an average rate of filtration of three gallons per square foot of cloth per hour was obtained and the gummy residual matter was sufficiently broken up to permit the filter cloth to be readily cleaned by reversal of current. Upon completion of the tests, a filter was installed in the plant and has fully demonstrated the practicability of the method on a working scale. It was found that any one of several substances could be used as an aid to filtration, among which are fine sand, fuller's earth, kieselguhr, sulfate or carbonate of lime, sawdust, wood pulp, etc.

It is not argued that such methods are applicable to all cases, but there are unquestionably many problems that will find solution in similar schemes, which make possible rates of filtration such as are usually obtainable only in sand filters, with the added advantage that the leaf filter offers an enormous filter area in a small space, combined with extraordinary ease of cleaning.

Another method of filtering materials containing a gummy residue that tends to choke the cloth is that of depositing a protecting layer on the cloth before commencing filtration. For instance, we may first fill the filter body with a very thin slurry of carbonate of lime and filter this mixture for a few seconds until a film of lime, say $^1/_{32}$ inch in thickness, has been deposited. This coats the cloth as completely and evenly as a deposit could possibly be made. The lime slurry is then drained off and filtration commenced. The coating of lime forms a complete film between the cloth and gummy residue, so the latter never even touches the cloth. When ready to clean the cloth the reversal of current is effective because the coating of lime breaks away readily.

It is frequently asked how we can tell when cakes of sufficient thickness have been formed, especially when the material filters and builds up the cake rapidly. This is not as difficult as would be imagined. The usual way is to work at a given pressure, say forty pounds per square inch, and pump for a certain number of minutes, determined by practice to form the required cake. Another way is to pump a certain number of inches from the supply tank for each charge. As in all processes, the operative soon becomes expert, and can judge from the general conduct of the filter when the charge is sufficient.

The usual skepticism which attends the introduction of any new machine was encountered at first, but so many installations are now in successful use as to establish fully the usefulness of the methods described. A noteworthy point is the fact that many of the filters of this type in use are of much larger size and capacity than it is found practicable to build filter presses. Many have been built with a capacity of 133 cubic feet of cake per charge and several others ranging from 80 to 120 cubic feet per charge. One especially large one was built which dumps over 25 tons of cake per charge.

That this apparatus is now far beyond the experimental stages is demonstrated by the fact that a large beet sugar factory in California installed three large hydraulically operated machines for the 1913 campaign. They were installed almost at the last minute before the campaign started and were at once placed in service at full capacity, and no difficulty was encountered, in spite of the fact that none of the employees who operated the machines had ever seen one before. The time required to open, clean and close one of these filters is about five minutes, which minimizes labor to such an extent that one operator can take care of several large machines, even though each machine has to be cleaned hourly.

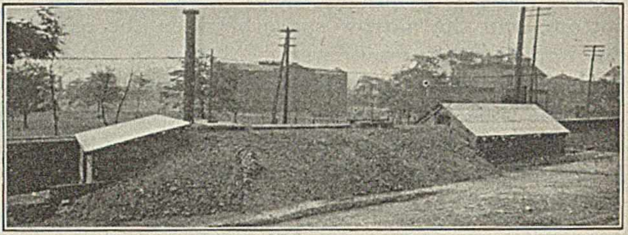
Sweetland Filter Press Co.
149 Broadway, New York

IMPROVISED MINE FIRES ON AN EXPERIMENTAL SCALE

Received January 15, 1914

The Bureau of Mines has recently installed at its Pittsburgh experiment station an underground chamber or furnace in which to carry on experiments relating to mine fires and spontaneous combustion as occurring in mines.

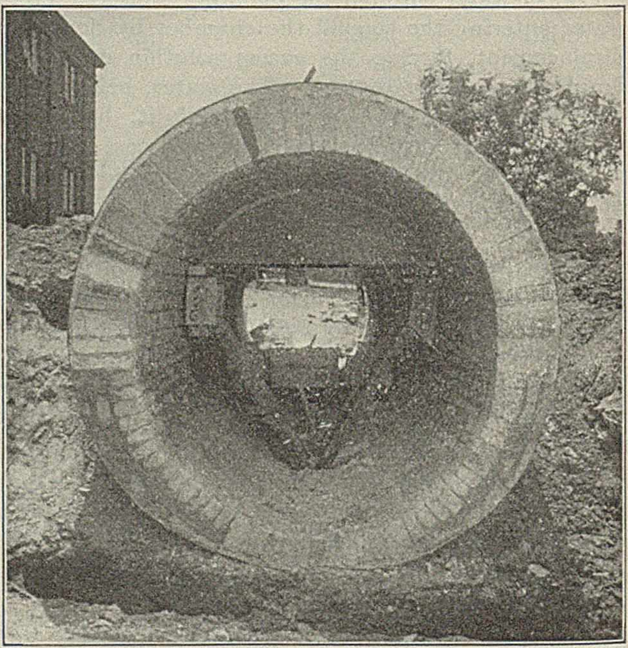
A section of steel tube cylindrical in shape, $6^1/_2$ feet in diameter and 27 feet long, was laid on its side in a deep trench, and after lining this shell with firebrick and mineral wool and stopping the ends with 13-inch brick walls, it was covered with two feet of earth. The chamber was constructed so as to be as nearly air-tight as possible, and in such manner as to retain to the greatest degree practicable any heat generated within its walls.



Side View of "Combustion of Coal" Apparatus

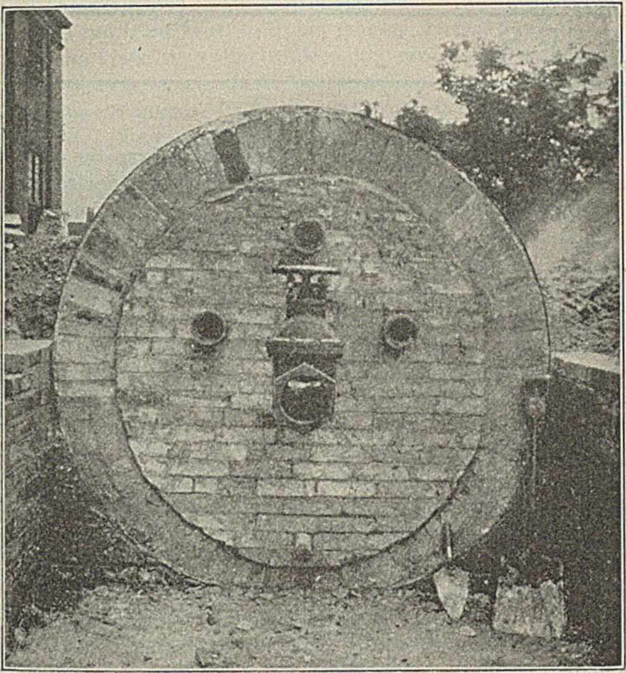
At one end a motor-driven fan will blow in air at a rate which can be accurately measured, and at the other a stack is provided which can be opened or closed as desired. Through the top of the chamber, at frequent intervals, pass small pipes for withdrawing samples of air or gases and for inserting pyrometers for temperature measurement in the interior.

The chamber will hold 6 to 8 tons of coal when one-third full. It is expected that different kinds of coal or of the gob or waste material from mines will be placed in the chamber and a study made of spontaneous development of heat in them under various conditions. After an active fire has been started in the chamber either by this means or artificially, experiments will be made on controlling the fire by reducing the air supply or by sealing it off entirely. The progressive changes in composition of the fire gases or of the air surrounding the coal will be followed and temperature measurements made, in an endeavor to apply the data



Cross Section of "Combustion of Coal" Apparatus Showing Method of Construction of Brick Lining thus obtained to solving practical problems in the treatment of mine fires.

Investigations have been made in other countries and to some extent also in this country, of the gases produced in actual cases of mine fires both before and after sealing off a burning area. The bureau is now making, however, probably the first attempt to investigate such problems in an experimental apparatus which permits careful control of conditions and yet is on a scale nearly commensurate with mining operations. These investigations are being carried on by Horace C. Porter, chemist, of the Bureau of Mines.



"Combustion of Coal" Apparatus Showing Gas and Air Connections to Combustion Chamber

A SHAKER FOR THE MECHANICAL ANALYSIS OF SOIL

By Freeman Ward

Received October 23, 1913

INTRODUCTORY.—In the mechanical analysis of soil one of the prime requisites is the complete separation of all the particles before sorting them into groups or grades according to size. The tendency in the natural soil is for the finer particles either to gather among themselves as aggregates or to cling to the larger grains. If a complete separation is not effected the per cent of the finer grades of soil will be below, and that of the coarser grades above the truth.

The separation can be effected mechanically in one of two ways—pestling and stirring; or shaking, as advocated by the Department of Agriculture[1]—water (very slightly ammoniacal) being added in either case. The essential idea of the latter is to place bottles containing soil and water in a horizontal position in trays which are jerked backward and forward by means of an eccentric attachment.

The purpose of this article is to describe a different type of shaker used by the writer and believed to have certain advantages.

DESCRIPTION.—The principle is as follows: The bottles with soil and water are ended over and over, thus allowing the contents to fall from one end of the bottle to the other. This is accomplished by having the bottles attached radially to a wheel which is rotated slowly in a vertical plane.

The machine used by the writer is "home-made" and consists of two small cart wheels sixteen inches in diameter, both on the same axle and touching hub to hub: this leaves the edges of the tires about three inches apart. Strips of tin fastened to the fellies serve not only to hold the two wheels together, but also with the fellies act as a broad groove ($1^1/_2$ inches wide) for a belt to run on.

The bottles used are the kind known commercially as "four ounce sample oil bottles:" they are about six inches long and one and one-half inches in diameter, and are fitted with rubber stoppers: they have a capacity of 120 cc. The base of each is slipped into a sleeve of tin fastened near the hub: a wire clamp secures the bottle at the neck.

The wheel thus constructed will hold sixteen of these bottles arranged radially—eight on a side. It may be attached to a motor by means of a belt. Plate I is a photograph of the machine.

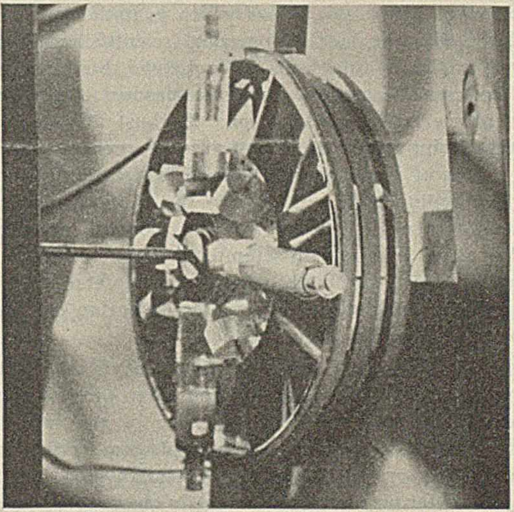


Plate I

To operate—put weighed (10 grams) sample of soil in bottle; fill one-half full of water which is slightly ammoniacal; attach bottle to wheel and revolve at the rate of twenty-five revolutions a minute; let run for three hours.

ADVANTAGES.—Separation by stirring and pestling is too laborious, consumes too much time, does not always result in a clean separation and has a tendency to mechanically fracture the particles of soil. Both the shaker methods are not only safer, and more effective, but, since they can be run by machinery, are convenient. And in either case the removal of the grades silt and clay by sedimentation and decantation

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[1] C. C. Fletcher and H. Bryan, "Modification of the Method of Mechanical Soil Analysis," U. S. Dept. Agr., Bur. Soils, *Bull.* **84**, 1912.

can be undertaken directly after the shaking without transferring the whole sample to another vessel.

The writer believes that his method is better than the one used by the Bureau of Soils in two respects. In the first place the machine is simple and inexpensive. A greater advantage is the saving of time. Clean separations can be effected in three hours, and in some cases two hours: this is a saving of at least four hours over the Bureau method. If the quantity of the water used in the bottles is reduced one-half, a clean separation results in much less than three hours, but there is a tendency for the grains to suffer some abrasion.

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ADDRESSES

THE PRESENT STATUS OF THE WOOD TURPENTINE INDUSTRY[1]

By E. H. French and James R. Withrow

In treating a subject that has as many phases as this one, it will be necessary to discuss briefly an allied industry, namely, that of Gum Turpentine as distinguished from Wood Turpentine, in order that the reasons calling for the development of this latter industry may be seen with the proper perspective.

That the Wood Turpentine Industry is at present at an extremely low ebb is unquestionably true. Nevertheless, it is likewise true that its scientific development is an economic necessity for certain localities, in order that waste may be conserved, that the products from waste replace those from the fast disappearing pine and fir forests and that cut-over land may be cleared at a profit instead of at a loss. Therefore, in this instance, as is often the case, necessity compels development.

The fact that thousands of dollars have been expended and lost in the incubation of this industry has been due, in our opinion, to three main causes, any one of which in itself would account for failure: *first*, the lack of practical scientific engineers experienced in this or analogous fields; *second*, financing for the sale of stock and securities rather than product; and *third*, lack of efficient marketing organization. It must also be borne in mind, that owing to the number of different processes, there was caused a lack of uniformity of product, which naturally tended to increase selling costs. Except to the U. S. Navy, little, if any, wood turpentine has been sold on thorough specifications. There has as yet been no real attempt by manufacturers to effect a general standard, although a few years ago the producers of the practically defunct steam process turpentine did make an attempt to standardize their product.

One of the important influences that tended at first toward the development of the industry and later proved extremely detrimental, was the speculative nature of the naval stores market. This was made up entirely of gum turpentine and rosin, upon the prices of which the relative wood turpentine values were determined. This market in the past has been subject to violent price changes, a fluctuation of from 30 cents to over $1.00 per gallon having been experienced, which was due almost wholly to speculation. Naturally, therefore, during the upward swing of prices an unnatural development occurred, and plants using costly processes and with inefficient management were profitably operated and exploited. It followed, of course, that when the national government, through criminal prosecution, put a stop to excessive speculation, a corresponding reaction occurred, ruining many concerns which required abnormal prices for financial success.

Unreasonably high prices not only encouraged the development of the wood turpentine industry, but also caused an expansion in operations by the gum turpentine manufacturers so that a larger percentage of trees, and many very young trees, were boxed, causing overproduction.

GUM TURPENTINE

The method of producing oil of turpentine from the resins of coniferous trees, consists in cutting a broad wedge-shaped notch or cup at the base of the tree and removing the bark immediately above the notch for about 18 to 24 inches. The resin exuding from the peeled area runs into the cup at the bottom and is collected from time to time. Each succeeding season the barked area is increased until it reaches about the height of one's head, usually taking five or six years. As many as four "boxes" are thus cut on one tree, depending on its size, permitting only enough of the original bark to remain to prevent the death of the tree.

After collecting sufficient quantity of the resin, it is distilled in a copper still, usually a "fire still," equipped with a live steam jet or a water supply. The turpentine thus produced is not carried farther in any refining process, but is ready for the market. The residue in the still is the rosin of commerce and is barreled at the still. The dross obtained by filtering sticks, dirt, etc., from the rosin is in many places being worked into cheaper grades of rosin. With rosin at an average price, it is generally figured that to make the operation profitable, about 42 cents per gallon must be obtained for the turpentine.

The marketing of the products is done through "factors" as they are called; that is, companies or individuals who contract with the producers for their output, supply them with funds for pay-rolls, etc., and advances when necessary. These "factors" take the product when produced, but usually have no other connection with the producer. Savannah, Georgia, is the leading naval stores center in the world and usually Savannah prices are accepted as the standard. Jacksonville and Pensacola, Florida, Brunswick, Ga., and New Orleans, La., are also large "factor" centers for this industry.

This method of producing turpentine is generally conceded to give the best turpentine and rosin, but unless more scientific methods are very widely adopted the time is rapidly approaching when it will be necessary to supply these products from another source, for present methods of operation are beginning to be looked upon as directly antagonistic to all ideas of conservation under American lumbering conditions, as they so weaken the trees that the loss from windfalls is extremely large. In fact, many large lumber companies have given up "boxing" for this reason, and also because they feel that the growth of the young tree is retarded.

Modifications of the old "boxing" methods are being used in some places. Metal cups are substituted for the box cut in the base of the tree and light chipping is being tried. It is claimed that the loss from windfalls is considerably reduced by some of these modern improvements. At least one large Southern lumber company is at present experimenting on 5,000 acre units in order to determine definitely, if possible, the merits of these new cups and other modifications as to yield and influence on windfalls, and also to decide the effect "boxing" may have on finished lumber.

WOOD TURPENTINE

Wood Turpentine came into commercial notice about the year

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[1] Presented at the 6th Annual Meeting of the Amer. Inst. of Chem. Eng., The Chemists' Club, New York, December 10-13, 1913.

1900. The name was, and is, applied to the product obtained from dead and down timber, a waste product called "lightwood." The live or green wood is not so suitable for this manufacture, owing to the moisture content and also to the fact that the bark still remains. Stumps, however, are very valuable, as they contain a much larger proportion of resins than "lightwood." Nevertheless, the cost per cord of stump wood is considerably more, as the stumps usually require the additional expense of removal by explosives. The cost per cord of "lightwood" at the works will run from $2.00 to $3.00, making, however, no allowance for its value as waste; while stump wood will vary from $3.50 to $5.00 per cord, the price depending on acre stumpage and hauling distances. The manufacture may be divided into five general processes; steam process, solvent process, alkali process, bath process and distillation process.

Before entering into a description of these various methods we desire to emphasize the statement that the manufacture of wood turpentine necessarily will become of far-reaching importance in the future. This is for the reasons that it is utilizing an absolutely waste product and is at the same time clearing cut-over lands and rendering them fit for occupancy. We wish also to emphasize the statement already made that many past failures were due to the unreasonable speculative condition of the markets. Abnormally high prices of naval stores induced promoters and unscrupulous persons to capitalize their concerns on the earning capacity during this period, thereby making them "stock jobbing" propositions rather than legitimate manufacturing institutions. This kind of financing while apparently expanding the industry really retarded development, as the energies of the management were expended primarily in the office and at the expense of the manufacturing organization.

We have seen from time to time figures of promoters, regarding yields and manufacturing costs of the different processes, which are not in accord with the results obtained from continuous operations. It may not be entirely without value therefore to cite some comparative yields and operation costs in these different processes, especially since there does not appear to be any published data of this nature. While the records themselves of individual plants would be interesting, such records are often misleading and in view of actual or possible competition, the location of plants must be withheld.

In submitting data as to yields, values and productive costs, we have complied them mainly from the actual results obtained during continued operation of a number of large plants. As so many elements making up these figures are variable, owing to location, construction and raw material, our endeavor has been to average them so that a comprehensive idea may be had as to actual results obtained commercially.

STEAM PROCESS

This process was the first to be extensively placed in commercial operation, and is very simple in its construction and handling. It consists merely of "hogging" the wood and placing it in a steel cylinder, holding usually about a cord, distillation being carried on with live steam and under varying pressure. However, there probably was little difference in results whether a maximum of five pounds or twenty pounds pressure was used. Distillation was carried forward until oils ceased to be obtained in quantity.

It should be borne in mind that there is a decided variance in the resinous content of wood; therefore, it was quite possible to make a selection that would run as high as 30 gallons of turpentine to the cord. We believe the following figures, however, based on a cord of long leaf yellow pine lightwood, weighing 3500 pounds, would be the average.

The fuel cost is only the labor of handling the treated chips. However, there is no allowance made for the office, upkeep, depreciation, insurance, etc. Therefore, it can be seen that the steam process, in order to be profitable, necessarily demands a market price considerably in advance of the present markets.

The price of Wood Turpentine is always a few cents per gallon under that of Gum Turpentine. The quality of the product produced by the steam process, however, is excellent. Our opinion is, nevertheless, that at least 50 cents per gallon is necessary as a minimum for successful operation.

Turpentine—9½ gals. at 35 cents	$3.32
Pine Oil—3 gals. at 35 cents	1.05
Total value of products	$4.37
Production Cost Per Cord	
Wood	$3.00
Labor	1.00
Barrels	0.42
Freight (approximate)	0.20
Selling Commission	0.25
	$4.87

SOLVENT PROCESS

In the early development of this process the wood was subjected to the old steam treatment and subsequently treated with carbon disulfide for the recovery of rosin. The loss of solvent rendered it impractical. In the next stage of development the wood was hogged and placed in digestors for the recovery of turpentine and pine oil. Then the solvent (a low grade of gasoline) was added, live steam was applied recovering some turpentine, pine oil, and solvent by distillation and the dissolved rosin drawn off, its volatile matter being recovered by distillation. This has been improved, in some instances, by omitting preliminary steaming, adding solvent direct and recovering this with the turpentine and pine oil by live steam in the primary distillation, obtaining rosin alone when the still is drawn. The rosin, however, is soft, and difficulty has been experienced in obtaining a hard product, but this is overcome by subsequent treatment. In either method a considerable loss of solvent is always entailed, varying from 17 to 30 gallons per cord. The approximate yields and operating costs per cord are as follows:

Turpentine—9½ gals. at 35 cents	$3.32
Rosin—400 lbs. at $4.00 per 280 lbs.	5.72
Pine Oil—3 gals. at 35 cents	1.05
	$10.09
Production Costs per Cord	
Wood	$3.00
Labor	2.50
Loss in solvent at 15 cents (17 gals.)	2.55
Barrels	.42
Rosin Barrels	.25
Selling Costs	.50
Freight	.75
Total	$9.97

Again the actual fuel cost in this process is negligible as use is made of the "treated chips." No allowance is made here for insurance, upkeep, overhead and interest charges, refining costs or depreciation; therefore, it is plainly evident that, at present market prices, at least until improvement is made in yields or in minimizing costs, there is not sufficient margin for successful operation. However, it is quite possible that by using the "treated chips" for paper pulp manufacture this process can be made of commercial value. The operation in this case would have to be maintained on an enormous scale in order to supply treated chips for a pulp plant unit of an economic size. A plant using this solvent system and built on a very elaborate scale, was in operation in southeastern Georgia, and, despite the most advantageous financial backing, was unable to operate profitably on a weakened market, and is now in the hands of receivers. This citation alone probably would not necessarily condemn the process, but as several smaller plants are either in like position or shut down, it indicates the necessity of research or development if ultimate success is to be attained. As with the steam process, many claims of higher yields than we have above credited are made by interested parties, but these claims are still subject to substantiation.

ALKALI PROCESS

This process is essentially one to be applied to the alkali processes for manufacturing paper pulp from resinous woods with the recovery of turpentine and rosin and at the same time improving the quality of the pulp, and promoting ease of manufacture. The process is well covered by patents.

The basis upon which this method rests is the fact that the sodium hydroxide saponifies the resins in the wood and the sodium resinate thus formed may be separated from the spent soda pulp liquor by temperature regulation. The wood is handled in the same manner as in soda pulp manufacture, except that after digestion the spent liquor is cooled for the separation of sodium resinate before the liquor proceeds to the evaporators. This product has been so purified and refined, commercially, as to produce a good quality of paper size. The resinate may if desired be manufactured into resin by acid treatment, or destructively distilled to produce rosin oils. The turpentine is recovered from the digester blow-off during the digestion operation. This process is apparently theoretically sound, but requires the outlay of capital to develop thoroughly the mechanical details. Fifty to seventy thousand dollars were expended in one case to demonstrate its commercial possibilities and some results were obtained. However, the enterprise has not been financially successful and the plant has been dismantled, a fact which may be due to faulty engineering or other causes; and even though the process appears enticing from a theoretical viewpoint the fact remains that the trial was not successful and there is no process of this kind in actual operation. Nevertheless, it is our opinion that eventually it will be of commercial importance and ultimately the combination of the two industries, paper pulp and turpentine-rosin recovery, thus utilizing resinous wood, will be successful. Unusual yields of turpentine are claimed by a Florida plant using an alkali bath but satisfactory arrangements have not yet been made regarding rosin recovery.

BATH PROCESS

This process must not be confounded with the recently suggested process using a bath or envelope of oil external to the oven for the purpose of heating the same. This external bath process has not been long enough in operation to demonstrate its future and it will be interesting to note whether certain fundamental operation difficulties can be overcome.

By Bath Process we refer to the process commercially so called which has been in operation for some time and in which the bath is *within the oven* or retort in contact with the wood itself. Three plants using this method have been built, the first in North Carolina, which has been dismantled, the others at Mt. Pleasant, Georgia, and Jacksonville, Florida, which have not been successful owing to low market conditions and both of which have gone into receivers' hands within the last few months.

The process itself was divided into two separate general operations: first, the recovery of turpentine and pine oil, or "sweet spirits," and subsequently the destructive distillation of the wood itself, although this second operation was not contemplated in the original process.

The operation has a decided advantage over the solvent and steam processes in that it does not require the "hogging" of the wood.

The general construction used in this first operation consists of steel cylinders at Mt. Pleasant, and concrete ovens at the Jacksonville plant, each holding five to nine, one or two cord steel cars, similar in construction to those in common use in hard wood distillation; thus each oven holds about nine cords of wood. Placed at the side of the oven is a heater equipped with a large cast iron worm joined to the bottom of the oven. To the rear of the heater is placed a large steel or concrete reservoir connected by cast iron pipe with the top of the oven, and also with rotary pumps which in turn are joined to the heater pipes.

The loaded cars are placed in the oven and melted rosin or pitch is run into the reservoir and circulated by the pumps through the heater and the bottom oven connection. This pitch after filling the oven *in contact with the wood* overflows into the reservoir and is thus continually circulated through the heater and oven, thereby vaporizing the volatile resinous bodies, without dissociating the wood fiber. The turpentine and oil vapors are carried through a "vapor" chamber in which the high boiling liquids that are mechanically carried by the vapor are separated, the vapor continuing to an ordinary tubular condenser, where the crude "sweet spirits" are obtained. Afterwards the "sweet spirits" are refined, the products being turpentine, pine oil and a tarry residue. The time required to treat a charge varies in the plants mentioned from seven to ten hours, and the product obtained is of high quality, though not so good as steam process turpentine.

At first sight it would appear that in this process the rosin from the wood treated would gradually increase the volume of the bath and rosin be thus manufactured. The reverse of this, however, is the case, as a serious loss of bath is actually realized. This is in fact a very serious drawback to the process, and is probably due to the formation of volatile rosin oils when the liquid bath encounters the high temperature of the heater. These rosin oils are volatilized and pass into the "crude spirits," and are lost in the refining residue, as only from 65 to 70 per cent of the spirits is received as turpentine and pine oil. By proper arrangement this difficulty could be avoided.

This process is also seriously handicapped by the fuel consumption of the heaters and the heavy upkeep for heater pipes and pumps. Nevertheless, with proper design, operation costs would be much reduced from that actually experienced.

After refining, the results from this "sweet process" could be averaged as follows:

Turpentine, 7$^{1}/_{2}$ gals. at 35 cents	$2.62
Pine Oil, 2.5 gals. at 35 cents	.87
	$3.49

After the charge is withdrawn in this first operation the "treated" wood is placed in ovens similar to those used in the hard wood industry and there subjected to destructive distillation. The results obtained here are very important as a good market has been created for these products. An average of from 68 to 70 gallons of oils is obtained, together with a like volume of "acid water," the latter a "waste," although its utilization was accomplished just prior to the receivership of one of the mentioned companies. In addition there remains in the cars approximately 900 pounds of charcoal and there is produced about 10,000 feet of non-condensible gas per cord which is of fuel value.

This crude distillate above mentioned is called "destructive distillate" or "D. D. Product" to distinguish it from the product derived from the resins, called "sweet spirits." On refining there are obtained the following products per cord:

Tar, 41 gals. at $.08	$3.28
Light Oil, 6.8 gals. at $.12	.81
Heavy Oil, 10 gals. at $.12	1.20
Charcoal, 36 bushels at $.075	2.70
From "sweet process"	3.49
Total	$11.48

Costs of Production per Cord

Wood	$ 3.00
Fuel	3.25
Labor	2.75
Cooperage	1.00
Selling Costs	.60
Freights (approximate)	.75
	$11.35

Again it can be seen that this process handled as it has been in the past cannot be operated successfully on a low market, as no allowances have been made for upkeep, insurance, interest charges, refining costs, management or depreciation. Although the loss in bath is partially made up by the pitch obtained, it can be seen from these costs that improvement must be had before this process can exist during low market conditions. It is not to be inferred, however, that the principles upon which the process is based are entirely faulty. The reasons for its failure appeared to be lack of knowledge as to the chemical nature of the products and troubles consequent to improper construction and operation. As is common with approaching dissolution strenuous efforts at improvements were made in this process, and despite well known prior failures, experiments were completed and operation commenced for the utilization of the waste "acid water" just before the closing of one of the plants. The results proved interesting and promised excellent recovery, as the products recovered, including acetate of lime and wood alcohol, represented a net gain of well over $1.50 per cord.

DISTILLATION PROCESS

As the wood turpentine industry now stands, the destructive distillation process apparently has the best chance of commercial success, as it is not only more simple in construction and operation, but yields more in volume of products. Chemical and engineering skill, nevertheless, are necessary for this success.

The distillation process may be subdivided into three divisions: *first*, that division analogous to hard wood distillation. This method in its primary operation is very similar in equipment and design to the usual hard wood distillation plant, the wood being placed in steel cars and run into ovens. The products derived from the resins and those from the dissociated wood are collected together, and separation is made during refining, although some attempt has been made at fractional distillation in this primary stage. This method gives a much inferior grade of turpentine, etc., owing to the commercial difficulty of eliminating the pyroligneous bodies, and the product will not answer to the permanganate test which indicates pyroligneous matter. The tar produced in this operation is usually resinous and for some uses, therefore, objectionable.

The *second* division is merely a modification of this process, the ovens being in duplicate, and distillation for the resinous bodies being carried out in one oven, so designed or "set" that the temperature can be maintained approximately uniform. After the resinous bodies have been obtained the "treated wood" is withdrawn and placed in a second oven and in this oven the distillation is carried at a higher temperature for the destructive distillation of the wood itself.

The *third* division is that using concrete ovens containing 12 inch heater pipes running the length of the ovens. These ovens have dutch-oven connections and the flue gases travel through these pipes, and it is claimed that temperature regulation is more easily accomplished.

In all these processes the products obtained are the same, except so far as the degree of purity is concerned.

The first distillate, or that from the resins in these methods, will run on an average 22 to 24 gallons of "sweet spirits." This on refining will give from 50 to 60 per cent or from 12 to 14 gallons of marketable turpentine and from 9 to 10 per cent or from 2 to $2^1/_2$ gallons of pine oil, and also 100 pounds of a very resinous pitch.

The destructive products are the same as those from the "bath process;" thus it can be seen that the gross total in this operation should be materially higher than in the other processes, while the operating expense is very much lower. This, including wood, upkeep, and in fact all expense, should not, under proper design, construction and management, run over $9.00 a cord.

The particular objection raised against the destructive distillation process is that the products are difficult to market, and this has been true to a certain extent in the past, but when it is considered that many of these products were new to the trade this condition cannot be wondered at, and at present the marketing is not more difficult than products of other processes. In fact, just now there is an unusual demand for these products.

MARKETS

It may, perhaps, be of interest to call attention to the various developed markets for the D. D. Products, for we all realize that the marketing of products is at least equal in importance to the manufacture; and this industry shows many instances where comparative merit of process and operation was wholly lost by inferior marketing facilities, and, on the other hand, instances in which unsound operation was maintained for a considerable time by a remarkably efficient selling organization. The latter cases, while losing ventures to those financially interested, have no doubt succeeded in creating a growing demand for the products, as indicated by the prices now obtained for them, with many plants closed down. At the present time tar could be easily sold for 12 cents per gallon as compared with the 8 cents allowed in the cost data in this article, but which should be considered maximum, as the future will undoubtedly increase supplies so as to bring these prices back to a more nearly normal condition. This fact, however, does show that a demand has been created that did not exist prior to the quite recent establishment of plants of this nature. Perhaps this condition is more clearly evidenced in the heavy D. D. oil, for which 22 cents per gallon is being obtained. The tar demand had in a measure been previously supplied by that known as "kiln tar" made at works using the kiln system for charcoal manufacture from resinous woods.

The product mentioned as D. D. light oil is at present most difficult to market profitably. It is on the market in this form and is used to some extent by manufacturers of disinfectants. However, it has been fractionally distilled and has been used locally as a substitute for gasoline for use in engines and has proven itself to be more efficient than gasoline. The comparatively small amount of this product makes its use in this manner merely of local interest but it indicates a real value of the product.

The heavy D. D. oil has been in consistent and increasing demand, particularly in the paint industry, and notably for shingle stains; also for the manufacture of tar oils for which there is a large foreign demand. The necessity of an energetic market agency for this product was in one case well illustrated within the past year. One large concern, having nearly 100,000 gallons in storage, and finding it impossible to market, was offering it for 5 cents per gallon, while at the same time another company was unable to supply its customers at 18 cents per gallon. Of course, the latter considered the purchase from the former, but feared future competition in case, as seemed dangerously probable, the former concern should learn of their customers.

The pitch produced in the distillation process and distinguished from the tar has a firm market demand from ship chandlers and also is sold for uses such as coating silos, rendering them impervious to moisture.

The tar, of course, has its established used with rope manufacturers as well as with paint producers, while the charcoal consumption, particularly in the south, is very steady both for domestic use and manufacturing. Of the number of suggested specialties based on the use of tars and oils, doubtless a few will ultimately contribute a steady demand for a portion of these products.

COSTS OF INSTALLATIONS

The various processes have in most instances exceeded reasonable installation costs. Undoubtedly the same is true in any newly established industry, and more particularly in cases where, as pointed out in this one, prices could be obtained that were out of all proportion to production costs.

The entire equipment of a steam process plant should come well within $750.00 per cord capacity, while the solvent process complete should be approximately $2,000.00 per cord. This also should be approximately that of the bath system, while the destructive distillation method ought to be very close to $1500. In making these general estimates neither working capital nor purchase of timber or stumpage is considered.

CONCLUSION

When your attention is brought to the fact that the destructive distillation plants alone have been able to survive recent price depression, it is reasonable to conclude that, in the present state of the art, this method has inherent advantages. Nevertheless, in this type of process there is room for much improvement, particularly in refining and the utilization of waste products that were ignored in the past. Constructive chemical engineering in this industry apparently has opportunity to create an unusually profitable business, provided it utilizes the unfortunate mistakes of the past, by combining parts of the various processes.

It is not to be inferred from this article that recommendations are made for the encouragement of any particular process. The motive is merely to outline present conditions or, broadly, to show cause and effect; and also to show, if possible, that in order to attain success, many elements are as necessary in this industry as in any other. Statements have been made to the effect that failures in most instances were due to lack of real engineering skill, and this is partly true, but lack of skill is not wholly accountable for even the engineering failures, as no amount of theoretical engineering skill can replace the knowledge acquired from continued intimate contact with the going operation.

Neither does this statement take into consideration the marketing organization, which is also an essential, and is always confronted with the general economic situation, although this does not affect directly the operation.

It can be seen from this outline of the industry that its very existence was primarily due to an unnatural market condition, and as the field for profit and exploitation was so enormous it can hardly be wondered at that there was unusual activity in its promotion.

Ohio State University, Columbus

CHEMISTRY AS AFFECTING THE PROFITABLENESS OF INDUSTRY[1]

By G. W. Thompson

In the preparation of this paper I had thought of considering chemical industry as if it were distinct from other industries, but, as the subject developed, it became very apparent that no such distinct line could be drawn. Properly speaking, all industries must be considered as chemical. It is next to impossible to imagine the existence of an industry in which chemical reactions or considerations, either directly or indirectly, do not enter. It is possible that we could define chemical industry in a somewhat restricted sense, but such a definition would hardly be other than arbitrary. The lines of demarcation would be indistinct and shadowy. The only basis for such a definition would be the attitude of the popular mind. This attitude of mind has been steadily growing towards the recognition of the fact that chemistry is an important factor in every industry, and when, in any particular case, it becomes popularly recognized that chemistry is a factor in an industry, then that industry becomes a chemical industry. Ultimately, this popular recognition will extend to all industries and the rapidity of the growth of such recognition indicates that the time is not far distant when all industries will be generally and popularly recognized as chemical.

My plan had been to discuss the profitableness of chemical industry, but if we accept the conception that all industries are chemical, it would seem better that our discussion should be broadened so as to consider the general effect of chemistry upon the profitableness of industrial operations, using the words "industrial operations" as including all phases of the actual production of wealth.

Perhaps it would be well to make clear the conception that all industries are chemical in one or more phases. By way of illustration, let us consider the relation of chemistry to the production of power. I think we can show that there is a very close connection between chemistry and such production, and also that there is no industry which does not depend upon the consumption of power; this being the case, it becomes very evident that, from the power standpoint alone, all industries are chemical industries.

Our first impressions of power are those which we ourselves are conscious of exercising, and, in practice, the simplest form of power is man power as manifested in manual labor. It is not customary, perhaps, except from the humanitarian standpoint, to consider the chemical changes in the human body, converting food into work, as factors in industry. Nevertheless, they deserve serious consideration. It is being learned daily that properly fed employees are more efficient as workmen, and the study of food problems is surely a phase of the application of chemistry to industry. In some industries, the study of the food consumed by employees has a direct bearing upon the health of the employees as affected by the industry. It is found that certain foods act as prophylactics towards certain industrial diseases, and that other foods (perhaps improperly so called) act in the opposite manner. The scientific study of foods in connection with efficient manual labor is a phase of welfare work that has not been considered to the extent it deserves. Take, on the other hand, the horse. It is true that the horse is being displaced by the locomotive and automobile, and as a power factor, has been almost completely superseded by mechanical appliances; still, so far as the horse is used for the power he furnishes, his proper feeding is a phase of the application of chemistry to industry. Perhaps it may be considered that these two illustrations, the feeding of employees and the feeding of horses, are trivial as compared with the study of the production of power through the use of the steam boiler, the steam engine, the gas producer, and the internal combustion engine. Probably this is so, for, in the production of power by these mechanical means, we have clearly recognized chemical reactions, and the understanding of these chemical reactions is essential to the proper economy of fuel and the production of power with the least outlay. In these cases, chemistry teaches us the need of a proper balancing of the combustible material used and the air supply, so that the loss of heat in effluent gases may be reduced to a minimum. In the steam boiler, chemistry has taught much of great value in relation to the refractory materials used, the utility of water consumed, and how to correct its scale-forming tendencies. In recent years, numerous excellent devices have been developed for automatically giving information as to the composition of flue gases, with the result that great savings in the cost of power have been made. The study of the composition of coals has resulted in a better classification of coals, a truer connection between price and quality, and the purchase of coals by specifications involving chemical examination is becoming more extensive each year. The small power plant cannot perhaps give as much attention to chemical factors as can a large plant, but in large power plants, the economy resulting from the study of the chemistry of combustion has enabled such plants to furnish power to outsiders with a profit to themselves and to those to whom they sell it. Chemical considerations led to the use of blast furnace gases in the gas engine for the production of power; and if the chemist's dream comes true, there will come a time when power will be more directly produced from coal than it is to-day. It is, of course, recognized that in the utilization of the energy in our

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[1] Chairman's Address before the New York Section of the Society of Chemical Industry, The Chemists' Club, October 24, 1913.

great waterfalls, chemistry is an unimportant factor, but here there is the compensating fact that many of our great chemical industries have been dependent for their existence and growth upon the cheap power thus produced.

This is as far as our time permits us to speak of the influence of chemistry upon the production of power. The scope of this paper will not allow a more detailed treatment of this subject, and what we have said is more as a matter of obvious illustration of one point of the dependence of the profitableness of industry in general upon chemical factors; hence, we shall proceed to recount other phases of the relation of chemistry to industry.

The simplest phase is undoubtedly that relating to the purely commercial end of industry, wherein goods are bought and sold subject to analysis, the analysis being presumed to indicate the commercial value of the goods. These goods may be in the raw state, partially finished, or finished and ready for consumption. The oldest form of this kind of analytical control was undoubtedly for the valuation of precious metals and the ores containing them. The accuracy with which gold and silver can be determined by fire assay was recognized in the early stages of metallurgical development. The fire assay corresponded on a small scale to the actual recovery of gold and silver in smelting operations. It was natural, therefore, to assume that a similar correspondence existed between the fire assay of other metalliferous substances and the smelting operations then practised. What could be done with gold and silver, however, could not be done with the same accuracy with the more readily oxidized metals, and while the fire assay method is still applied in some places to metals other than gold and silver, in general, these processes have been superseded by wet methods, which are more obviously chemical in their character, and of greater accuracy.

The chemical testing of commodities sold under specifications is primarily for the purpose of protecting the purchaser, although accuracy of testing is necessary in order that justice may be done to the seller. Practically all raw materials dealt in in quantity are sold subject to chemical analysis. Chemical analysis may not be specified in the sale or made use of by the purchaser, but, in some form or other, the purchaser has the right to test out the products received, to see whether the terms of the sale have been lived up to. Very few commodities are sold to-day in regard to which there is not some recorded information on which a purchaser can base claims, if chemical analysis shows these commodities to be different from those described in the order or contract.

If we consider, however, the whole question of the purchase of commodities on either tacit or openly acknowledged chemical requirements, we shall see that chemistry has had a great influence in determining the profitableness of industry, in preventing the delivery of inferior raw or semi-raw materials, which would ultimately affect the yield or quality of the finished product. The whole operation of our pure food and pure commodity laws depends upon the availability of chemical analysis and testing, and it is only natural that the rapid growth of sentiment in favor of these laws should have produced some commercial hardships which have led to the criticism of chemical control and standards as being too rigid and unsuited to popular requirements. Nevertheless, such pure commodity laws have been of great profit to the purchasing public.

But if chemistry has had a great influence upon the profitableness of industry in the purchasing of commodities, what shall we say as to its effect on the profitableness of industry in the sale of commodities? In the popular mind, profits are made on sales, not on purchases, and the salesman seems to be, to use the language of the streets, "the whole thing." Most businesses are dominated by the salesman, be he proprietor, manager, or drummer. According to this idea, in the making of profit, the salesman is a factor greater than the purchasing agent, or even the manager of the manufacturing department, considering that these are distinct from each other. There is undoubtedly a great deal of truth in this conception and the popular idea rests on fairly well established facts. Taking this to be the case, what has been the influence of chemistry on the sale of commodities as affecting business profits? It is generally admitted that the old-fashioned personal influence of the salesman over the sale of his goods is growing less year by year. In place of this old-fashioned personal influence is coming a newer influence in which the salesman secures his sales, not by debauching the purchaser, but by his intelligence and the helpful knowledge which he possesses about the goods he sells, and, we must add, the confidence which the purchaser has in the salesman because of his possessing that knowledge. It is no longer the general practice to keep salesmen ignorant of processes of manufacture and use, but salesmen are being educated in many cases by technical men, often chemists, on the merits of their goods and how they may properly meet complaints. Then, too, the chemist's influence in improving the quality of products assists the salesman by giving him more salable products. I cannot take more than passing and regretful notice of the fact that there are some few chemists whose occupation appears to be mostly that of showing how goods may be debased without easy detection. The influence of the chemist in improving the quality of goods shows itself in the increased price which may be obtained for such goods. Perhaps, also, we should mention the general effect upon the commercial atmosphere of a business that has trained chemists in its employ, who give confidence to the general public that its products are made as well as possible with the assistance of the best that science can give.

With reference to actual manufacturing operations, we shall consider what the chemist has done in controlling manufacturing processes, correcting losses in manufacture, assisting in the invention of new methods and in the development of new uses for regular products, waste products, and by-products. Work along this line is particularly attractive to the chemist, and, in some cases, can be conducted profitably only by the chemist. The extent to which chemical knowledge is necessary or desirable can, of course, be determined only by considering each case by itself. There are, in all cases, practical limitations, in regard to which the chemist should be reasonable. Simply because, in general, chemistry is helpful, it must not, therefore, be assumed that in every case the chemist can increase the profitableness of manufacturing operations, because it must be remembered that the chemist is worthy of his hire, and that hire may more than absorb the value of what he may accomplish. In the control of manufacturing processes, if uniformity of product is desired, there is probably no one better qualified than the chemist to establish such control. This he will accomplish by the systematic study of all the materials entering into the process and the product in all stages of manufacture, discovering the chemical reactions of the process, where these reactions occur, and how they can be accelerated to advantage or made more complete, if that is desirable. Considering in the abstract the manufacturing operation involving a consumption of raw materials, heat, power, and labor, the fundamental units of cost are the time consumed and the quantity of product made. The chemist should possess an analytical mind, and, in the study of a manufacturing process, he will endeavor to develop the effect of these fundamental factors and seek to control the other cost factors, keeping in mind the preservation of the full value of the chemical reactions taking place. Chemistry has been a great help and profit to industry in the control of manufacturing losses, and the business man who fails to recognize its value cannot be considered as practical. For the avoidance of such losses, the chemist is peculiarly fitted. Some industries, it is true, can be conducted profitably with large losses of some of the constituents contained in the raw materials, but, in the course of time, these losses must be controlled, for the industry that applies the best control will be the most profitable and the best able to withstand competition. This can be done only by systematic chemical examination of the materials used and by systematic study of the chemical reactions entering into the processes. But the work that chemistry does in preventing losses in manufacture is not merely the direct prevention of such losses. Chemistry impresses itself sooner or later upon the manufacturer if he is awake, even though he be not technically trained, and he realizes that his manufacturing operations are not shrouded in mystery. The question of yield comes under the law of the conservation of matter. Matter does not disappear without going somewhere, and if it does disappear, it has been stolen, or some mistake has been made in accounting, or the matter has been changed in form, or actually lost in some of the refuse products. This is an exceedingly important subject. Many untechnical men think that yield, as they would express it, is "purely a practical question" and that losses in manufacture, like taxes and death, are something that we cannot get away from. The chemist valiantly attacks this belief. He asserts that losses occur for material reasons. This attitude of the chemist is simply a rational attitude which increases very materially the profitableness of industry. In developing new uses for regular products, waste products, and by-products, the chemist has left his indelible mark upon industry. Here, he is in the lead, and his constructive mind is not satisfied with announcing his immediate discoveries, but in pointing the way to the rich fields of possible discovery that lie before him.

It is proper here to elaborate a little on the value of chemical societies and their journals. Chemical societies, seeking at all times to bring out the most recent information bearing on chemical problems, obtain numerous papers, which, published in their journals, are available, in most of our large public libraries, to business men whether technically educated or not. Frequently, the information which they may want is obtained in complete form in these journals. In other cases, the information has to be interpreted by chemists, and in still other cases, the information is so distantly connected with the problems involved as to be available only to chemists who open up vast possibilities of profit to industry. It is hardly to be expected that the chemist will be acquainted with all the published facts relating to any problem, but if he knows where these facts may be obtained, and if he knows how to interpret them, they soon become available, no matter how long they may have remained buried in the literature of the subject. The application of such facts frequently develops new ones, which in their turn may have high potential value. So valuable are these chemical records that I must not lose this opportunity of pointing to the great service chemists are doing and to urge them to enlarge this service to the greatest practicable degree by further contributions. The knowledge which we may possess is of value to us individually, but in the general service of mankind, we can frequently impart some of this knowledge, without hurting ourselves, at the same time extending a helping hand to others.

Much has been written upon the influence of the research chemical laboratory on the profitableness of industry. Valuable information is on record showing how, in numerous cases, the research laboratory has been a tremendous profit to industry. In some cases, the research laboratory is devoted almost entirely to the development of new processes and products, and it would appear that the Germans have most successfully applied this method, and that their commercial high standing in chemical manufacture has been more due to this than to any superiority in methods or economies in manufacturing. While this is true, it appears to the writer that the research laboratory has another function not usually recognized. If I were to try to define this function of the research laboratory in popular language, I would say that it keeps the industry "ahead in the game." It is not only in the concrete things which the research laboratory does that its profitableness is to be measured, but its real value is also in the general advance work that it does. It gives to an industry a proper understanding of the needs of the trade. The industry that does not keep itself informed as to these needs is sure to lag behind. The fundamental information as to the needs of the trade can be furnished only by the chemist who has studied the possibilities, theoretical and practical, of both processes and products. The research laboratory is destroying trade superstitions which have hindered progress. It has furnished information to salesmen which they have been able to use to practical advantage. It has been in many respects the reflective organ of industry. The research laboratory could not have been any of these things if it were not continuously studying the problems presented directly and indirectly to it and availing itself of the invaluable records preserved in our chemical journals.

In those industries involving the manufacture of chemicals or in which chemistry is a predominating and obvious influence, the chemist is, of course, appreciated, although there are many such industries which do not utilize the chemist as fully and as completely as would be to their advantage. The really successful and profitable chemical manufacturing industries avail themselves of the services of the best chemists obtainable.

The indirect influence of chemistry upon the profitableness of industry should not be overlooked. The philosopher who once said something to the effect that the man who made two blades of grass to grow where only one grew before is a public benefactor, stated a truth that applies with a special force to the chemist. The discoveries of chemistry which have been of no direct value to the discoverer, but have been of great indirect value to humanity, are innumerable. Sometimes a chemist is looked upon with scorn because he has not made personal profit out of his discoveries, which he has published to the world and made common property. This form of communism is idealistic. The discoveries of Pasteur have added immense profit to the fermentation industries and have been the saving of innumerable lives. I know of no class which contributes, as chemists do, so freely to the fund of general knowledge on which profitable business is based. Then too, there is the indirect saving which the chemist is responsible for in the conservation and utilization of industrial products. The studies relating to the corrosion of iron and steel and indeed to all of the phenomena of decay have resulted in greater permanence and durability of the products of industry, the benefits of which all industries may share.

In arguing, as we have, in favor of the proposition that chemistry is a powerful factor in making industry profitable, we must not close our eyes to its limitations. The chemist should be a business man in the best sense of the words, and should recognize that in all successful business operations a proper balancing and coördination of all its factors is necessary. The study of power problems should be made, but the extent to which expenditure for the study of power factors should be made depends upon the importance of the power factor. The testing of materials purchased and used should be made, but the extent to which such testing should be made can be determined only by the proper consideration of its relative importance. New processes and products should be developed, but there is a limit to expenditure for these ends, which limit is in the hope of profit to be derived. After all, all industry depends upon the production or exchange of articles that are desirable, and the desirability of an article is a determining factor in its value. But not merely must a product be desirable, it must be produced with proper economy, for that is a limiting factor affecting its marketability.

We have discussed this subject in an abstract manner. Many illustrations could have been introduced of how industries have profited through the assistance of chemistry. We have thought it better, however, to omit such illustrations, but hope that during the coming year we shall have many papers practically demonstrating that what we have presented in the abstract is concretely true. When we speak of chemistry as affecting the profitableness of industry, we must bear in mind that, while all chemical knowledge may be said to come from the chemist, such knowledge is often made use of with profit by those who are not chemists. This is something that is unavoidable, and it seems to me no attempt should be made to make it avoidable. The benefits which chemists derive from the more general diffusion of chemical knowledge are very much greater than would be the case if chemists were successful in an attempt to make their profession esoteric. The progress of humanity cannot be accomplished by making the study of chemistry and the benefits that come from it profitable only to the chemist. It is proper that the chemist should seek to obtain profit from his knowledge and ability, but he cannot hope to do this except in some few cases, unless he is willing to give to others at least a portion of the knowledge that he possesses. All industries and occupations are interdependent. All industry depends upon the chemist and the chemist depends upon all industry. The more this interdependence is recognized, the greater the profit accruing to industry, and the greater the return to the chemist.

129 York St., Brooklyn.

PERKIN MEDAL AWARD

The Perkin Medal was conferred on John Wesley Hyatt for his distinguished services in the field of applied chemistry and engineering at the regular meeting of the New York Section of the Society of Chemical Industry, held at The Chemists' Club, on January 23, 1914.

The meeting was opened with an address by Dr. G. W. Thompson, Chairman of the Section, and the presentation address was made by Professor Chas. F. Chandler, Senior American Past-President of the Society of Chemical Industry. The acceptance by Mr. Hyatt was followed by an address by Dr. Frank Vanderpoel.

The inventive genius of the medalist together with an intimate description of the history of his developments was ably treated by the various speakers, and the addresses are printed in full in the following pages. [Editor.]

CHAIRMAN'S ADDRESS

By Gustave W. Thompson

At this meeting of the New York Section of the Society of Chemical Industry, it becomes the pleasant duty, through established methods, to award the Perkin medal to the person selected as most worthy for valuable work done in applied chemistry. It seems hardly necessary that a statement be made as to the origin and history of the annual presentation of this medal further than to say that the medal was founded in commemoration of the fiftieth anniversary of the coal tar color industry, the cornerstone of which was work done by the man whose name is attached to the medal. There are, however, certain features which are forced upon our attention annually in the selection of the person to whom this medal should be awarded, which it may be desirable to consider in opening this meeting.

As stated above, the medal is awarded for valuable work in applied chemistry. Whatever the future may have as interpreting the grounds for merit, in the past it has generally been considered that this work should be in the nature of original or inventive work which has proved of great public value. The questions I would propound to you to-night are: What is the mental faculty which has made the recipients of the Perkin medal what they are? In what respect, which has enabled them to be so successful in the application of chemistry to the arts, do these men differ from their fellow chemists? I have given considerable thought to these questions, and I wish to submit my conclusions for your consideration, believing that they may be of some suggestive value.

In 1870, Tyndall delivered his famous discourse on the "Scientific Use of the Imagination." In this discourse, he showed the value of the imagination properly made use of in solving some of the most difficult problems of physics. Tyndall has shown us how the imaginative mind, seeing resemblances in things, can supply the missing parts in such resemblances, those missing parts being hidden from the senses. It was this power of the imagination which enabled Kekulé to form the basis for the working out of the structure of many complex organic compounds; that work has been of incalculable benefit to chemical science and industry. Thousands of instances could be given showing that practically all of the progress made in the science of chemistry has been due to this proper use of the imagination.

Considering the work done in applied chemistry, we see clearly that it was the imagination of Herreshoff that enabled him to develop the metallurgy of copper; and of Behr in his work on the separation of the oil contained in the germs of corn; and of Acheson, who saw in his imagination that, if flocculating agents existed, there were probably also *de*-flocculating agents; and of Hall, who believed that somewhere there was a solvent for alumina from which aluminum could be obtained electrolytically; and of Frasch, who saw in the oil and salt wells the suggestion of the possibility of recovering sulfur from the bowels of the earth; and of Gayley, who saw the possibility of the dry blast in increasing the output and decreasing the cost of the blast furnace; and ——— of Hyatt, who saw in the drop of dried collodion the possibility of producing a plastic mass, which was finally obtained in celluloid.

It was Tyndall who emphasized the extreme value of the two little words "as if" when used by the scientific mind, showing how, from things seen, a scientific imagination can lay bare things unseen and make possible discoveries of great value. Discoveries often come by accident, but it is the imaginative mind that sees in these discoveries future possibilities. It is the imaginative mind which, following our discoveries so made, is led into unlimited fields of usefulness. We must not think, however, of imagination as being the sole factor, although it is probably the principal factor, in the production of valuable materials. There must be energy, concentration, and persistence, which will carry such a mind across the Jordan into the promised land. Nevertheless, the imagination is the most important factor here, because, without it, there would be no promised land.

As we look around about us upon those with whom we are intimate, we see this imaginative faculty in all degrees of development, and I have this word of suggestion to offer—those of us here who are educators, in whose hands are being moulded the minds of future chemists—should we not ask them whether the work which they are doing tends to develop this imaginative faculty, or whether it is indeed possible for them to sow in the minds of their students the seeds of imagination if they do not already exist there? It seems to me that there is no better place, no better occasion, than this place and this occasion, when we are honoring, by the presentation of the Perkin medal, a man in whom the imaginative faculty was highly developed, to put before you the need of the imaginative faculty in as emphatic a manner as possible and to urge that in our educational institutions this faculty should be developed to the highest degree. For, if we are honoring Mr. Hyatt on account of his possession of this faculty, should we not seek to increase the number of those who possess the faculty in a high degree? Is not the real purpose of the Perkin medal something more than the honoring of its recipients—great as that purpose is—is it not all done for the purpose of encouraging those faculties on which the presentation of this medal rests?

PRESENTATION ADDRESS

By Charles F. Chandler

Mr. Chairman, Distinguished Guest and Brother Chemists:

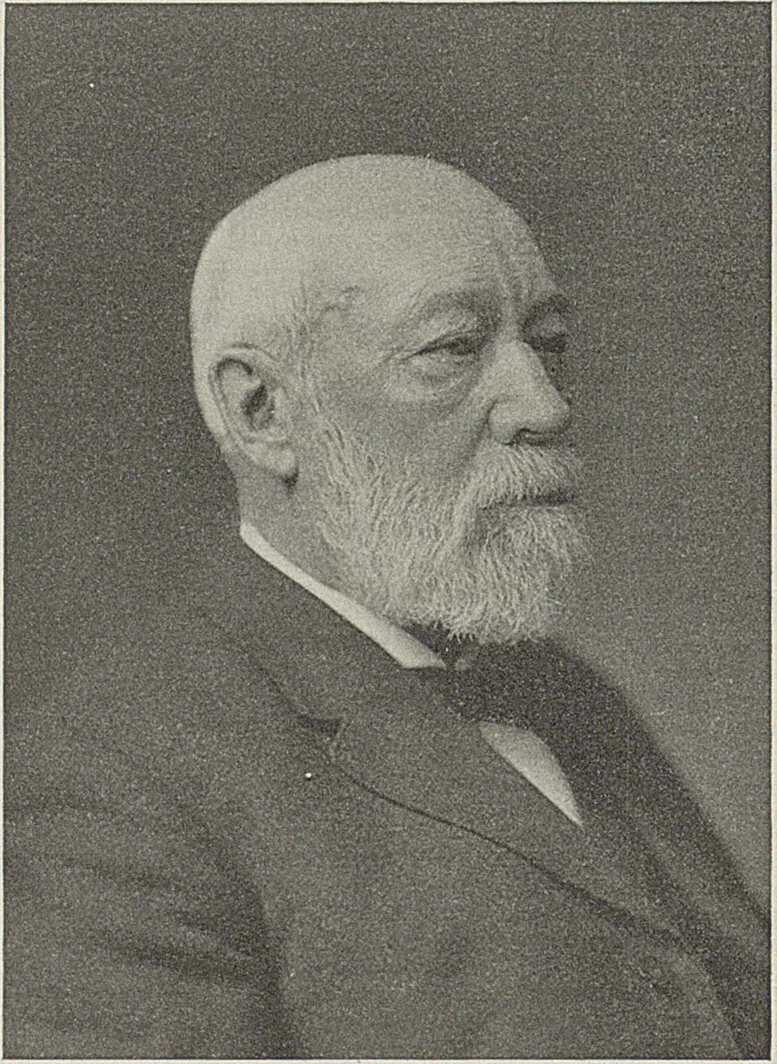
It is my very pleasant privilege as the senior Past-President of the Society of Chemical Industry, residing in this country, to present to John Wesley Hyatt the eighth impression of the Perkin gold medal, in recognition of his most valuable work in applied chemistry.

Mr. Hyatt was born at Starkey, Yates County, New York, in November, 1837. He was educated in the public school and later in the Eddytown Seminary where he excelled in mathematics.

In his early boyhood he acquired a strong taste for mechanical affairs in his father's blacksmith shop. In his sixteenth year he went to Illinois and learned the printing business, working at this trade for the following ten years. During this period he made his first invention, a family knife sharpener which included a new method for making solid emery wheels.

He then went to Albany and worked as a journeyman printer for about two years. Seeing a $10,000 offer for a substitute for ivory for billiard balls by Phelan & Collander of New York, he began experimenting nights and Sundays in the hope of gaining the reward. He made a number of useful plastic compositions, none of them however good enough for billiard balls, but he started to make checkers and dominoes of pressed wood and with his two brothers established in Albany, New York, what is now the Embossing Company which has been a highly successful concern for more than 40 years, under the mechanical management of Mr. Hyatt's younger brother, C. M. Hyatt.

In 1870 he invented and patented a machine for turning billiard balls, by which an unskilled workman can do as much as a dozen skilled workmen could accomplish by former methods, securing at the same time perfect accuracy.



JOHN WESLEY HYATT, PERKIN MEDALIST, 1914

His attention having been called to the character of the solid nitrocellulose left by the evaporation of liquid collodion, or artificial skin as it was called when collodion was first put upon the market, for covering cuts and other wounds, he turned his attention to the subject of nitrocellulose as a suitable material for producing plastics. It should be remembered that gun cotton or nitrocellulose was first discovered by Schoenbein in 1845. In 1847 Maynard announced the discovery that while nitrocellulose is not soluble either in alcohol or ether alone, it is soluble in a mixture of the two and he gave the name collodion to the solution, which has since found its way very extensively into medical use. It also served to solve the problem of producing photographic pictures, either positives or negatives, upon glass, practically sounding a death knell for the beautiful though expensive daguerreotype process. The wet collodion process was introduced by Scott Archer in 1851.

Hyatt was entirely ignorant of the various efforts which had been made by Parks, Spill and others to utilize soluble nitrocellulose or pyroxyline for the manufacture of plastic materials, and consequently he started out without any hints or suggestions as to how he should proceed. His first success resulted in the manufacture of billiard balls by first making a solid core of another plastic material and covering the same with nitrocellulose dissolved usually in ether and alcohol. The process was so successful that a good business was established in 1870 which continued for several years.

In the meantime Hyatt invented celluloid and began the manufacture of celluloid and bone dust billiard and pool balls. At this time his brother, Isaiah S. Hyatt, joined him and they worked together until the brother died in March, 1885.

I do not propose to give a detailed history of the progress made by Mr. Hyatt and his brother in establishing the celluloid industry. I shall merely remark that Hyatt's patent 88,633, dated April 6, 1869, was for a molding composition to imitate ivory and other substances composed of fibrous material and gum shellac or other solid fusible adhesive gum. His patent No. 88,634, dated April 6, 1869, was for an improved method of coating billiard balls, consisting in dipping the billiard balls made of some suitable composition into a solution of collodion which might be given any desired color beforehand. His patent 89,582, dated May 4, 1869, was for a composition consisting of ivory dust or its equivalent mixed with collodion and subjected to pressure during the evaporation of the solvent. Patent 91,341, dated June 15, 1869, taken out by the two brothers jointly, was for manufacturing solid collodion with very small quantities of the solvent dissolving the pyroxyline under heavy pressure, thus securing great economy of solvents and a saving of time.

Their patent 105,338, dated July 12, 1870, shows the fundamental invention of celluloid. It is entitled "Improvement in Treating and Molding Pyroxyline." The three claims of the original patent are:

1. Grinding pyroxyline into a pulp, as and for the purpose described.
2. The use of finely comminuted camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described.
3. In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

This patent was reissued three times in order to avoid ambiguities. The claims of the last reissue are as follows:

1. The use of finely-comminuted camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described.
2. In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

The specification fixes the proportions at about 1 part of camphor to 2 parts of pyroxyline. Modifications of this process were embodied later in U. S. Patents 156,352 and 156,353.

From this time on celluloid became a most important plastic, superior in almost every respect to any other plastic hitherto proposed, for the manufacture of the greatest variety of articles, useful and ornamental.

Seventy-five different patents were taken out either by John Wesley Hyatt alone or in association with his brother Isaiah S. Hyatt, and an enormous establishment grew up at Newark in the hands of the Celluloid Company.

I should not take up your time by enlarging further on the history of celluloid were it not that in one of our most important and most recent works on applied chemistry, I find it stated as follows under the head of celluloid:

"The substance was first produced by Daniel Spill of Hackney, England, and come into commerce under the name of 'Xylonite.' Spill's method of converting the nitrocellulose has been followed for more than forty years."

I have had occasion, in connection with celluloid and nitrocellulose litigation, to study most carefully the history of the pyroxyline industry and there is no logical ground for making the above statement. Celluloid was invented by the brothers Hyatt, and not by anyone else. This whole matter has been thrashed out in the Federal Courts as long ago as 1886, and the Hyatt patents have been sustained although everything that had been patented or published was carefully studied and discussed during the litigation.

It is quite true that many other experimenters sought to prepare useful plastic compounds with the aid of pyroxyline prior to the Hyatt invention of celluloid. Most prominent among these experimenters, we find Alexander Parks and Daniel Spill but neither one of them ever suggests the essential features of the Hyatt method for manufacturing celluloid. Parks' patents relate to the following points: (1) Making liquid solutions by the use of various solvents, rendering the material less inflammable by adding chloride of zinc or tungstate of soda or gelatine dissolved in acetic acid. (2) Making sheets by pouring the solution on glass and allowing it to evaporate. (3) Dehydrating wood alcohol or naphtha as a solvent by distilling over chloride of calcium. (4) Adding castor or cottonseed oil, gums or resins or oil previously treated with chloride of sulfur to his solvents. (5) Introducing nitrobenzene or glacial acetic acid or hydrocarbon solvents. In one patent he proposed to remove the solvent from the solution of pyroxyline by adding water, mineral naphtha or other liquids. In another patent he gives compositions to be used as a varnish. There is nothing whatever in any one of these patents that anticipates Hyatt.

As for Daniel Spill, his patent 2666 of 1867 (English) suggests as substitutes for dehydrating alcohol or wood naphtha as a solvent for pyroxyline: fish, vegetable oils, essential oils, resins, gum resins, spirits of turpentine, fats, light oils and naphtha from coal and mineral naphthas. One example of a suitable solvent contains 80 per cent alcohol and 20 per cent of rosin. Another contains 60 per cent of alcohol, 3 of castor oil, 1 of essential oil of lavender, 3 of resin and 34 of coal naphtha or benzole.

The Spill patent 3984 of 1868 claims the production of compounds of "Xyloidine" by the employment of nonvolatile solvents, mentioning animal, fish, vegetable, or mineral oils, as mineral tar, lard oil, cod liver oil, camphor oil or liquid camphor, linseed oil or heavy coal oils or mixtures of the same. He further states that the following substances may be added: paraffine, camphor, resins, fat, wax, india rubber, gutta percha or balata gum or mixtures of the same. He gives the following example:

Camphor, camphor oil, or liquid camphor..........	20 parts by weight
Oil, such for example as castor or linseed oil, either before or after such oils have oxidized or boiled....	40 parts by weight
Xyloidine..	40 parts by weight

The claim of the patent is for the production of compounds of Xyloidine by the employment of nonvolatile solvents. This is also the essential feature of the claims of Spills' American patents 91,377 and 91,378 in 1869.

Spill took out another British patent 3,102 of 1869, substantially identical with U. S. Patent 97,454 of the same year. This does not differ materially from his prior patents. He mentions a great variety of solvents, many of them given in his previous patents and these he groups under eight numbered paragraphs and gives the following as the only example of his invention:

Xyloidine....................................	27 parts by weight
Castor oil...................................	27 " "
Camphor......................................	6 " "
Solvents, either of the Nos. 1, 2, 3, 4, 5, 6, 7, 8......	40 " "

The Spill patent 180 of 1870 is for bleaching Xyloidine. His patent 787 of 1870 and his U. S. patent 101,175 of 1870 are for the employment of evaporating and concentrating apparatus, to remove the solvent from the fluid preparations and convert them into masses of a greater degree of consistency, at the same time recovering the volatile solvents evaporated.

These inventions give a fair picture of the condition of the efforts to make a useful plastic from pyroxyline prior to the date of Hyatt's invention of celluloid which was patented July 12, 1870, and which in the clearest and most unequivocal language sets forth the nature of his invention. His claims are as follows: (1) Grinding pyroxyline into a pulp, as and for the purpose described. (2) The use of finely comminuted camphor-gum mixed with pyroxyline pulp, and rendered a solvent thereof by the application of heat, substantially as described. (3) In conjunction with such use of camphor-gum, the employment of pressure, and continuing the same until the mold and contents are cooled, substantially as described.

Considering the claim that Daniel Spill was the inventor of celluloid, it is very significant that as late as the 11th of May, 1875, he took out a British patent 1739 of that year, for producing and applying Xyloidine. In this patent he makes no references to any material that could possibly be called celluloid. On the contrary, he recommends the following mixture as a suitable solvent for soluble guncotton or Xyloidine:

250 parts by weight of alcohol.
150 parts by weight of ether.
10 parts by weight of nitrobenzole.
33 parts by weight camphor or camphor oil.
250 parts by weight hydrocarbons, from coal, shale or other bituminous substances boiling between 220 and 400° F.

Or he says the following solvent may be employed:

400 parts alcohol.
200 parts of hydrocarbons, before referred to, and 33 parts of camphor or of camphor oil.

Now this patent was taken out nearly five years after Hyatt's celluloid patent and although Spill in this patent suggests adding a small quantity of camphor to large quantities of other solvents, volatile and nonvolatile, he always mentions it as camphor or camphor oil, regarding them as equivalents. They certainly are equivalents for Spill's purposes to produce liquid solutions of pyroxyline, but camphor oil is not equivalent to camphor in Hyatt's process for making celluloid and it would be absolutely impossible to make celluloid by any process suggested in any one of these patents of Spill or Parks, or any other inventor prior to Hyatt, and this is what the federal judges decided when the matter was tried out in court.

Mr. Hyatt's activities were not limited to celluloid. Among his other inventions also of great importance, we find a sugar cane mill, very superior to any mill previously used, in its efficiency both in increasing the percentage of juice extracted from the cane and in greatly diminishing the time necessary to extract it, and in giving a higher value to the refuse bagasse as fuel.

In the early 80's, Mr. Hyatt and his brother Isaiah took up the subject of water filtration and started a company called the Hyatt Pure Water Company. Isaiah Hyatt invented and patented a very important feature of the filtration process, February 19, 1884, Patent 293,740. It marks the beginning of a new era in water purification. Coagulants had been previously used to purify water, but the difficulty was that the water was held in large tanks or cisterns. The coagulant was added to it, the whole was thoroughly agitated and then it was necessary to allow it to stand 12 to 24 hours for the coagulum to settle to the bottom. The Hyatts conceived the idea of employing a coagulant which could be added to the water while on its way to the filter, so that no large settling tanks or basins are required and no time is lost. The claim of this patent is as follows:

"The method herein described of arresting and removing the impurities from water during an uninterrupted passage of the same from a supply pipe into a filtering apparatus, thence through a filter bed contained therein and out through a delivery pipe leading therefrom, which method consists in introducing into the water simultaneously with its passage to or into the filter a substance which will sufficiently coagulate or separate the impurities to facilitate their arrest and removal by the filter bed, thus obviating the necessity of employing settling basins.

I was connected with a litigation which followed the issue of this patent, and studied the process and apparatus at Somerville, N. J., Niagara Falls and Elmira. The process was unusually successful. At Somerville the river water exhibited a milky opalescence caused by such fine particles of clay that no filter would clarify it. By a proper attachment of an alum box to the feed pipe to the filter, a minute quantity of alum was added to the stream of water on its way to the filter, less than one grain to the gallon, and in the few seconds that elapsed before the water reached the filter bed of the ingeniously constructed Hyatt filter, coagulation had taken place and the coagulum including the alumina of the alum and the clay, bacteria and other suspended impurities of the water had been converted into such flocks as made it possible for the bed of sand in the filter to arrest it completely. These Hyatt filters are so constructed, whether they are on a large scale or small scale, that they can be washed completely at any convenient moment by simply reversing the current through the filter. This churns up the sand and separates from it the accumulated coagulum.

Nearly all the paper mills and woolen mills in the country were and still are supplied with these filters, as are also more than 100 cities and towns.

The validity of this patent was established through lawsuits which were brought against the cities of Elmira and Niagara Falls. These cities attempted to evade the Hyatt patents by constructing a chamber underneath the filter through which the water passed on its way to the filter, but we found by examination that while a portion of the coagulum accumulated in the chamber, one-third of it passed on and was separated by the filter. Judgments in favor of the Hyatt patent were given by the Circuit Court of the United States, Judge Shipman presiding, in 1894; by Circuit of Appeals, Judge Wise presiding, in 1895; again by Judge Coxe in 1896; and again by Judges Wallace, Lacomb and Shipman in 1897.

In 1891–2 Mr. Hyatt took up the subject of antifriction roller bearings with great success.

I have really occupied far more time than I should have done, but I felt it a duty to take advantage of this opportunity to present the facts with regard to Mr. Hyatt's priority of invention in connection with the celluloid and water purification, which I was in a position to do owing to my experience and knowledge gained in the litigations which arose in both cases.

I think that the facts to which I have called your attention, although very briefly expressed, will satisfy you of the great achievements of Mr. Hyatt and will fully justify your committee in placing Mr. Hyatt beside Sir William Henry Perkin and the six American chemists who have already received the Perkin medal.

To Mr. Hyatt:

It gives me great pleasure, as the representative of the Society of Chemical Industry, and the affiliated chemical and electrochemical societies, to place in your hands, Mr. Hyatt, this beautiful token of the appreciation and affection of your fellow chemists.

ADDRESS OF ACCEPTANCE

By John Wesley Hyatt

Mr. Chairman, Ladies and Gentlemen:

I have never looked forward to any such honors as you have bestowed upon me, and I do not know how fittingly to express my gratitude. You have overlooked my lack of early training in the sciences with which you are all familiar, and look only to results which have been obtained mainly by persistent, and many times mistaken, experiments. Some successful experiments I might never have made if I had been familiar with the danger theories of some learned men.

CELLULOID

From my earliest experiments in nitrocellulose, incited by accidentally finding a dried bit of collodion the size and thickness of my thumb nail, and by my very earnest efforts to find a substitute for ivory billiard balls, it was apparent that a semi-liquid solution of nitrocellulose, three-fourths of the bulk of which was a volatile liquid and the final solid from which was less than one-fourth the mass of the original mixture, was far from being adapted to the manufacture of solid articles, and that I must initially produce a solid solution by mechanical means. The only useful solvent known to me at that time was a mixture of alcohol and sulfuric ether; with the old formula (about equal parts of ether and alcohol) I mixed in a closed mill a thick paste of soluble cotton, made by the old firm of Charles Cooper & Co. After mixing, the cover of the mill was removed and the mass evaporated down to a thick dough, which was then forced accurately around the ball (made of another substance), and allowed to dry. This I found resulted in a rather brittle coating, owing, as I found, to the unequal evaporation, leaving only the alcohol, a poor solvent by itself, at the final shrinkage. This was remedied by using only the least amount of alcohol (five parts ether to one alcohol) necessary as a solvent. Even this coating shrunk to less than half of its original thickness and required to be dried immersed in water under several hundred pounds' pressure per square inch to insure its solidity and freedom from bubbles. It became necessary to strain the mass by forcing it through a very fine sieve to exclude the unnitrated fibers. All these difficulties stood in the way of success, except in high-priced articles like billiard balls. Other seriously objectionable features became apparent. In order to secure strength and beauty, only coloring pigments were added, and in the least quantity; consequently a lighted cigar applied would at once result in a serious flame, and occasionally the violent contact of the balls would produce a mild explosion like a percussion guncap. We had a letter from a billiard saloon proprietor in Colorado, mentioning this fact and saying he did not care so much about it, but that instantly every man in the room pulled a gun.

I next had a small beating engine made, to pulp the nitrocellulose. In one experiment I placed a small quantity of this dried pulp in a strong cylinder and forced quickly a minimum quantity of liquid solvent into it with high pressure. The result was a solid substance, as hard as sole-leather, which soon dried, leaving a fine, hard disc about three-fourths of an inch in diameter and one-half an inch thick. While no explosion ever resulted from this, there was real danger to be feared, and the matter was dropped.

My brother, I. S. Hyatt, joined with me at that time, and finding it stated in some patents to which I was referred, that a little camphor added to the liquid solvent was beneficial, we conceived the idea that it might be possible to mechanically mix solvents with the pulp and coloring matter while wet, then absorb the moisture by blotting papers under pressure, and finally submit the mass to heat and pressure.

To our surprise, we noticed a slightly solvent action of the precipitated and washed camphor upon the pulp, even before the heat and pressure, and without other solvent we succeeded in producing a transparent slab one-fourth of an inch thick, fine, and as hard as a piece of wood. My brother took some samples to the American Hard Rubber Company, with the view of interesting them. They employed the late Professor Charles A. Seeley, who had made collodion for the government during the Civil War, to investigate the matter. He came to our place in Albany, N. Y., and we conducted the whole process for his inspection, very successfully. He remarked that he had come prepared to detect some chicanery, but could see no deception, and expressed himself as satisfied. He kindly advised us that if, accidentally or otherwise, we were to apply a little too high temperature, the quantity we were dealing with would inevitably destroy us with the building and adjacent property. While we did not accept this as true, it was disturbing. The following day between 12 and 1, when all were out, I rigged up a four-inch plank used as a vice-bench, braced it between the floor and ceiling, between the hydraulic press and the hand pump, intending it to shield me from possible harm. I then prepared the mould, heating it to about 500° Fahrenheit, knowing it would certainly ignite the nitrocellulose and camphor, and thinking I would abide by the result. The gases hissed sharply out through the joints of the mould, filling the room with the pungent smoke. The mould, press, building and contents were there, including myself, very glad that I did not know as much as the Professor.

The next step was to make a small stuffing machine, consisting of a cylinder, four-inch bore, about a foot long, terminating in a tube three-fourths of an inch bore, ten inches long, immersed in an open oil-jacket, with a gas burner and thermometer. A capnut with one and one-fourth inch screw forced a plunger upon the cakes of incipient celluloid, which were heated at the outlet end of the cylinder passing through the heated tube into moulds, and also through nozzles forming rods, tubes, etc.

We found it advisable to lower the melting point of the camphor by adding a small quantity of alcohol or other solvent of camphor. A much larger hydraulic stuffing machine was then made. Dental plate blanks were the principal part of our early business.

My brother interested some New York capitalists—principally composed of General Marshall Lefferts, Joseph Larocque and Tracey R. Edson—and we removed to Newark, N. J., in the winter of 1872–73. We had nearly all the appliances and machinery to design and build, which progressed with some halts and mistakes for two or three years, when a fire occurred in our four-story and basement building, utterly destroying all our stock and machinery, pushing out the whole front of the building (which was very weak), and severely injuring several of our men, who all finally recovered, although one—Mr. Charles S. Lockwood—was in great danger for a long time. We then started our present works, acquiring knowledge and experience; my brother started a separate factory for making brushes, mirrors and combs. Early in 1878, my brother went to Paris and started the French Celluloid Company.

Before we left Albany we began the use of tissue paper in place of carded cotton or bleached flax, which finally resulted in getting tissue paper of definite thickness and materials, and breaking it up into small, separate pieces by a machine I constructed, drying these separate pieces in a loose mass and nitrating them instead of the carded cotton.

In 1876, I was allowed to employ a chemist for determining our acids and to systematize our nitration, instead of merely using hydrometers and thermometers, and Mr. Frank Vanderpoel was selected by me. So far as I know, the analyses of mixed spent acids was not reduced to practical work. Professor Seeley proposed that we separate the nitric and sulfuric acids by distillation, and then bring these to the proper strength before mixing, which was not adopted. Vanderpoel first removed the gelatinous flock by adding finely powdered natural barium sulfate and allowing the barium and flock to subside, which was a great success. I had previously tried filtration, which was impractical. After much labor Vanderpoel perfected a quick and accurate method of determination of the spent acids, and then added the required fresh acids. An elaborate and extensive battery of tanks was constructed, the acids being moved through copper pipes, where required, by means of air pressure. The tanks for mixing the comminuted tissue paper with the prepared acids were arranged on a turntable supporting a dozen or more tanks, each holding hundreds of pounds. A rotating stirrer was arranged to stir in the requisite amount of paper in one tank, the turntable being revolved to the next tank, and so on. At a distance embracing about half a dozen tanks from the stirrer was located a centrifugal machine, which separated out most of the acids. The nitrated paper was then thrown into a washing device, and the partly washed paper then fell into large tanks of fresh water and was thoroughly washed. A very considerable number of tons of paper per day were and are treated in this way.

The next procedure was to grind this nitrated paper in a beating engine. The water was then mainly removed by a centrifugal machine. The mixture of pigments, camphor and nitrocellulose was then made, according to the results required, and ground together in a mill, then pressed into slabs or cakes, still further deprived of moisture by great pressure, and finally deprived entirely of moisture by blotting papers, repeatedly changed. These cakes were then broken up and alcohol or other desired solvents added and allowed to soak in. The partly dissolved mass was then masticated in heated rolls, turned out into necessarily rough sheets, cut into strips and rolled up into cylinders, ready for the stuffing machine.

The great need was for Celluloid in solid perfect sheets, and this neither the rolls nor the stuffing machines could possibly do, with all our experience. I constructed a special nozzle for the stuffing machine, to form a slab about one and one-half inches thick, seven inches wide and several feet long, which was pressed between steam plates, one of them with under-cut grooves to hold the slab. A machine was made with shaving knife and reciprocating bed, and by it the slab was shaved into sheets of the desired thickness. These slabs were necessarily imperfect, and were too small. After showing this result to the other directors, I proposed building a hydraulic pressure steam-heated mould, to make a slab or block about two feet by five, and three inches thick, in which to weld and press a pile of rough sheets from the masticating rolls.

General Lefferts, our much beloved president, had suddenly died a year or more before. To those who knew the least about Celluloid my suggestion looked pretty good, but to others came a great fear of possible danger and failure to weld up such a mass. At last they gave me authority to build the apparatus, limiting me to less than half its cost if fairly estimated. With this authority, which consisted more of the privilege of trying such an apparatus than in providing for its cost, I ordered the machine, agreeing to pay the machinist all above the appropriation if it failed to work. The machine was built and most carefully tried in the presence of only the new president, who knew little about celluloid, and Mr. Stevens and Mr. Lockwood from among the employees. The mould was cooled and opened, and nice sheets were at once made, considering that only scrap material was used, though less than half the block was welded. This meant reheating, which was at once done, and the whole was known to be a success.

I dwell upon this because of its vast importance to us. It multiplied the value of celluloid many times, making a much stronger and finer material than was produced by the former means.

About this time we were enjoined from bleaching the iron out of the pulp, caused by the iron-beating knives, and it was up to me to remedy the serious difficulty. A large revolving drum of copper, through the axis of which was a shaft with beating arms rotating at a very high speed, in which the mixture of nitrated paper, camphor and pigmets was placed, and the whole beaten to a pulp without the discoloration of the iron and water, and without the loss in washing and bleaching the fine pulp from the beating engine.

In order to clearly differentiate my work in celluloid from that of others in the nitrocellulose industry, I will summarize as briefly as I can.

First: The idea of combining with the nitrocellulose only the exact or approximate amount of solvent required for a solid solution. This required a nearly perfect mechanical mixture before very much solvent action could take place.

Second: Completing the solution by means of heat and pressure.

Third: Eliminating the practically unnitrated fibers by pulping.

Fourth: Employing tissue paper in place of carded fiber.

Fifth: Avoiding the terrible danger of drying out the moisture by exposure in a drying room.

Many years ago I patented the process of first pressing out all the water possible and displacing the remainder by forcing alcohol through under pressure. This, I understand, is now used by other nitrocellulose workers, but we prefer the method herein described.

Sixth: The stuffing machine process.

Seventh: The sheeting process, most essential.

ACKNOWLEDGMENTS

Mr. Stevens has been with me ever since he was fourteen years old, has invented solvents and many other things of great importance in the art, and stands at the head of nitrocellulose workers at the present time.

Mr. Harrison, in his department, has invented the method of imitating the grain of ivory, of smoked pearl, of onyx, as well as many other beautiful colors and effects. He has been with us nearly forty years

Others are entitled to much credit, but it is impossible to name them here.

SUGAR-CANE MILL

In the old method of milling sugar cane the cane is passed between rolls which are generally 34 inches in diameter and 84 inches long. These rolls are grooved and roughened so as to draw all the cane in between them that is possible. Owing to the comparatively obtuse angle formed by the contact of two rolls, the quantity of cane is limited and they are very nearly together at the passage of the cane through the last pair of rolls. The last, say 15 per cent, of the juice is forced out through five or six inches of highly compressed fiber in the opposite direction from which the cane is moving, so that in practice a considerable portion of the juice is carried through the rolls. For this reason it is repeatedly passed through rolls, at each passage removing a small proportion more of the juice. It is found profitable in most cases to add water to the bagasse between each set of rolls so as to dilute the juice that necessarily remains in the bagasse. In order to get the desired quantity of work from the mill, the rolls are of great length, from seven to seven and one-half feet. There are generally from 30 to 40 tons of pressure for each foot of face of the rolls. It is not practicable to get any greater pressure than this. I employ four or five times as much pressure per lineal foot.

With my apparatus and method the angle formed between the chain and the upper roll is far more acute and the cane is forced through rolls so that five times more cane goes through the rolls of a given face than is possible with the old mills. If this chain belt were impervious to the juice little or nothing would be gained by this method, but inasmuch as the chain forms a massive screen through which the juice may readily escape from the underside, the juice has only to pass downward through the mass perhaps one and one-quarter inches at the most to escape, instead of five or six inches in the opposite direction to the progress of the cane, as in the old mill. It does not take any more powerful apparatus to press the cane fiber when it is one inch thick than it does to press fiber that is one-eighth of that thickness, and as I get quite as much cane through my rolls with 12-inch face as will pass through the old rolls of 84-inch face I can readily afford to put several times as much pressure upon each foot of face as is practicable with the old mills. I employ upward of 150 tons on rolls with 12-inch face.

For the same amount of cane passing six times through the present rolls my mill will not require more than one-third as much power and instead of getting with the best milling a bagasse with 50 per cent of moisture and 50 per cent of fiber, I can easily produce a bagasse which has 60 per cent of fiber and 40 per cent of moisture. This bagasse is so dry that a quantity of it, either a handful or a bushel, placed upon the ground can be lighted with a match and will burn like carpenter's shavings. My mill is about one-eighth the weight of the present mills with the same capacity, and as the machine work is of the same character the machine will not cost one-quarter as much as the present mills.

In Cuba, 71 per cent of extraction without dilution is as good as can be obtained. With my mill, without dilution, I can easily get 78 per cent extraction. With Louisiana cane, which has less fiber, I can easily get 84 per cent extraction without dilution. Of course, if the bagasse is passed through a second mill with 12 per cent dilution, I can get 88 per cent extraction.

The joints of my sprocket chain belt are self-cleaning and cannot clog; as shown in practice, each revolution of the chain rubs the screen surface together several times. All the links of the chain are alike, and are of drop-forged steel. The concave edges of these links absolutely fit the under roll. The smaller pressing roll is provided with annular grooves coinciding with the longitudinal joints of the chain so that even the last small percentage of juice has a perfectly free outlet.

There is no danger from irregular feeding, as the mass of bagasse between the rolls is about one and one-quarter inches thick, and no loose or open space can possibly exist. The springs yield or follow up, according to the feed. No crusher or shredder is necessary or desirable.

The speed of the surfaces of the rolls and chains is designed to be 30 feet per minute, although I did practically as good work on my previous machine at 40 feet per minute, and it will probably be proved that this machine can do equally as good work at 40 feet per minute, but to be safe, I have calculated it for 30 feet per minute. The ordinary cane mills are run at anywhere from 16 to 25 feet per minute, according to the choice of the owner or engineer.

The increased value of the bagasse as fuel, and the avoidance of any peculiar kind of bagasse burner with forced draft, etc., are quite important items. Furthermore, as was shown by my machine at Adeline, Louisiana, the purity of the juice is considerably improved, as the cane is not ground up as in the ordinary mills, but merely flattened by the great pressure.

I have taken out 238 patents (a few of them being joint inventions with others), and several new industries have resulted. The one of next importance to celluloid is the Hyatt Roller Bearing. I have received considerable liquid money, most of it having been of a volatile and inflammable nature. Age ought to bring wisdom.

PERSONAL REMINISCENCES

By Frank Vanderpoel

Mr. Chairman, Ladies and Gentlemen:

It is a great pleasure, I can assure you, to be present this evening, at a time when, in company with the preceptor whom all the boys of Columbia love, we are to do honor to my friend of later years, when what was taught me by the former became the equipment for my work with the latter. Every young fellow who had the good fortune to study chemistry under Dr. Chandler will bear me witness that the days thus passed were very enjoyable indeed: the memory of them will last long in our minds, no matter where, or in what circumstances we may find ourselves. When the request came to me from our worthy chairman to say something this evening at the presentation of this medal, I could not help feeling that there were other members of the societies which we represent who could do the subject more justice than I. There is no other, however, who is more gratified at the awarding of the medal. The only reason that I can think of for the selection of the speaker is that for a long term of years he has been the intimate friend and associate of the recipient of the medal.

Let me say, further, that when I was asked to take part in the exercises, it seemed almost as if I had been requested to assist at the obsequies of an old friend who had departed this life; for, of course, no one could be expected to say anything at such a time as this except in praise; anything else, even if it were possible, which it is not, would seem very ungracious indeed, and so, the recipient of the medal must listen, perforce, like Tom Sawyer and Huckleberry Finn, in Mark Twain's humorous story, when they came to their own funeral, to words of eulogy and praise of which he has never dreamed. However, let us dismiss from our minds the thought that our friend is a departed one. He is very much alive: we haven't come here to bury him, and what we are about to say we are going to tell him to his face, and not apologize for it either. If you will permit personalities, Mr. Chairman, without which I don't believe I could get through with my talk, I should like to say that it was about three years after leaving Columbia that I had the good fortune to meet our guest of the evening. It happened at a time when I was desirous of locating myself where I could do laboratory work on a somewhat larger and more efficient scale than I had been able to do before. Without going into details, let me say that I met Mr. Hyatt, had a chat with him, found that he had discovered the need of an analyst at the works of The Celluloid Manufacturing Company, as it was then called, applied for such a position, and secured it through his kindness and influence. From that time until the present, and this means a long series of years, we have been friends, and our friendship has stood the test of sun and rain, of bright and cloudy days, of the ups and downs which every manufacturing business must have, and I think that we are as strong friends as ever, at this moment. In fact, I don't believe that there is anyone present who is more pleased than I am that the Perkin Medal has been awarded to him—unless it be Mr. Hyatt himself.

To refer to the early days of the celluloid business in Newark, where the factory was located, I should like to say that there seemed to be a good deal of prejudice against it in that city. On account of an unfortunate fire which took place there shortly after the company began operations, the people of Newark did not, as a rule, take kindly to a material which was reported as being made of guncotton and camphor. Of course, such a statement would never lose in transmission, and the people would look askance at any article of commerce which contained, as an ingredient, this high explosive. I remember hearing a story told of a man who happened to touch, with a lighted match, one of a pair of cuffs made of celluloid when, to his amazement, there was a terrible explosion, and he barely escaped with his life. Well, this and other stories of a like nature produced a strong feeling against the manufacture of this new substance, to say nothing of its *use* by the public, and, of course, some one had to bear the brunt of it. Naturally, the inventors (The Hyatt Brothers) and those most intimately associated with them in the business, had to carry the burden; and it wasn't a very light one, either. But our friend had the enthusiasm of the inventor, an enthusiasm which he imparted to those who were associated with him, and without which success would have been long delayed, if not impossible. I suppose that, in the minds of some, even at the present day, the idea exists that the principal ingredient in the material referred to is true guncotton, the highly-nitrated compound of cellulose. This is because the public, as a rule, is not given to distinguishing between the compositions of different chemical compounds. If, in order to make true guncotton, you treat cotton fiber with a bath composed of a mixture of strong sulfuric and nitric acids, why, it stands to reason—so some of these people think—that cotton fiber treated with a bath of these same acids, no matter what their percentage composition may be, will be converted into the explosive compound. You know that this is not the case, but the general public does not, or did not, some thirty years ago. If you will pardon the digression, I should like to say that, shortly after I became associated with the Celluloid Company samples were made of these two varieties of nitrocellulose, using raw cotton fiber in each case, and their solubility tested in a strong solvent, and thus compared. Any nitrocellulose which would not dissolve in this solvent would be utterly worthless as a basis for the manufacture of our product.

Upon making the test, the fibers of the lower nitrated compound disappeared in the solution upon the instant that they touched the solvent. This was the variety of nitrocellulose which was the principal ingredient in the manufacture of celluloid. How long do you suppose it took the other, the true guncotton or trinitrocellulose (or, as some call it, hexa-nitrocellulose) to dissolve? It was kept in the bottle of solvent for more than six years without showing the slightest evidence of a solvent action—each fiber showing up bravely—then it was thrown away. But the public did not know of this difference and thought that the product of our friend's brain was a menace to every one who came near it. Prejudice goes far, and it takes courage and pluck to fight it. If I said much more on this point, you good people would think that the company had paid me to boom its product, which is not the case.

Mr. Hyatt's share in the work of making celluloid did not consist in merely getting out the various patents and handing them over to the company. He was often at the works, superintending, advising, assisting in the manufacture and always on call if things needed his attention. We all felt confidence in his judgment, and found afterwards that this confidence was not misplaced.

The inventor's enthusiasm is a valuable asset or adjunct in bolstering up the faint-hearted employee who may sometimes think that he has an idea of his own which he would like to have exploited. I think that more than one of the men employed at the works received encouragement from our friend, Mr. Hyatt, in certain lines of work in which they were engaged and which they might have been inclined to give up if it had not been for *his* enthusiasm and optimism. It not infrequently happens, in this world, that the succcess which a naturally timid person achieves is due, in some degree, to the encouragement which he may receive from one who has more courage and backbone. As the boys would say, "He doesn't get cold feet," and this means the difference between success and failure. We sometimes need optimistic friends who will help us over the rough places, or the thin ice—put it whichever way you will. Mr. Hyatt was one of these, I can assure you, and to his cheering influence is due, in great measure, I think, the success of the Celluloid Company. This comforting way of looking at things does not mean, let me say, that everything that a fellow would think of and suggest, would be endorsed by him. I well remember a remark made by him one day when I had occasion to relate how a certain so-called or self-styled chemist had utterly failed in the solution of a problem which he was *absolutely* certain he could solve. In fact, he claimed to have solved it some time before, but when a second attempt was made, the result was not in the least satisfactory. (Mr. Hyatt will pardon tales told out of school.) "Yes," said Mr. Hyatt, "a man may say to you, 'if I put this brick which I have here on this side of the street with that one over across the way, I'll have two bricks;' but when he goes across the street he finds that what he saw on the other side was not a brick, after all!" Very likely, Mr. Hyatt does not remember this occurrence, but, I assure you, it is true, as is also another one which happened at the works and illustrates his practical way of looking at things.

You know it is just as important, sometimes, to know what to omit as to know what to do: what to leave out of your invention as well as what to put into it. A mutual acquaintance, an employee of one of the branches of the Celluloid Company, went to our friend one day and told him of an invention which he had almost worked out in his mind, and asked his opinion of its value. He was going to make billiard balls out of celluloid, these balls to have a hollow centre, and this small cavity was to be partly filled with mercury, which, when the ball was struck, would act as a sort of brake on the motion of the ball and cause it to slow down. Mr. Hyatt's reply was: "Well, if billiard balls came ready-made and partly filled with mercury as you suggest, and you could find some way of getting that mercury out, I think that it would be a fine thing."

There was one element in Mr. Hyatt's make-up concerning which I cannot speak too highly, for the reason that you don't find it everywhere: it is, I believe, the exception and not the rule. It was his willingness to give every one credit for his own idea and not attempt to appropriate it himself. Sometimes he went further than this: he would take the thought that you gave him, enlarge upon it or improve it, and then hand it back to you as your own. How many do that to-day? I think that if you counted them on your fingers, you would have some fingers left over when you had finished counting.

No, indeed, there are probably several of us here to-night who can tell of cases where the true inventor has been coldly shoved to one side, and all the glory and honor appropriated by some one else.

There is another quality or characteristic possessed by the successful inventor which is a most important asset. Something which happened not very long ago on a train running across the Arizona desert may, in a slight degree, illustrate the point.

The day was hot and dusty, and anybody who has ever traveled those alkali deserts with nothing much in the way of vegetation but sage brush in sight, can tell you what that means. It is decidedly uncomfortable, to say the least, and you look in vain for a cool spot where your eyes may rest—a clump of trees, or a little running water. One of the passengers kept looking out of the window every minute or two, pulling the shade to one side as he did so, and then letting it drop back again into place. Another passenger, noticing the interested look on his face, asked him what he saw.

"I see miles and miles of corn, acres of wheat and cotton, and the whole country covered with farms," he said. "When the supply of water back of the tops of those mountains is tapped and brought down here to this prairie, we shall have it blossoming as the rose."

"What is your name?" the passenger asked.

"Luther Burbank," was the reply.

Now, what shall we call this quality or element in the composition of the successful inventor and advanced thinker along these lines? Some might say, "Efficiency." Well, that is a good name for it. It means making two, three or twenty cornstalks grow where none, or at the most only one, grew before. It means causing the dry and dusty desert to become a veritable garden. It means taking a product of the laboratory which, before, had been only a chemical curiosity, and working upon it in such a fashion, and with such determination that it shall become a most useful article of commerce which shall find application in a multitude of ways, and bring comfort, yes, and happiness to many a home.

Time will not permit me to tell of our guest's other achievements; his process for the continuous filtration of water; the roller bearings invented by, and named for him, and many other inventions for which the world is indebted to him. They are matters of record, and we know that they represent the product of a mind that is not content to remain idle but is at all times at work in the interests of the general public.

He has the faculty, often lacking in many well-meaning persons, of putting the right thing into the right place. You remember the story of the school boy who was reading "What a good time I am havin'." "What! Repeat that!" said the teacher. "What a good time I am havin'." "Why," said the teacher, "you are leaving out the 'g'." "Gee! What a good time I am havin'." Now, Mr. Hyatt differs from the boy, inasmuch as he generally gets the "g" in the right place. And, Mr. Chairman, ladies and gentlemen, I think that by placing the well-earned Perkin Medal in the hands of Mr. John W. Hyatt, you have put it in the right and proper place.

CURRENT INDUSTRIAL NEWS

EVALUATION OF PULPWOOD

In an address delivered by Martin L. Griffin, Chief Chemist of the Oxford Paper Co., before the Maine Section of the American Chemical Society in Bangor, Oct. 17th, Mr. Griffin shows how unsatisfactory the prevailing units of measurement in the lumber trade have come to be, when applied to the valuation of wood for pulp and he says: Dimension measure units are only properly applicable to dimension products, as lumber. When wood is to be valued for its yield in pulp, it should be measured in terms of its useful products like other commodities: as coal in heat units; ores in terms of their metallic content; fertilizers in terms of potash, phosphoric acid and ammonia.

Up to the present time manufacturers of pulp, buying wood upon the cord dimension unit, not only suffer by the variation in yield of pulp in the same, and different species, as spruce and balsam, but also by the uncertainty as to the solid contents of the cord.

VALUATION BY VOLUME—A cord of wood is defined to be a stack 4 ft. high and wide and 8 ft. long containing 128 cu. ft. The solid contents of such a cord are affected by various conditions, such as:

1. LENGTH OF STICKS—Sticks are never entirely straight and smooth, and in piling them one above another there always remain cracks, which become larger, the longer the sticks are and *vice versa.* With four feet sticks as standard, changes in the stick length, from one foot to six feet, vary the difference in the solid volume of the same stack measure from 14 per cent to 35 per cent.

2. DIAMETER OF STICKS—The smaller the sticks, the greater the number, and number of cracks to the cord and consequently less wood. The difference in solid volume of two stacks, whose sticks are twice as large in one case as in the other, may amount to 13 per cent; and if the sticks of the one are four times as large as those of the other, this difference may amount to 25 per cent.

3. SPLIT WOOD—Large sticks are often split to facilitate handling and drying. After splitting they cannot be stacked as closely as before. This swelling amounts to 5–6 per cent. As a rule, the longer and thinner the sticks split, the greater is the swelling of the stack.

4. FORM OF STICK—The straighter and smoother the sticks, the smaller the air spaces between them and consequently the greater the solid contents.

5. SPECIES—Soft woods contain on the average about 3 per cent more solid wood to the cord than hard woods, due to straighter habits of growth and smoother bark.

6. GREEN AND DRY WOODS—With the drying of wood there is a consequent shrinkage in volume. Green hard wood will shrink by completely air-drying from 9–15 per cent and dry soft, 9–10 per cent.

7. PILING AND FIXING THE STACK—The higher the stack the less closely can it be piled. The heavier the stick and the weaker the piler, the less close is the piling.

It has been observed that there is more solid wood in a stack when only one end supporting stake is used than when two are used. There always remains some space between the stakes holding the stacks together and the wood, therefore, the fewer the stakes supporting ends or the longer the piles, the more solid wood. Just here arise many controversies over wood measurements where the method of scaling in cars is employed. An ordinary freight car will hold three crosswise stacks in each end and one short lengthwise stack between, making the equivalent of seven short staked piles having fourteen ends, about a cord to a stack. There are also many minor details which affect the amount of solid wood in the unit measure.

Since it is obvious that each stick of wood involved cannot be scaled and the sum total in solid feet obtained, a method of drawing representative sample cords may be employed and these measured. A sample may not only truly represent a grade of quality, but when drawn at a proportional rate, it may as truly represent a quantity. Thus if every fifth stick is drawn as wood is running on a conveyor or in a sluice until one cord is gathered, we know that four other equal portions, alike in all particulars, have passed. Such a sample can be measured by any standard of value, including quality and substance. If such a mode of sampling is applied according to the theory of averages, the sample will represent the quality, and there remains only the counting of the whole number of sticks to determine with precision the total quantity in terms of any unit by which the sample is valued.

If all pulp wood were equally dry, of the same specific gravity, and would yield the same amount of fiber per unit volume, this method would be adequate. Such is not the case.

VALUATION BY WEIGHT—Bulk commodities are now very generally bought and sold by weight. Wood can be so valued and in many instances this method is easily applicable and has its advantages. According to the plan of valuing wood by solid volume as outlined, if we take the weight of the sample volume we approach much nearer the measurement of the substance. Such a sample weighing would be accurate and applicable alike to wood driven in the rivers or freighted by rail.

Where wood is shipped by rail, its weight adds another important factor, namely—the freight, and this must be paid by the mill. Here the weight and moisture test reveal the substance and the water upon which freight must be paid. A cord of spruce wood will weigh from 3300 lbs. to 4400 lbs. according as it has 35 per cent to 50 per cent moisture, and this difference in moisture may add 50 cts. per cord to the cost of the wood at the mill.

The author concludes his address by suggesting that buyers and sellers of wood get together and study their joint interests and at least save a large sum of money now paid to the railroads for hauling wet and green wood.

PROGRESS IN THE FIXATION OF NITROGEN IN SCANDINAVIA

The London Times Engineering Supplement for Oct. 15, 1913, refers to the successful commercial development of the process for oxidizing ammonia to nitric acid by means of the catalytic action of platinum (see Eng. Pats. 698 and 8300 of 1902, and Addition to Fr. Pat. 317,544 of 1902; *J. S. C. I.*, 1902, 548; 1903, 93, 420). The carbide works at Odda, Norway, when operations were started, comprised 10 furnaces, each with a capacity of 7–8 tons of carbide per 24 hours. Ten more furnaces, of 16–18 tons capacity each, have recently been added. The temperature is maintained at 5720° F. (3160° C.), the electrodes of the older furnaces taking 1400 kilowatts and those of the newer ones, 3500 kilowatts. It is stated that the radiation of heat from the new furnaces is less than from a steam boiler. The hot gases from the furnaces are used in the lime-kilns instead of producer-gas. The annual output, 32,000 tons up till recently, is now 80,000 tons of carbide. Most of this carbide passes direct to the calcium cyanide works of an associated company, which, at the present time, has an annual output of 80,000 tons, the number of furnaces having been increased nearly sevenfold since the opening of the works four years ago. The nitrogen used is prepared by the Linde process, 100 tons of air being liquefied daily. The furnaces have a capacity of 1 ton each: the nitrogen is supplied through valves in the side, and a current at 60–75 volts through an electrode in the center. After about 24 hours at 1650° F. (900° C.), the carbide is converted into cyanamide, the resulting product containing 20 per cent of nitrogen. In addition to these developments, a company formed to acquire the rights of the Ostwald process (except in Westphalia and Rhineland) is erecting new works for the manufacture of carbide and cyanamide (and nitric acid) at Aura, Norway, with an estimated output of 200,000 tons of calcium cyanamide, and has acquired waterfalls at other places in Norway and also in Iceland, capable of furnishing power for an annual output of nearly 2 millions ton of calcium cyanamide. Works are to be erected at Dagenham on the Thames, at Trafford Park, Manchester, in Scotland, and in Ireland for producing from calcium cyanamide 12,000, 12,000, 9000 and 3000 tons of nitric acid, respectively. In the event of the supply of calcium cyanamide being curtailed or stopped, it will be possible to use the ammoniacal liquors from coke ovens, blast furnaces, residual recovery plant, and gas works as sources of ammonia.

STANDARD SPECIFICATIONS FOR THE PURITY OF RAW LINSEED OIL FROM NORTH AMERICAN SEED

The American Society for Testing Materials, affiliated with the International Association for Testing Materials, has just issued a compilation of the reports of the Committee on Preservative Coatings for Structural Materials, D-1, 1903–1913. The following specifications for the purity of Raw Linseed Oil from North American Seed were adopted August 25, 1913:

PROPERTIES AND TESTS

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

	Maximum	Minimum
Specific gravity at 15.5°/15.5° C.	0.936	0.932
or		
Specific gravity at 25°/25° C.	0.931	0.927
Acid number	6.00	......
Saponification number	195	189
Unsaponifiable matter, per cent	1.50	......
Refractive index at 25° C	1.4805	1.4790
Iodine number (Hanus)	......	178

METHODS OF TESTING

2. The recommended methods of testing are as follows:

GENERAL—All tests are to be made on oil which has been filtered at a temperature of between 60° and 80° F. through paper in the laboratory immediately before weighing out. The sample should be thoroughly agitated before the removal of a portion for filtration or analysis.

SPECIFIC GRAVITY—Use a pyknometer, accurately standardized and having a capacity of at least 25 cc., or any other equally accurate method, making a test at 15.5° C., water being 1 at 15.5° C., or a test at 25° C., water being 1 at 25° C.

ACID NUMBER—Expressed in milligrams of KOH per gram of oil. Follow the method described in *Bulletin No.* 197, revised 1908, Department of Agriculture, Bureau of Chemistry, page 142.

SAPONIFICATION NUMBER—Expressed as with acid number. Blanks should also be run to cover effect of alkali in glass. Follow method given in *Bulletin No.* 107, revised 1908, Department of Agriculture, Bureau of Chemistry, pages 137–138.

UNSAPONIFIABLE MATTER.—Follow Boemer's method taken from his "Ubbelohde Handbuch der Ole u. Fette," pages 261–262. "To 100 g. of oil in a 1000 to 1500 cc. Erlenmeyer flask add 60 cc. of an aqueous solution of potassium hydroxide (200 g. KOH dissolved in water and made up to 300 cc.) and 140 cc. of 95 per cent alcohol. Connect with a reflux condenser and heat on the water bath, shaking at first until the liquid becomes clear. Then heat for one hour with occasional shaking. Transfer while yet warm to a 2000 cc. separatory funnel to which some water has been added, wash out the Erlenmeyer with water, using in all 600 cc. Cool, add 800 cc. of ether and shake vigorously one minute. In a few minutes the ether solution separates perfectly clear. Draw off the soap and filter the ether (to remove last traces of soap) into a large Erlenmeyer and distil off the ether, adding if necessary, one or two pieces of pumice stone. Shake the soap solution three times with 400 cc. of ether, which add to the first ether extract. To the residue left after distilling the ether add 3 cc. of the above KOH solution, and 7 cc. of the 95 per cent alcohol, and heat under reflux condenser for 10 minutes on the water bath. Transfer to a small separatory funnel, using 20 to 30 cc. of water, and after cooling shake out with two portions of 100 cc. of ether; wash the ether three times with 10 cc. of water. After drawing off the last of the water, filter the ethereal solution so as to remove the last drops of water, distill off the ether, dry residue in water oven and weigh."

REFRACTIVE INDEX—Use a properly standarized Abbé refractometer at 25° C., or any other equally accurate instrument.

IODINE NUMBER (HANUS)—Follow the Hanus method as described in Bulletin No. 107, revised 1908, Department of Agriculture, Bureau of Chemistry, page 136.

URANIUM, RADIUM AND VANADIUM REPORT

The U. S. Bureau of Mines has just issued *Bulletin No.* 70. "A Preliminary Report on Uranium, Radium and Vanadium," by Richard B. Moore and Karl L. Kithil, of the Denver Laboratory of the Bureau of Mines. The bulletin describes the carnotite deposits, and gives the commercial methods of the treatment of ores.

Charles L. Parsons, Chief Division of Mineral Technology, says in the preface of the bulletin: "It has been shown that, although the Austrian Government has conserved its own resources of uranium and radium by purchasing the Joachimsthal mines and by carefully supervising pitchblende production, the deposits of radium-bearing minerals in the United States are being rapidly depleted by wasteful exploitation, chiefly for the benefit of foreign markets.

"Seemingly the country has been quite unaware of the extent to which uranium ores have been sent abroad. Investigation has developed the fact that during the year 1912, carnotite ores carrying 28.8 tons of uranium oxide were produced and that practically the entire amount was exported. The major part of this ore carried between 2 and 3 per cent U_3O_8, as it appears that no ore carrying less than 2 per cent can at present prices bear the cost of transportation. This means that 8.8 grams of radium chloride, or 11.43 grams of radium bromide, may be obtained from the ore shipped from this country in 1912. Only one American company has been preparing radium salts of a high degree of radioactivity and its product has only recently been offered for sale. The American ores exported were purchased for their radium content. It can probably be definitely stated that in 1912, there was obtained from American ores nearly two and one-half times as much radium as from all other sources combined.

"France, Austria, England, and Germany have their radium institutes fostered by their Governments or by philanthropic foundations. Up to the present time, although the United States has been furnishing a large part of the material for these foreign investigations, comparatively little has been done in the hospitals and laboratories of this country."

THE APPROXIMATE MELTING POINT OF SOME COMMERCIAL COPPER ALLOYS

As very little information on the melting points of commercial brasses and bronzes can be found in either scientific or technical literature, tests of a few typical alloys were made by H. W.

Gillett and A. B. Norton, of the U. S. Bureau of Mines. The results, summarized, in *Technical Paper No.* 60, are as follows:

	Approximate composition				Melting point	
Alloy	Copper	Zinc	Tin	Lead	° C.	° F.
Gun metal	88	2	10	..	995	1825
Leaded gun metal	$85^1/_2$	2	$9^1/_2$	3	980	1795
Red brass	85	5	5	5	970	1780
Low-grade red brass	82	10	3	5	980	1795
Leaded bronze	80	..	10	10	945	1735
Bronze with zinc	85	5	10	..	980	1795
Half-yellow-half-red	75	20	2	3	920	1690
Cast yellow brass	67	31	..	2	895	1645
Naval brass	$61^1/_2$	37	$1^1/_2$	..	855	1570
Manganese bronze	..	..	..	..	870	1600

The melting point given is the "liquidus," or point where the alloy is completely molten. The temperatures are thought to be accurate within ±10° C. or ±20° F.

BUREAU OF MINES BUDGET

The estimate of appropriations for the United States Bureau of Mines, for the fiscal year ending June 30, 1915, as approved by Secretary Lane and forwarded to Congress, is as follows:

For general expenses, $70,000.
Investigating mine accidents, $347,000.
Equipment of mine rescue cars and stations, $30,000.
Equipment of testing plant at Pittsburgh, Pa., $10,000.
Testing fuels, $135,000.
Mineral mining investigations, $120,000.
Investigations of petroleum and natural gas, $30,000.
Inspection of mines in Alaska, $7,000.
Books and publications, $2,000.
Lands, leases, etc., for mine rescue cars, $1,000.

The total is $752,000, an increase of $90,000 over the fiscal year ending June 30, 1914.

PLATINUM DEPOSITS IN GERMANY

Consul Thomas H. Norton reports that in several localities of the Ural Mountains, notably in the neighborhood of Nizhni Tagilsk in the Perm Government and about Mount Blogdat, platinum is found in sufficient amounts to allow of systematic mining operations. Very small quantities of platinum have been found in Borneo, Sumatra, Brazil, Colombia, Australia, and California, but the contributions from all these regions to the world's demands form a small fraction of the Russian supply—5 per cent or less. The total production is now about 13,250 pounds annually.

Every effort has been made in Russia to locate new deposits of the metal, but without success. The annual quantity tends to decrease, and an exhaustion of the deposits at no very remote date seems almost a certainty. At the same time, the demand for platinum has far outstripped the supply, and has naturally caused an enormous increase in the price. In 1892 platinum cost $89 per troy pound, about one-third as much as gold. Four years ago the price had risen to $338 per troy pound, and at present (October, 1913) it is $488 per troy pound.

Under these circumstances a large group of industries will welcome the discovery in Germany of extensive deposits of platinum, susceptible of easy exploitation. The location of these deposits is at Wenden, in Westphalia, in a section where iron, lead, copper and zinc mines are abundant. While prospecting by drill in the neighborhood of Wenden, metallurgical chemists unexpectedly discovered appreciable amounts of platinum in the layers of rock covering the ores of the common metals. Over 100 analyses of different borings were made and all showed the presence of the metal in sufficient amount to guarantee profitable extraction. The amount of platinum present in the rock varies from 0.9 to 1.9 troy ounces per cubic yard, which is very rich compared with the Russian deposits. Thus far a territory of 500 acres has been examined and the borings from nine different drill holes give on analysis the results cited. This tract alone will assure profitable extraction for many years. The depth to which the platiniferous rock reaches has not been announced.

Steps have already been taken to begin the regular metallurgical extraction of platinum at Wenden on a large scale. It is thought that careful prospecting will reveal the presence of other extensive fields in the Westphalian ore region, where geological formations similar to those at Wenden are wide-spread.

Surprise may be expressed that in a country where chemical investigation is so highly developed, the existence of easily accessible platiniferous rock deposits should have remained so long unsuspected. The reason is as follows: In the usual analytical methods, gold and platinum, as well as most of the rarer metals allied to platinum, are separated from the ordinary metals—iron, copper, silver, etc.—by treatment with nitric acid, in which the latter are soluble. Metallic gold and platinum remain behind as an insoluble residue after such treatment. They can be brought into solution by the aid of aqua regia, and be separated from one another, or the gold can be extracted by means of mercury. It happens, however, that platinum when alloyed with silver can be dissolved by treatment with strong nitric acid. As thus far platinum has been found in nature almost exclusively in the elementary form, no attempt has been made in ordinary ore analyses to test for the presence of the rare metal in the nitric acid solutions obtained as just described.

It seems, however, that in the Westphalian deposits platinum is present in the form of an alloy, and in the customary course of analysis entered into solution in the form of a nitrate. A chemist decided to test the solution of nitrates obtained in the normal course of an analysis for the possible presence of platinum, and this led to the unexpected discovery. There is every possibility that not only in Germany, but in all other countries, rock analyses will promptly be submitted to revision, and the greatest care taken to ascertain whether platinum is present. Deposits containing much less platinum than occurs at Wenden can still be worked most advantageously.

U. S. MINERAL PRODUCTION, 1912

The value of all minerals produced in the United States in 1912, according to figures just compiled by Edward W. Parker, statistician, of the United States Geological Survey, reached the record-breaking total of $2,243,630,326. This is more than six times the value of the production in 1882, 30 years ago. During that period the population has not quite doubled, but the per capita output of the mines has increased from $7.27 to $23.47.

OIL-HARDENING PLANT IN NORWAY

Commercial Agent Erwin W. Thompson states that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head offices at Christiania. The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1,000 barrels a day with the expectation of hardening cottonseed and peanut oils for the margarin makers. The Norwegian firm will purchase the best grades of cottonseed and peanut oils, and will also harden on toll.

CONCENTRATED NITRIC ACID IN NORWAY

Consul General Charles A. Holder reports that 98 per cent nitric acid is being produced at the Notodden and Rjukan plants where they now manufacture calcium nitrate. The acid has already been used successfully by factories manufacturing explosives. The manufacture of this concentrated acid is expected to prove of great importance.

PROPOSED BEET-SUGAR FACTORY FOR CHILE

Consul Alfred A. Winslow, Valparaiso, reports that the cultivation of sugar beets is receiving much attention of late in Chile, and a movement is on foot to interest capital for the erection of a beet-sugar factory. Sugar beets have been successfully raised at several points in this Republic, yielding 15 per cent and more of sugar.

As early as 1880 beet sugar was manufactured in a small way at Nunoa, Chile, and again from 1885 to 1891 at Los Guindos, and as late as 1901–1904 at Membrillo. While production on such a small scale was not found profitable, it was demonstrated that a factory of a capacity of 700 or 800 tons of beets per day could be made to pay well at the present rate of protection of 68.5 cents or 59.9 cents United States gold per 100 pounds on raw sugar, according to quality.

The following table shows Chile's imports of the different classes of sugar:

Pounds of sugar	Refined	White	Granulated	Crude
1906	17,714,521	1,449,363	95,567,956	1,994,740
1907	10,989,207	2,174,744	108,258,612	1,942,589
1908	6,873,592	2,659,778	94,607,942	1,134,760
1909	10,265,046	2,353,340	136,874,188	2,313,410
1910	9,233,046	1,678,732	143,935,352	1,684,595
1911	4,797,045	4,050,464	154,984,306	2,589,510
1912	6,009,861	3,262,116	136,327,268	1,749,440

Practically all of the crude sugar comes from Peru and is refined in Chile, since the duty on refined sugar is \$1.64 or \$1.09 United States gold per 100 pounds, according to quality.

PRODUCTION OF PORTLAND CEMENT IN 1913

It is estimated by Ernest F. Burchard, of the United States Geological Survey, that the quantity of Portland cement manufactured in the United States in 1913 was approximately 92,406,000 barrels, compared with 82,438,096 barrels in 1912, an increase of about 9,967,900 barrels or 12 per cent. The estimated shipments of Portland cement during 1913 were 88,853,000 barrels, compared with 85,012,556 barrels in 1912, an increase of about 3,840,400 barrels, or 4.5 per cent. On account of a large surplus of production over shipments, stocks of cement at the mills apparently increased more than 45 per cent, or from 7,811,329 barrels in 1912 to 11,375,000 barrels at the close of 1913. In 1913 the relations between production and shipments were the reverse of those for 1912, when shipments exceeded production. It may be necessary to revise considerably the estimates of stocks, but it is believed that these figures for production and shipments are very close to those that will be shown by complete returns from all producers.

Although few definite statements as to selling prices are at hand it is evident that the average value per barrel was appreciably higher than in 1912. Increases of 10 to 25 cents a barrel are reported from several plants in the central and eastern states, but there were slight decreases reported from a few plants in the Rocky Mountain district.

NATURAL GASEOUS MIXTURES RICH IN HELIUM

According to the *Journal of the Franklin Institute*, the follow- mineral springs evolve gas containing a large percentage of helium. The natural gas from the springs at Sautenay contains from 8.4 to 10.1 per cent of helium, that from springs at Mazières contains 5.9 per cent; from springs at Grisy, 2.18 per cent; from Bourbon Lancy, 1.84 per cent; from Néris, 0.97 per cent; and from La Bourboule, only 0.1 per cent. The quantities are too large to be considered as nascent helium evolved immediately it is produced; and it is more probable that the immediate source is dissolved helium, evolved by the disintegration of minerals in which it has been absorbed. These sources are grouped in the neighborhood of Moulins, Dijon, and Vesoul, France.

NOTES AND CORRESPONDENCE

PURIFICATION OF WATER BY ADSORPTION. PRELIMINARY ANNOUNCEMENT

Lead may be removed from water by shaking the water with fuller's earth, or similar adsorbent, and then filtering through paper. A sample of water drawn from a lead pipe which contained 1.5 mg. lead per liter, and which was entirely free from turbidity, so that the lead was probably present in true solution, required 0.05 mg. earth per 100 cc. and exposure to the earth for three minutes exclusive of the exposure incidental to filtering for complete removal of the lead. Lead was also removed from dilute solutions of lead acetate by means of fuller's earth, powdered charcoal, powdered pumice stone, powdered talc, ferric oxide, and marine clay, but quantitative determinations have not yet been made. Of these substances fuller's earth appears to remove lead best.

Bacteria are also removed from water by agitating it with adsorbents and then filtering through paper. Water containing 24,000 bacteria per cc. was rendered entirely sterile by treating 100 cc. for 15 minutes with 1 gram powdered charcoal. The same amount of fuller's earth per 100 cc. water reduced the total count very much but did not remove all bacteria. Larger amounts of earth effected complete sterilization. The complete removal of bacteria by means of any of the substances, fuller's earth, charcoal, or pumice, depends upon the two factors, amount of adsorbent, and length of time the water is treated before filtering. Fuller's earth appears to serve best for removing lead, and charcoal for bacteria.

Fuller's earth imparts a decided taste to water which cannot be removed by several previous extractions of the earth with water either hot or cold. It may be removed, however, by heating the dry earth, or by extracting the earth with concentrated hydrochloric acid containing a little nitric acid, and then with boiling water. The taste from charcoal is much less marked than that from raw fuller's earth, but charcoal is much more dirty to handle. Water treated with the sample of pumice used acquired only a slight taste, which can be removed by heating the pumice first. Clay and ferric oxide both gave a strong taste. In deciding whether a particular adsorbent gives a taste, it should be remembered that many varieties of filter paper, unless previously extracted for some time, will impart a slight taste to a solution passed through them. It is believed that treating with some adsorbent and filtering through paper, can be used to purify small amounts of water for drinking purposes, and may be adapted especially to the needs of travelers, and to household use during epidemics.

We are indebted to Dr. F. N. Whittier for assistance in making some of the bacteriological tests. The work will be continued.

MARSHALL P. CRAM
HENRY D. EVANS

BOWDOIN COLLEGE
BRUNSWICK, MAINE
January 7, 1914

NOTE ON CERTAIN UNPUBLISHED WORK ON ELECTROLYSIS USING SUPPORTED MERCURY KATHODE[1]

I commenced work towards a commercial solution of the wet electrolysis of common salt in 1888 and my first efforts were devoted to the mercury kathode, the results obtained in that year being what I propose to describe. At that time all the

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[1] Presented at the 6th Annual Meeting of the American Institute of Chemical Engineers, The Chemists' Club, New York, December 10-13, 1913.

rugged appurtenances of a successful commercial apparatus were yet to be developed in order to lift any process for the purpose out of the laboratory. It, therefore, came about that, in considering the immense distance to be traveled in order to surround the invention of the supported mercury kathode with the necessary concomitant equipment, and in the light of certain simplifications possible when using the diaphragm process, I gradually worked over to devoting myself exclusively to the development of the latter. It may not be out of place to say that it was this development which became, less than five years later, the first commercial contributor of caustic soda and chlorine to the world's markets[1] and which, if I may be allowed to say so, embodied those essential features of diaphragm success (such as excess liquid pressure on the anode side) which have since been used by everyone working in this field.

Referring to the 1888 work, it seemed to me obvious that, with a view to eliminating sodium from the solution, the worst possible place to put it was on top of a layer of mercury exposed to contact with said solution. The point is that, although sodium dissolves in mercury, the initially formed amalgam is of very low specific gravity compared with mercury itself and naturally tends to stay on top of the latter save as a sluggish tendency to diffusion operates otherwise. It seemed to me that the obvious alternative was to use the under side of the mercury as the kathode, the upper side being completely exterior to the electrolyzer as such, with the idea that the sodium, as fast as it was delivered to said under side, would bob up to the upper side and be thereby removed from relation with the electrolyzer and its contents.

This I proceeded to do, using a horizontal square frame of paraffined pine wood, a supporting sheet of a special cotton fabric carried by the under side of said frame, and additional support supplied to the fabric by a paraffined wood grating. Mercury was placed on the fabric to a depth just sufficient completely to cover it and a current supplied from a primary battery of three large two-fluid bichromate cells between a carbon anode and the under side of the mercury, saturated salt brine being the electrolyte.

The first run made with this cell will always be a painful memory. I started it on a certain Sunday morning in July and then went off for a walk to a point 7 miles distant. Returning in the evening I looked at the cell and saw to my disgust that the mercury was covered with liquid and that there were grains of some white material resting on the mercury in said liquid. I jumped to the conclusion that the layer of mercury had become discontinuous and that hydrostatic pressure had forced brine up over it and that partial evaporation had precipitated crystals of salt. Just to see what it tasted like I put my finger in the liquid and touched it with my tongue and then removed it with speed because the liquid was an oily 50 to 60 per cent solution of C. P. caustic soda and the white grains were undissolved particles of same. Of course what had happened was that sodium had entered the mercury from the under side and oxidized and hydrated, in moist air, from the upper side, and a portion had deliquesced in additional moisture abstracted from the air. I have always felt convinced that this general principle would work up to the best possible type of mercury kathode electrolyzer, but I also took the view, at least in the 90's, that unless some great commercial advantage accrued from being able to supply C. P. caustic, the best diaphragm process could, on the whole, do better than any process using a mercury kathode. However, seeing that mercury cells are in considerable use I am unable to understand why the apparently obvious principle above described has not been employed. In the light of the principle so clearly grasped in connection with the above quarter century old work, it is curious to note, in Wilderman's address before the World's Congress last fall, the repeated remarks on the disadvantages all processes previous to his have labored under of putting the light sodium in on the top layer of mercury and leaving it there.

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[1] Parsons, *J. Am. Chem. Soc.*, **20** (1898), 868.

SYNTHETIC RESINS

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, **6**, 3 appeared a paper by L. V. Redman, A. J. Weith, and F. P. Brock, which is supposed to be a general review of the literature on phenolic-methylene-condensation products, together with the results of personal research work of the authors.

The paper in question would have had increased importance if some of the opinions and statements expressed therein were more in accordance with facts.

The paper, although dated from the University of Kansas, is no more nor less than one of the so-called industrial research fellowships inaugurated by Professor Duncan, and which are paid for in the interest of purely commercial enterprises. In the paper, the author refers to "our firm, S. Karpen & Brothers, of Chicago," which tends to offset somewhat any prestige the mention of the name of the University of Kansas may bring about.

Among the several erroneous statements which are to be found in the paper, I shall mention more particularly the following:

On page 6, second column, paragraph 11, referring to the use of hexamethylentetramin, it is stated that the British patent Wetter (Lebach) "shows clearly that this reaction is no other than a water process to which a condensing agent has been added." In reality, the patent in question says nothing of this kind; the text clearly (on page 3, lines 50, etc.) reads as follows: "The 40 per cent formaldehyde may be replaced also by its polymerization products, as well as by substances which yield formaldehyde, such, for example, as hexamethylentetramine."

On page 7, first column, the paragraph entitled "Problem," recites a problem where the authors show a fertile imagination, untrammelled by mere cold sober facts. For instance, they state: "The resins formed (by the dry process as claimed by the authors) have very great commercial possibilities on account of their uniformity, chemical inertness, dielectric properties, mechanical strength, high refractive index (luster), plasticity at certain stages and the cheapness and supply of the raw materials from which these resins are manufactured."

In how far this statement is in accordance with the real facts, is shown further by direct comparative measurements and tests; it will be demonstrated that it matters not whether the process is carried out wet with my older process, or dry according to the directions of the authors.

The last sentence, referring to "the cheapness and supply of the raw materials," looks rather awkward in so far as it refers to hexamethylentetramin, which is manufactured from formaldehyde and ammonia, followed by evaporation, crystallization and drying. How this is a cheaper raw material, or a better supplied material than a plain mixture of ammonia and formaldehyde, is beyond my understanding.

Further down (page 7) a rather narrow and arbitrary construction is put on the definition of the word "bakelite." The fact is overlooked that "bakelite" is merely a registered trademark name for phenolic condensation products. It is true that in my first publication on this subject[1] I have referred, as a typical example of bakelite, to a product resulting from the union of 6 molecules of phenol and 7 methylen groups, which shows good resistance to acetone, while similar products containing more phenol seem to contain, at the same time, saliretin products which weaken their resistivity to acetone. For tech-

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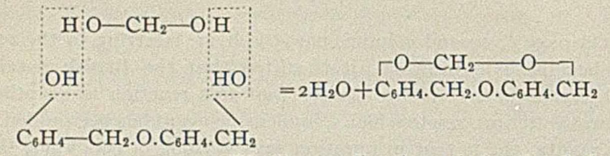
[1] This Journal, **1**, No. 3 (1909), page 149.

nical purposes, however, many kinds of bakelite are manufactured, some of them containing more phenol, others containing homologs of phenol, others again containing a considerably larger amount of methylen-groups.

In my Willard Gibbs lecture[1] I pointed out this fact as follows: "This simple way of interpretation has the advantage that it accounts for the possible existence of any number of similar bodies made with a varying proportion of formaldehyde. For instance, it leaves the possibility of imagining that a product may exist which is derived from more than six molecules of oxybenzylalcohol and one molecule of methylenglycol, which then would show less chemical resistivity. In the same way, it allows conception of varieties of the same product with a smaller number of molecules of phenol-alcohol entering into reaction with one molecule of formaldehyde or methylenglycol.

"Numerous facts point to the existence of such modified bodies of which the chemical and physical inertness increases with the lesser amount of molecules of phenol-alcohol, which enter into reaction with one molecule of methylenglycol; or to put it simpler, of which the resistivity increases with the larger amount of formaldehyde which reacts with a given amount of phenol. Dr. H. Lebach [*Z. angew. Chem.*, **22**, 1599 (1909)] called attention to the existence of a condensation product resulting from the action of one molecule of methylenglycol (formaldehyde) on disaligenosaligenin:



Disaligenosaligeninmethylenglycolether.

"The latter corresponds, in practice, to condensation products resulting from the direct reaction of two molecules of phenol on three molecules of formaldehyde."

Some of these varieties of bakelite, containing more methylen groups, have been manufactured here and abroad for certain purposes, and are characterized by a considerably increased resistivity, especially towards caustic alkalies.

The statement that dry hexamethylentetramin and dry phenol heated together evolve no water, may have a theoretical significance, but it does not alter the fact that large amounts of gaseous ammonia are set free, and that the ammonia is even more troublesome than water, as far as the technical applications are concerned. But right here my patented process for the conjoint use of heat and pressure becomes of paramount value, because its practice obtains homogeneous articles, where otherwise a porous useless mass would be the result.

With the use of much smaller amounts of ammonia, or other alkalies, homogeneous products can be obtained at relatively low temperatures, without the use of pressure, and this is one of the advantages of the use of small amounts of bases.

On page 8, paragraph 3, the authors avoid the disturbing influence of ammonia, by producing a porous mass of material B, or "intermediate product," and then welding together the ground-up material in a hot hydraulic press. They omit, however, to refer to my two United States patents Nos. 939,966 and 942,700, where this process is very accurately described.

On page 8, second paragraph, second column, the statement occurs: "This reaction between a phenolic body and an active methylene group may be followed by simply measuring the amount of ammonia which has been evolved." Instead of stating: "This is especially true if the phenol is in excess," the correct thing would be to state that it is *only* true in case phenol is in *large* excess. Under the latter conditions, a permanently fusible, soluble resin is formed—a "novolak."[2] Then indeed, the elimination of ammonia during the heating process is complete, and the amount of ammonia evolved becomes an accurate indication of the progress of the reaction. But such is not the case if less phenol be used, because then an infusible, insoluble product is formed, which is totally different in chemical composition and in general properties, and which retains a considerable amount of ammonia in the final product. The evolution of this ammonia gas keeps on to the moment when the product solidifies to an infusible porous mass. But here again, my patent for the conjoint use of heat and pressure, No. 942,700, comes in most handy whenever technical applications are concerned.

That part of the paper which describes the method of producing Novolak by the action of small amounts of hexa, on an excess of phenol, gives also the analysis of the resulting fusible resin. If we take into consideration the difficulty of this class of chemical investigation, the recorded results confirm, to a remarkable degree, the data and conclusions at which I arrived in my paper, "On Soluble, Fusible Resinous Condensation Products of Phenols and Formaldehyde."[1] The authors substitute the long name of "phenyl-endika-saligeno-saligenin," for the shorter name "novolak."

It seems to me that the authors might have done better justice to Dr. C. P. Steinmetz, of Schenectady, N. Y., by mentioning that this method for making a permanently fusible resinous condensation product, was described in all its details, by him, in his pending patent application of which Dr. Redman got knowledge during the interference proceedings before the United States Patent Office, in which Dr. Steinmetz, Mr. Byron Goldsmith, as well as Dr. Redman, and myself are contesting parties.

As to the transformation of this or any other Novolak into infusible products by further heating with methylen-containing bodies, like paraform, hexamethylentetramin, etc. (see page 10, column 2, last paragraph) this is a well known and well described process, patented by Mr. Aylsworth, as well as by myself.[2]

On page 9, second column, occurs this statement: "We have, at present, in our laboratory rods of this material 2 feet long and 1$^1/_2$ inches in diameter which have been produced by simply pouring the material while liquid into open molds and allowing it to harden under suitable heat treatment without the application of external pressure. These rods in the final condition are homogeneous, almost water white transparent and free from fractures or gas bubbles." This statement would be more significant if it were accompanied by some data as to tensile strength or brittleness of this product, or if it were stated at the same time, that its method of production was not borrowed from some other existing patents.

As to the table of analyses published on page 11, first column, some of the results relating to bakelite products are strikingly inconsistent with all the theoretical speculations of Dr. Redman; for instance, "a bakelite pipe stem bought in the open market" shows a higher percentage of material insoluble in KOH than any of the materials made with dry phenol and dry hexamethylentetramin, although the latter product is vaunted to be an improvement over the first.

The apparatus described on page 11, for determining whether water is set free when reacting with an excess of phenol on hexamethylentetramin, seems to invite a very serious objection as to the suitability of this method. Indeed, the inverted condenser designated by 8 seems to be the best means for *preventing* any formed water to enter into the train of absorbing tubes where the water is supposed to be determined. Furthermore, it is a well known fact that pure phenol has a decided tendency to retain small amounts of water and this even at high temperatures.

It should be noted that in these condensation products, it is not a matter whether 10 or 5 per cent or even 1 per cent of

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[1] This Journal, **5**, 506.

[2] *Ibid.*, **1** (1909), page 545.

[1] This Journal, **1**, 545.

[2] Aylsworth, U. S. Patent No. 1,020,593; Baekeland, U. S. Patent No. 1,038,475.

water is evolved, but whether such small quantities as 0.5 or 0.1 per cent are retained in the mass. It is easy enough to drive off any amount of water up to the last traces, even if one starts with water-containing materials. In some cases, the removal of these last traces of water is not necessary. In other cases, for instance, when the material has to be used as an insulator for high-voltage–high-frequency currents, then it is very important that even the smallest traces of water should be eliminated. When it comes to that point, the presence of free ammonia is just as objectionable, because the latter attracts water and increases the surface conductivity.

On paper, the reaction between phenol and hexamethylentetramin ought to occur without setting free anything but NH_3. Yet, we know in practice, that organic reactions are seldom, or ever 100 per cent; in other words, any organic reaction is ordinarily accompanied by the formation of some by-products. Many organic chemists in their rather inaccurate ways of expressing themselves are apt to speak of "a quantitative reaction" when the reaction shows $99^1/_2$ per cent or even much lower. I have heard reference made to quantitative reactions, when in reality 5 and even 7 per cent of by-products were formed.

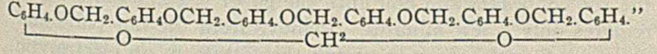
In relation to the question whether water is necessarily present in the end-product when starting from wet materials, I can state that there is no trouble in producing bakelite by means of water-containing substances, like formalin (or so-called aqueous formaldehyde solutions) and of which the infusible end-product showed incomparably better dielectric properties than what we obtain in making a material by means of dry phenol and dry hexamethylentetramin, as described by Dr. Redman and his collaborators.

On page 12, column 2, it is stated that anisol will not react on hexamethylentetramin, and some arguments are advanced to that effect. This statement, by itself, might make some impression, but for the fact that a few lines further it is asserted that anisol will react with hexamethylentetramin. "Anisol" is certainly an exemplary well behaved substance, which does not react when the authors desire it to behave so, but which obediently reacts when for some theoretical argument, it should react, providing it be in the encouraging company of 6 molecules of phenol. It then obeys discipline as a Prussian soldier, and ranges itself exactly on the extreme end of a row of benzol groups, military fashion, and stands there like a corporal on a battlefield, to ward off any attack on the line.

As a result of this exemplary behavior, it is stated that a lacquer film made with some anisol, stands 72 hours a solution of *N* caustic potash solution, without loosening.

Unfortunately, for all this argument, nothing is easier than to prepare lacquer films from ordinary cheap cresols containing enough metacresol, which will not detach neither in 72 hours nor in 90 hours.

On page 13, column 2, paragraph 2, I read: "Dr. Baekeland concludes that the final product is not obtained through the polymerization of novolak as an intermediate product, but that the growth of the chain stops when six phenols have entered and that an extra hydrated formaldehyde forms with the six phenol chain an inner anhydride as shown by the following formula:



$C_6H_4.OCH_2.C_6H_4OCH_2.C_6H_4.OCH_2.C_6H_4.OCH_2.C_6H_4.OCH_2.C_6H_4.$"

I am not aware that I ever took the initiative of commanding this molecular chain to stop or not to stop. My molecules do not seem to be as obedient as anisol is to Dr. Redman and his collaborators. In my former publications I have stated that we can conceive molecular chains shorter or longer.[1] Furthermore, experience has taught me enough sober sense not to be dominated exclusively by any purely theoretical considerations, when referring to such complicated substances as these condensation products. When, in my first publication, I proposed a straight chain formula, I had no presumption whatever of calling this a final explanation. In offering this formula, I was careful to add "until we have something better." In my Willard Gibbs lecture (*loc. cit.*) I repeated these same thoughts. I also quoted: "Even Dr. Raschig warns us with the natural conservatism of an able chemist of long and wide experience, when he says: 'Ueber die Chemie des Bakelit tappen wir noch vollständig im Dunkeln.'"

That the "chain formula" does not explain everything is clearly shown by the rather large formation of such secondary products as dioxydiphenylmethan, which in its turn can be converted by the action of more methylen groups into bakelite as announced by me last year.[1] In this case, the dioxydiphenylmethan acts simply as a diphenol. Lately a similar reaction has been described by Beatty,[2] who starts from a similar phenolic body, dimethyldioxydiphenylmethan, obtained after the method described in 1891 by Dianin, consisting in reacting with acetone upon phenol in presence of an acid.[3]

All this should warn us against too one-sided theoretical interpretations in regard to the constitution of the process of reaction of any of these colloidal bodies, which undoubtedly are composed of several substances, all intermixed and in such a condition that it is impossible to separate or purify them by our usual chemical methods, which are available for crystalline or volatile substances.

The negative properties and general inertness of these hard, infusible condensation products is the very reason why we can not apply to their study the accepted scientific methods, and why it becomes practically impossible to establish their constitution beyond mere conjectures.

But a very practical question presents itself. Are the condensation products obtained by the action of anhydrous hexamethylentetramin on anhydrous phenols, really different from those obtained by the so-called wet processes?

This question, at least, is easy to answer: The so-called phenyl-endika-saligeno-saligenin, notwithstanding its long name, is identical with the permanently fusible shellac substitutes of Blumer, DeLaire and others, which I have called Novolak. In fact, for substances so difficult to purify, its properties, as well as its chemical composition, as recorded by Dr. Redman and his collaborators, are strikingly similar to Novolak.[4]

As to the infusible products obtained by the use of more hexamethylentetramin, let us compare their physical and chemical properties with those of bakelite obtained by the use of the so-called "wet-process."

TENSILE STRENGTH

Redman product	*Bakelite*
Tensile strength between 2000 and 4500 lbs. per square inch.	Tensile strength average, 5000 lbs. per square inch. Highest, 7350 lbs. per square inch.

CRUSHING STRENGTH

20,000 to 30,000 lbs. per square inch.	Averages 26,000 lbs. per square inch.

DIELECTRIC STRENGTH

$^1/_2$ millimeter thick gave voltage puncture from 40,000 to 50,000 volts.	$^1/_2$ mm. thick gave voltage puncture 40,000 to 50,000 volts.

SPECIFIC ELECTRIC RESISTANCES AND SURFACE CONDUCTIVITY

Recent comparative tests have shown that plates of bakelite and the material made by the method described by Dr. Redman,

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[1] THIS JOURNAL, **5** (1913), 506.

[1] THIS JOURNAL, **5**, 506.

[2] Beatty, French Patent No. 447,647.

[3] *Berichte*, **25** (1892), Referate p. 334–37; Dianin (*Journ. d. russ phys.-chem. Gesellsch.*, **1891** (1), 488–517, 523–546, 601–611).

[4] THIS JOURNAL, **1**, 545.

have practically the same specific electrical resistance and the same surface conductivity.

If we add that all the infusible materials made from phenol (hydroxybenzol) and formaldehyde and ammonia, or hexamethylentetramin, dry or wet, have the same specific gravity, the same color, the same appearance, the same resistivity to solvents and chemicals, and that up till now, no property has been mentioned which is not common to all these products, it becomes easy to draw conclusions as to their absolute identity.

L. H. Baekeland

Yonkers, New York
January 10, 1914

OZONE

Editor of the Journal of Industrial and Engineering Chemistry:

Referring to the editorial, on the above subject (This Journal, 5, 882), commenting on tests of ozone published recently in the *Journal of the American Medical Association*, I wish to call to your attention that the manner in which these tests were conducted, leaves large room for doubt as to the reliability of the conclusions drawn by the authors and that the readers of your valuable paper should be warned against accepting them without more convincing proof.

After a careful study of the reports, I am impressed that many of the conclusions are imaginary and not proven by the results obtained. For example, tests were made on three men by placing them individually in front of a large ozone generator delivering a strong blast of ozonized air at high concentration, the face of the victim being only a few inches from the outlet of the ozone generator. One of the victims had a "sore throat" ("cold") at the beginning of the experiments. The experimenters concluded from the results of the test that breathing ozone in strong concentrations produces sore throat. When we consider the probable effect of the blast of air on the face and head, the wind pressure on the nasal passages and the dust carried by the blast, it seems rather far-fetched to make any definite conclusions regarding the effect of ozone, especially from such a small number of tests and subjects. Furthermore, the conditions of the tests were extremely abnormal as it has not been proposed to use in ventilation concentrations exceeding one-tenth of that used in these tests.

The results of the bactericidal tests indicate that ozone in dry air has little germicidal effect. There is, however, overwhelming evidence which proves beyond a doubt that it will destroy germs in water. This has been thoroughly tested out by the best scientific authorities in Europe in connection with the many municipal ozone water purification plants, as well as by Pasteur's Institute and the German Imperial Board of Health. The latter were able to destroy by means of ozone practically all germs in water containing as many as 30,000 cholera and 30,000 typhus bacteria per cubic centimeter. As there is always considerable moisture in the respiratory passages, it is perfectly logical to suppose that the breathing of ozonized air may have some beneficial effect.

The fact that the guinea pigs died in an atmosphere of strongly concentrated ozone is not surprising, as there is no substance known to science which will destroy bacteria without also destroying animal tissue. For this reason, antiseptics cannot be used full strength and the best that is expected from their use is to stunt the growth and prevent the propagation of the bacteria.

The tests on the animals in the cages supplied with mild concentrations of ozone showed practically neutral results, *i. e.*, there was no pronounced beneficial or detrimental effects noted. The duration of the tests was entirely too short to be conclusive.

The test these experimenters made of blowing ozonized air on a piece of paper covered with lampblack to determine the effect of ozone on tobacco smoke, was going a long way around. It seems to me the proper way to make such a test would be to make it on tobacco smoke instead of lampblack. Particles of carbon in lampblack are very many times larger than the floating particles of tobacco smoke and hence, the oxidation of the latter in its very finely divided state might take place when lampblack would not be appreciably affected.

W. H. Thompson

Westinghouse Electric & Mfg. Co.
East Pittsburgh, Pa.
December 16, 1913

RAPID DETERMINATION OF COPPER IN STEEL, CAST IRON AND ALLOY STEELS

Editor of the Journal of Industrial and Engineering Chemistry:

The steadily increasing use of copper in steel in the last year or so has created a demand for a more rapid determination of that element in steel than is possible by the present method of analysis.

Copper in steel is usually determined by being precipitated as copper sulfide by the means of hydrogen sulfide or sodium hyposulfite. The copper sulfide is then generally incinerated in a porcelain crucible, digested at a gentle heat with nitric acid, transferred to a platinum crucible and evaporated with hydrofluoric and sulfuric acids to remove silica.

The residue, if not soluble in sulfuric acid, is fused at a low heat with sodium or potassium pyrosulfate. The copper is then deposited electrolytically from the acid solution, or determined colorimetrically in an ammoniacal solution.

In the presence of titanium and molybdenum there are variations of this method which make it even more tedious and time-consuming. There is nothing new or original claimed for the method about to be described as it follows very closely Low's method for the precipitation of copper by aluminum, but so far as the writer is aware, it has never been used for the determination of copper in steels or irons.

METHOD

From three to five grams of steel, depending upon the amount of copper present, are dissolved in a mixture of 60 cc. of water and 7 cc. of sulfuric acid (sp. gr. 1.84) in a 250 cc. beaker. After all action has ceased, place in the beaker a piece of sheet aluminum prepared as follows: Cut a stout piece of sheet aluminum $1^{1}/_{2}$ inch square and bend the corners so that it will stand upon its edge in the beaker.

Boil the solution from twenty to twenty-five minutes which will be sufficient to precipitate any amount of copper liable to be present. Remove from the heat and wash the cover and sides of the beaker with cold water. Decant the liquid through a S & S 11 cm. filter. Wash the precipitate three times with cold water, then place the filter in a 100 cc. beaker. Pour over the aluminum in the beaker 8 cc. of nitric acid (sp. gr. 1.42) and 15 cc. of water and heat to boiling. Pour this over the filter in the 100 cc. beaker and boil until the paper is a fine pulp, which requires only a few minutes. Remove from the hot plate and filter, wash with water, receiving the filtrate in an electrolytic beaker, add 2 cc. of sulfuric acid (sp. gr. 1.84) and electrolyze, using 2 amperes and 2 volts. Gauze cathodes and anodes are used and the deposition is completed in from one to one and a quarter hours. The total time of the determination from the weighing of the sample to the weighing of the copper is about three hours, and with the proper equipment, a large number of samples may be run at the same time.

Below are some of the results obtained on the Bureau of Standards' samples.

Name	Average copper present Per cent	Copper found Per cent
Vanadium steel No. 24	0.022	0.020
Chrome nickel steel No. 32	0.056	0.056
Chrome vanadium steel No. 30	0.070	0.066
Nickel steel No. 33	0.150	0.150
No. 5 A iron (C)	0.060	0.063

As a further proof of the accuracy of this method, known amounts of pure electrolytic copper containing 99.88 per cent of copper were added to the Bureau of Standards' sample No. 14 A steel. The mixed drillings were dissolved in 20 cc. of (2–1) nitric acid, 8 cc. of sulfuric acid (sp. gr. 1.84) added and the solution evaporated until sulfuric acid fumes were evolved freely. The solution was allowed to cool and then 25 cc. of cold water were added and the solution was heated until all the sulfate was dissolved. The solution was filtered and the filter washed with hot water. The volume (not to exceed 75 cc.) was brought to a boil and the sheet aluminum introduced. Procedure was the same as stated before, except that after the solution was decanted through the filter and washed with water, the copper was dissolved on the filter and the filtrate received in an electrolytic beaker and electrolyzed as usual. The results obtained follow:

Copper added Per cent	Copper found Per cent
0.499	0.49
0.998	0.99
1.997	1.97
2.996	3.00
3.995	3.99
4.994	4.98

I wish to give credit to Mr. George Shuster of the laboratory force, who tried out this method and obtained the results stated above.

William B. Price

Waterbury, Conn.
Oct. 25, 1913

INTERNATIONAL ELECTRICAL CONGRESS, 1915.

The International *Electrical* Congress is to be held at San Francisco, September 13–18, 1915, under the auspices of the American Institute of Electrical Engineers, by authority of the International Electrotechnical Commission and during the Panama-Pacific International Exposition. Dr. C. P. Steinmetz has accepted the Honorary Presidency of the Congress. The deliberations of the Congress will be divided among twelve sections which will deal exclusively with electricity and electrical practice. There will probably be about 250 papers. The first membership invitations will be issued in February or March, 1914.

Attention is drawn to the distinction between this *Electrical* Congress and the International *Engineering* Congress which will be held at San Francisco during the week immediately following the electrical congress. The engineering congress is supported by the Societies of Civil, Mechanical and Marine Engineers and by the Institutes of Mining and Electrical Engineers, as well as by prominent Pacific Coast engineers who are actively engaged in organizing it. This Congress will deal with engineering in a general sense, electrical engineering subjects being limited to one of the eleven sections which will include about twelve papers, treating more particularly applications of electricity in engineering work.

The meeting of the International Electrotechnical Commission will be held during the week preceding that of the Electrical Congress.

SPRING MEETING OF THE AMERICAN CHEMICAL SOCIETY

The Forty-ninth General Meeting of the American Chemical Society will be held in Cincinnati, Ohio, April 8–11, 1914. The officers of the local section are: President, F. W. Weissmann, 2900 Vine St., Cincinnati, Ohio, and Secretary, Stephan J. Hauser, 1623 Maple Avenue, College Hill, Cincinnati, Ohio. A more complete statement of the meeting will appear in the March issue of This Journal. The titles of papers should be sent to the Secretary, Charles L. Parsons, Box 505, Washington, D. C.

The following chairmen of committees have been appointed:

Executive Committee, Frederick W. Weissmann.
Finance Committee, Archibald Campbell.
Transportation and Excursions, Gordon Farnham.
Press, Publicity and Printing, C. T. P. Fennel.
Reception and Registration, J. W. Ellms.
Ladies' Reception, Mrs. J. W. Ellms.
Entertainment, Richard Lord.
Smoker, F. C. Broeman.
Banquet, L. W. Jones.
Meeting Places, John Uri Lloyd.

Chas. L. Parsons

BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., is prepared to issue a sheet brass of the following composition, approximately:

	Per cent		Per cent
Tin	1.0	Zinc	27.0
Lead	1.0	Iron	0.3
Copper	70.3	Nickel	0.5

The fee, payable in advance is \$3.00 per sample of about 150 grams weight.

S. W. Stratton, *Director*

January 6, 1914

SYNTHETIC RESINS—CORRECTION

We note the following errors in our article under the above title, This Journal, 6, 3.

(1) Page 8, Column 1, four lines from the end, the equation should read:

"$2HO.CH_2.C_6H_4OH \longrightarrow HO.CH_2.C_6H_4O.CH_2.C_6H_4OH$."

(2) Page 10, Column 1, below the first table:

"$C_6H_5OCH_2.C_6H_4.OCH_2.C_6H_4(\ )OCH_2.C_6H_4OH$."

(3) Page 13, Column 2, line nine from the end:

"79 per cent" should read 76 per cent.

L. V. Redman
A. J. Weith
F. P. Brock

January 21, 1914

VEGETABLE OILS EXPORTED FROM CHINA, 1912

The *Oil, Paint and Drug Reporter* states that exports of vegetable oils from China in 1912 amounted to 35,046 net tons of bean oil, 20,281 net tons of peanut oil, and 44,815 tons of wood, tea seed and other oils.

ANNUAL TABLES OF CONSTANTS, ETC., VOL. III.

Volume III of the Annual Tables of Constants and Numerical Data, Chemical, Physical and Technological, published by the International Commission of the VIIth and VIIIth International Congresses of Applied Chemistry is now in press and will be issued in the first half of 1914. A descriptive circular with references to reviews of previous volumes may be secured on application to The University of Chicago Press.

The *subscription* to Volume III is *now opened* and *will be closed March 31, 1914*. The names of subscribers should be sent to The University of Chicago Press, the American agent for the distribution of the Annual Tables. Subscriptions are payable to The University of Chicago Press at the time of publication.

The subscription price of Volume III will be the same as for Volume II, namely, \$6 for the unbound copy, \$6.80 for the bound copy (carriage free). Members of contributing societies (*The American Chemical Society, The American Electrochemical Society, The Society of Chemical Industry, the American Academy of Arts and Science, the National Academy of Science*) and of contributing manufacturing establishments, are entitled to a discount of 20 per cent (but not on the binding) and will receive the volume unbound for $4.80, or bound for $5.60 (carriage free) *provided their subscriptions are received* by March 31, 1914. After March 31, 1914, the price will be raised to $6.40 (unbound) and $7.20 (bound) and a charge will be made for carriage and no discounts allowed.

JULIUS STIEGLITZ, University of Chicago
EDWARD C. FRANKLIN, Leland Stanford University
HENRY G. GALE, University of Chicago
ALBERT P. MATHEWS, University of Chicago
Commissioners for the United States

PERSONAL NOTES

Prof. Theodore William Richards, of Harvard University, has been elected President of the American Chemical Society for the year 1914. M. T. Bogert and A. D. Little have been elected directors, and C. H. Herty, Julius Stieglitz, L. H. Baekeland and W. L. Dudley, councilors-at-large, for a three-year period.

An Anglo-American Exposition to celebrate the centenary of peace and progress in the arts, sciences and industries of the United States and Great Britain, will be held in London, from May to October. A committee has been organized to represent the chemical industries.

Dr. C. E. K. Mees, Director Research Department, Eastman Kodak Company, gave a lecture illustrated with lantern slides, on the problems, equipment and organization for research, in their plant at Kodak Park, Rochester, before the New York Section of the A. C. S., on January 9th, at The Chemists' Club.

Mr. A. K. Comins, formerly in the leather department of A. D. Little, Inc., of Boston, is now with the A. C. Lawrence Leather Company, of Peabody, Mass.

The Wisconsin Section of the A. C. S. met on January 21st. Prof. David Klein gave an illustrated lecture on "Recent Developments in Colloid Chemistry."

Mr. H. E. Howe, of the Bausch & Lomb Company, gave an illustrated lecture on "Optical Glass" and "The Projections of Spectra," before the Western New York Section of the A. C. S. on January 13th.

Sir William Crookes has been elected President of the Royal Society. In view of the invariable practice that the President of the Royal Society should hold no office in similar learned societies at the same time, he has been obliged to resign the Presidency of The Society of Chemical Industry, to which he was elected at the annual meeting in 1913.

Dr. Rudolph Messel was elected President of The Society of Chemical Industry, by the Council, on December 22nd, to complete the unexpired term of Sir William Crookes.

The Philadelphia Section of the A. C. S. held their January meeting on the 22nd. The speakers were Dr. Carl L. Alsberg, Chief of the Bureau of Chemistry; Mr. Charles J. Hexamer, of the Fire Underwriters' Association, who gave an illustrated address on "The Chemistry of Fires, and Chemicals in Fires." Prof. Philip Maas, of the Central High School, exhibited a suite of liquefied gases.

Prof. R. A. Wetzel, of the College of the City of New York, spoke at a recent Colloquium of the General Electric Company Research Laboratory, on the "Relativity Principle," which he illustrated with the models recently described in *Science*.

Mr. Wm. Hoskins and Mr. H'V. Main gave a lecture illustrated with lantern slides, before the Chicago Section of the A. C. S. on January 16th, on "Atmospheric Pollution."

Dr. Reston Stevenson has been promoted to the position of Assistant Professor of Chemistry in the College of the City of New York.

Dr. Wolfgang Ostwald, of the University of Leipzig, Germany, is giving a series of six lectures on colloid-chemistry before various universities and chemical organizations in America, including: Columbia, Chicago, Johns Hopkins, Illinois, Cincinnati, Nebraska, McGill (Montreal) Universities, Indianapolis Section of the A. C. S., and others to be arranged later.

The Alabama Section of the A. C. S. was addressed at the January 24th meeting by Prof. B. B. Ross, on "The Occurrence and Composition of Some Alabama Phosphates," and by Prof. C. L. Hare, on "A Study of the Chemical Composition of Cotton Seed."

The International Petroleum Commission of Karlsruhe, Grand Duchy of Baden, Germany, desire to change the Commission into an INTERNATIONAL PETROLEUM INSTITUTE, and have requested the Imperial German Government to submit their plan to the countries represented or interested in the Commission.

Mr. Christian Dantsizen and Mr. J. A. Orange, of the General Electric Company Research Laboratory at Schenectady, have recently returned from Europe where they spent three months visiting plants of general interest to the electrotechnical industry.

The Johns Hopkins Medical School has announced the following changes concerning the admission of students: In 1913 the number of students in each class was limited to ninety. In order to receive consideration applications of incoming students must this year be made by July 1st. After that date the various applications will be sifted and the most likely ninety applicants chosen. The requirements for admission in chemistry have been increased so that in addition to the present requirement of 150 hours of laboratory work in inorganic chemistry, an additional 90–100 hours of laboratory work in organic chemistry will be required of all students desiring to enter the school after October, 1914.

Virgil Coblentz, Chief Chemist for Squibb & Co., took the lucky number in a raffle, entitling him to the library and chemical publications of the late William McMurtrie. The drawing was conducted by Dr. Charles Baskerville and was held at The Chemists' Club, New York City, on January 9, 1914.

The Southern California Section of the A. C. S. had as speakers at their meeting on January 16th, Dr. Elbert E. Chandler, of Occidental College, "The Universal Equilibrium," and Mr. H. J. Lucas, of Throop College of Technology, "The Sanitation Service of Porto Rico."

Prof. J. Howard Mathews, of the Chemistry Department of the University of Wisconsin, lectured on "Color Photography," before the Chicago and Indiana Sections of the A. C. S., on December 12th and 13th, respectively, and before the students of De Pauw University on the afternoon of December 12th.

Mr. H. J. Skinner, Vice-President of Arthur D. Little, Inc., Mr. Perry Barker and Mr. Vasco Nunez, of the same organization, spent two weeks in December examining a large industrial plant in Louisiana.

The Cornell, Rochester, Eastern and Western New York and Syracuse Sections of the A. C. S. held a joint meeting at Syracuse University on January 17th. The afternoon program was as follows: "Address of Welcome," Hon. Louis Will, Mayor of Syracuse; "The Use of Physical Measurements in

Chemistry," Dr. C. E. Kenneth Mees, Director Research Laboratories of Eastman Kodak Co.; "Hydrogen Telluride and the Atomic Weight of Tellurium," Dr. Ross P. Anderson of Cornell University; "The Dissociation of Hydrogen into Atoms," Drs. F. Langmuir and G. M. J. MacKay, of the General Electric Company; "The Oxidation of Ammonia to Nitric Acid," Mr. G. N. Terziev, of the Solvay Process Company; "Microscopical Demonstrations with Especial Reference to the Ultramicroscope," Dr. H. C. Cooper, Syracuse University. The evening program included a short organ recital, a brief welcome by Chancellor Day, of Syracuse University and a lecture on "Electrical Energy," by Dr. Charles P. Steinmetz, Professor in Union College and Chief Consulting Engineer of the General Electric Company.

Dr. E. G. Love was tendered a testimonial dinner by the members of The Chemists' Club and their friends, on January 17th, as a mark of appreciation of his long service as Chairman of the House Committee of the Club.

The Eastern New York Section of the A. C. S. held a symposium on "Electronics and Chemistry," at Schenectady, on January 23rd. The symposium was led by Dr. Saul Dushman with supplementary papers by Messrs. Whitney, Coolidge and Langmuir, of the General Electric Company.

Mr. C. F. Woods, secretary of Arthur D. Little, Inc., presented the Report of the Official Chemists to the American Institute of Metals, at the convention held in Chicago in October. On November 20th, Mr. Woods spoke before the New England Street Railway Club on "The Relation of the Chemist to the Electric Railway."

The Pittsburgh Section of the A. C. S. was addressed on January 22nd by Mr. E. R. Weidlein, of the Mellon Institute of Industrial Research, University of Pittsburgh, on "Adrenaline: Its Nature and Composition."

The Willard Gibbs Medal for 1914 has been awarded by the jury to Doctor Ira Remsen, Past President of the American Chemical Society, and President Emeritus of Johns Hopkins University. This medal was founded by William A. Converse, of Chicago, and is awarded annually by the Chicago Section of the A. C. S. to that chemist who is deemed worthy of recognition because of eminent work in, and original contributions to, pure or applied chemistry.

BOOK REVIEWS

Dictionary of Applied Chemistry, revised and enlarged edition. By SIR EDWARD THORPE and other eminent contributors. Five volumes, 3891 pages. Price per volume, $13.50; complete set, $67.50. Longmans, Green & Co., London and New York.

The fourth and fifth volumes of the set have now been issued by the publishers, thus completing the task of thoroughly revising, enlarging and republishing this great work. Volumes I, II, and III were reviewed in THIS JOURNAL, 4, 550, 698 and 5, 620.

Vol. IV containing 727 pages covers the subject matter in the usual alphabetical order from Oilstones to Soda. As in previous volumes, the old material has been revised and brought up to date and a number of new subjects have been included, the more important of which are Old Fustic, Olive Oil, Osmium, Oxydases, Industrial Uses of Oxygen and Ozone, Palladium, Palm Oil, Synthetic Perfumes, Phenanthrene, Phytosterol, Pitchblende, Plant Sprays, Polarimetry, Polonium, Potato, Proteins, Ptomaines, Pyrites, Pyrometry, Racemism, Radioactivity, Radium, Refractometer, Refrigeration, Rubber, Safrole, Salicylic Acid, Saponification, Sewage, Artificial Silk, Smoke Prevention.

In addition to this new material, the other articles show careful revision, correction and extension where the importance of the subject justifies it.

Volume V, 830 pages, treats the subjects beginning with Sodium and ending with Zymurgy. The more important new subjects which have been added to the text are Soils, Solubility, Sulfide Dyes, Synthetic Drugs, Thermite Process, Titanium, Toxins and Antitoxins, Urea and Uric Acid, Vat Dyes and Whiskey; and subjects which have gained in commercial importance since the older edition was published, such as Thorium, Vanadium, Uranium and Tungsten are entirely rewritten and extended.

The revision and publication of these volumes has been a great undertaking and it is gratifying to find that both the editor's work and the mechanical production have been accomplished with such promptness and success. Thorpe's "Dictionary of Applied Chemistry," in its present revised form, is doubtless the most comprehensive and complete book of reference now in existence covering the broad field of Applied Chemistry.

M. C. WHITAKER

Transactions of the American Institute of Chemical Engineers. Volume V. (1912) Office of the Secretary, Polytechnic Institute, Brooklyn, N. Y. Published by the Institute through D. Van Nostrand Company, New York, 1913. 8vo., iv + 284 pages.

The Institute held joint meetings with the Eighth International Congress of Applied Chemistry in September, and many of its papers were published in the Congress proceedings, which accounts for the smallness of the present volume.

The frontispiece this year is an excellent photogravure of the Institute's President, Dr. T. B. Wagner, The binding is uniform with the series. This work is either better done or appears to better advantage on the smaller volume. The present volume starts by giving in full the papers which have been read before the Institute, together with the discussions which followed. This throws to the rear of the volume such matter as the Institute's Constitution and membership list. This change in arrangement is an improvement, since the main value of the volume in future years will be the original communications read before the Institute. The Proceedings of the annual meetings have been omitted entirely from this issue. The volume on the whole is a pleasing one and a number of the articles are illustrated. Inspection reveals few errors, although the transcript of the discussions should be edited to give more meaning at times.

The following addresses and papers read before the Institute are contained in the volume:

"Phenol-Formaldehyde Condensation Products," L. H. Baekeland.

"Protection of Intellectual Property in Relation to Chemical Industry," L. H. Baekeland.

"Notes on a Study of the Temperature Gradients of Setting Portland Cement," Allerton S. Cushman.

"The Production of Available Potash from the Natural Silicates," Allerton S. Cushman and George W. Coggeshall.

"Potash, Silica and Alumina from Feldspar," Edward Hart.

"A Chemical Investigation of Asiatic Rice," Allerton S. Cushman and H. C. Fuller.

"The Beehive Coke Oven Industry of the United States," A. W. Belden.

"Action of Disinfectants on Sugar Solutions," George P. Meade.

"The Decomposition of Linseed Oil during Drying," J. C. Olsen and A. E. Ratner.

"Tests on the Opacity and Hiding Power of Pigments," G. W. Thompson.

"Control of Initial Setting Time of Portland Cement," E. E. Ware.

"The Effect of 'Lime Sulphur' Spray Manufacture on the Eyesight," James R. Withrow.

"Acetylene Solvents," J. H. James.

"The New Chemical Engineering Course and Laboratories at Columbia University," M. C. Whitaker.

"The Need of Standard Specifications in Oils for Paving Block Impregnation," John Haynes Campbell.

"The Presence of Oxygen in Petroleums and Asphalts," Sam. P. Sadtler.

"The Chemical Engineer and Industrial Efficiency," Wm. M. Booth.

"Water for Industrial Purposes," Wm. M. Booth.

"The Availability of Blast Furnace Slag as a Material for Building Brick," Albert E. White.

"Technical Accounting and Chemical Control in Sugar Manufacture," David L. Davoll, Jr.

"The Bituminous Rocks of the United States and their Use for Street Surfaces," S. F. Peckham.

Code of Ethics.

The diversity of interest shown here gives the assurance that the Institute has not become too highly specialized and indicates well the breadth of Industrial Chemistry and Chemical Engineering.

Special attention might well be called to the address by the retiring President of the Institute, Dr. Leo H. Baekeland, on "Protection of Intellectual Property in Relation to Chemical Industry," as the summing up of an important point of view in the matter of patent reform to which the author and the Institute have devoted much time. In the article on "Acetylene Solvents," Dr. J. H. James, probably the foremost investigator and inventor in this field, has broken his silence and given us some of his results and a hint as to the probable future of acetylene storage. The papers by Wm. M. Booth amply demonstrate the contention of this engineer that the *Chemical* Engineer is probably best fitted for all-round efficiency engineering work. Space is not available for noticing many of the prominent articles, but mention should be made of the excellent and well illustrated article on the new Chemical Engineering Laboratories at Columbia University by Professor Whitaker. He has been fortunate and energetic in securing the means to fulfill the dreams some of us have harbored for years in the matter of university industrial laboratory equipment. The average university industrial chemistry laboratory is equipped only with dreams, although it seems that some do not even believe in the dreams.

Grave doubt might be expressed as to the propriety, in view of the objects of the Institute, in admitting to its publication such an article as "A Chemical Investigation of Asiatic Rice." The nvestigation is avowedly for the purpose of contributing to the general knowledge of the chemical *composition* of rice, with an idea of assisting in the problem of "the relation of an exclusive rice diet to the etiology of beri-beri disease." The work is probably a noteworthy one in its field, but if the Institute once lets down the bars so as to admit articles of an analytical nature, or character other than of an industrial manufacturing and engineering one, irrespective of the standing of the authors, its reason for existence is swept away. In discriminating against analytical chemical articles the Institute is in no sense in the position of expressing any idea of degrading analytical chemistry. This branch of chemistry in the eyes of all thinking chemists has always held a position of honor. The present reviewer knows no field of chemistry that calls for more exercise of inventive genius as well as conceded accuracy of thought and manipulation. While Industrial Chemistry and Chemical Engineering are commonly considered the most promising fields for inventive genius, analytical chemistry really offers more frequent opportunity in this direction because of the time element. The confirmation of industrial ideas takes months or years while analytical ones can usually be confirmed or discarded in much more reasonable periods, and the investigator can proceed to other problems. Quite irrespective of all this, analytical chemistry is the faithful handmaid of industrial chemistry and chemical engineering. Many of the most important articles in these fields will contain much analytical data but it will always be secondary, though probably a necessary help, in the solution of the main problem of the paper or investigation. There is ample opportunity for the publication of such articles in other publications, whether they be researches in analytical chemistry or the analytical chemical investigation of an industrial product. The results of such work are often of the greatest interest to industrial chemists and by industrial chemists I mean manufacturing chemists and chemical engineers. The temptation for any of us to do just such work is often strong and even necessary. The work of drawing the line is, therefore, a difficult one for the officers of the Institute. They are to be congratulated in having so seldom become susceptible to criticism in this regard in the five years of the Institute's existence.

James R. Withrow

General Metallurgy. By H. O. Hofman. McGraw-Hill Book Co., Inc. $6.

Prof. Hofman covers more ground in this book than has been attempted recently in any similar work and has done it uncommonly well. It is what its title indicates and what similar works rarely are, a *general* metallurgy, and treates of the subsidiary branches which are usually slighted or ignored entirely.

The first chapter is very short, merely defining the scope of the work. Then follows a short but adequate chapter on the Properties of Metals. The third chapter is on alloys and is an exceedingly good and clear account of the present theories. It is fully illustrated with diagrams of cooling curves, typical micro-photographs and equilibrium diagrams. There is a curious error on page 59, where it states that in making alloys of copper and zinc "they are charged together in order that the readily fusible metal may dissolve the more refractory," whereas the copper is always melted first and the zinc added, and this is stated as the general process in the preceding sentence.

Chapter IV on Metallic Compounds is arranged in a rather novel method as the grouping is by the acid radicals. This has decided advantages for the purpose of this book.

The chapter on fuels is not as satisfactory as most of the others. A rather disproportionate amount of space is taken up in the description of methods and apparatus that are only of historical interest. As usual, we have long tables of the analyses of picked samples of fuel which, unfortunately, are much better than commercial deliveries. It is difficult to understand the reasons for the selection of the gas producers illustrated; some of those shown have not been exactly brilliant successes, and some of the best are not even mentioned. Prof. Hofman mentions that the depth of a fuel bed must be varied to suit the fuel "and is greater the lighter the fuel." He does not, however, mention that the size of the fuel has more influence in determining the proper depth of bed.

The chapter on Refractory Materials is very good, though perhaps an undue weight is given to composition. An ultimate, or even a "rational" analysis is a very poor guide in the selection of a refractory, as it is much easier to get bricks of good chemical than physical characteristics.

The chapter on Pyro-Metallurgical Processes and Apparatus is excellent. It starts with a rational and useful classification of furnaces and follows this with short descriptions of typical specimens of each: first of those heated by fuel, and then of the electrical. The methods of calculating the efficiency are described and examples given. The various classes of operations, roasting, smelting, refining, etc., are then taken up. Next is the best article on slags the reviewer has seen. They are treated from the point of view of their general similarity to alloys, and the result is excellent.

Wet processes and apparatus follow, and this chapter should be learned by heart by the numerous patentees of such processes who have never worked outside of a laboratory. While Dr. Hofman, of course, recognizes the great value of many of the wet processes, he fully appreciates and explains their disadvantages and difficulties.

Electro Processes and Apparatus come next. The general principles are well given but no attempt is made to describe special processes.

The eleventh chapter deals with mechanical operations and takes up more than a third of the book. It gives a condensed but clear description of the apparatus and processes of crushing, concentrating and briquetting ore, the mechanical treatment of alloys, handling of liquids, air supply, heating and drying, and, lastly, the purification of gases.

The concluding chapters are on Metallurgical Products and Economic Considerations. Both are very good and it is only a pity the author did not give more on these very important subjects.

Dr. Hofman's long experience in the field and as a teacher has eminently qualified him for the work, and he has produced a book of which he may well be proud, and one that no metallurgist can afford to be without. The bibliography, if alone, would be of the greatest value, and arranged as it is with the references for each subject on the page with the author's text, its usefulness is greatly enhanced.

Unfortunately the publishers have not treated the work as it deserved. The print and illustrations are fair, but the paper and binding are poor and will not stand the use that a book of this character is bound to receive. The proof-reading has been very careless and there are a number of annoying typographical errors. Most of them are obvious and, therefore, not serious, but there are several which make sense but do not convey the author's meaning and are, therefore, liable to mislead those not thoroughly familiar with the subject.

G. C. STONE

Plantation White Sugar Manufacture. By W. H. TH. HARLOFF, Manager of the Boedoeran Sugar Factory, Java, and H. SCHMIDT, Consulting Sugar Chemist and Engineer, Java. Translated from the second revised Dutch edition, by JAMES P. OGILVIE, F.C.S., Technical Editor of the "International Sugar Journal." Published by Norman Roger, 2, St. Dunstan's Hill. London. Small 8vo. 135 pp., 7s., 6d. net or $2.00 abroad.

The present translation of Harloff and Schmidt's "Handleiding voor Tropische Witsuikerfabrikatie," is exceedingly opportune. Discussions in technical journals regarding the influence of recent tariff legislation upon white sugar manufacture in the tropics and the growing tendency among cane planters themselves to produce sugars of higher purity indicate that this new treatise is one of the most timely sugar books of the year.

As stated by the authors in their introduction the purposes of the book are (1) to give the reader a practical insight into the most generally adopted methods of preparing white sugar and (2) to present the theoretical side of the subject and give "the reasons just why such and such a procedure and no other must be adopted." The authors very correctly observe that this second subject is of greater importance than the first since it forms the basis for independent thought and research without which all instruction remains a dead letter.

In their discussions of the principles of white sugar manufacture the authors omit, as is proper, all technical descriptions of sulfur-ovens, filter-presses, evaporators, and other equipments of the sugar house. A previous knowledge of such appliances is supposed to have been acquired; the treatise is, therefore, primarily a book for the experienced sugar manufacturer or advanced student and not for the beginner.

The first section of the book deals with the chemistry of white sugar manufacture. This phase of the question is presented clearly and concisely in 25 pages, 10 of which are devoted to the important subject of the coloring substances, derived from the cane or produced during manufacture. The second section of the book discusses the underlying principles of white sugar manufacture as practised upon the plantations of Java; the scope of this division is indicated by the six headings: Carbonatation, the Acid Thin-juice Process, Raw-juice Sulfitation, Treatment of Thick-juice, Centrifugal Syrup Treatment, and Curing.

The most casual reader will be impressed by the impartiality with which the claims of different processes are discussed. While the authors, for example, admit their preference, on grounds of safety, for double carbonatation, the disadvantages of this method of clarification are stated so fully and the advantages of single carbonatation set forth so fairly that the most partisan advocate of the latter process can find nothing to criticize.

It is to be regretted, however, that in preparing a book for circulation in English-speaking countries a somewhat fuller mention was not made of processes employed outside of Java. In the section, for example, upon raw juice sulfitation, the discussion is limited to the Java procedure, which consists in liming first and then sulfuring. The value of this part would be considerably increased, if the authors had discussed in this connection the merits and demerits of a method employed in the Western Hemisphere in which the sulfuring of the juice precedes the treatment with lime.

The general tone of the book is conservative and in strict agreement with most generally approved results of sugar house experience. Extreme boldness has been a characteristic of several recent departures in sugar-making and a considerable modification of old established principles has resulted. The Kestner evaporator is a practical refutation, if there ever was one, of the orthodox rule that high temperatures must always be avoided in sugar manufacture. A more recent and startling heresy is the Battelle white sugar process in which the raw cane-juice is treated with quicklime, to from 1 per cent to 5 per cent of its weight, and then boiled until all reducing sugars have been destroyed. This process, which has been favorably received in the Hawaiian Islands, is a most glaring violation of an old principle, summarized as follows by Harloff and Schmidt, on page 6 of their new book:

"By the action of lime on glucose at temperatures below 55° C. (131° F.) the chief product is lactic acid, a very stable acid, not subject to spontaneous decomposition, though at higher temperatures glucinic acid and saccharinic acid, with their colored decomposition products, are formed. Since the calcium (lime) salts of acetic acid (lactic acid?) on the contrary, are colorless, during carbonatation, when much lime is present with the glucose, care must be exercised that the temperature remains below 55° C. (131° F.), so long as the liquid is not neutral."

The conservatism of the book makes it, however, an altogether safe one for any manufacturer to follow. In a period when many sugar manufacturers are tending towards a hazardous radicalism the old admonition "Be not too bold!" may have at times a saving influence.

For the information and wealth of suggestions which it offers the book will repay most careful study; it should be read by everyone who is at all interested in sugar manufacture.

C. A. BROWNE

Metallurgical Analysis. By NATHANIEL WRIGHT LORD, E.M., late Professor of Metallurgy and Mineralogy, Ohio State University, and DANA J. DEMOREST, B.Sc. in Chemical Engineering, Professor of Metallurgy, Ohio State University. Third edition. McGraw-Hill Book Company, New York. Illustrations 24, pp. xiv + 334. Price, $2.50 net.

The first edition of this book was issued in 1893 by Prof. Lord, and consisted of notes, written for the use of students in the Metallurgical Laboratory of the Ohio State University. The object was to give, in a condensed form, the series of selected methods in metallurgical analysis which made up the course of study. The second edition appeared in 1903, and the writer endeavored to extend its scope and make it not only a text-book for students in technical schools, but also a book of reference for young men in metallurgical laboratories. The book was enlarged, due to the treatment of many of the subjects at greater length. The notes were extended and the book was brought up to the state of the science at that time. In this, the third edition, Professor Demorest has rewritten the book, so as to incorporate in the old methods the recent advances in knowledge bearing on them. Many new subjects have been added so as to include practically all the methods of chemical analyses likely to be used by the metallurgical chemist. In so doing, the writer has retained as closely as possible, Professor Lord's method of presentation of the subject. The method of presentation is an admirable one. The chapter usually opens by giving a brief outline of the theories of the method presented, followed by a clear detailed description of the method, giving references where necessary, and closing with a number of very practical notes.

The first chapter of 11 pages is devoted to Preparation of Samples. The second chapter of 9 pages is given to the Analyses of Limestone. Then follow 17 chapters, 160 pages, describing Methods of Analysis for Iron Ores, Iron and Steel, including Methods for Nickel, Vanadium, Tungsten, Chromium, Titanium, Copper, Arsenic, Aluminum, Nitrogen, Oxygen, Hydrogen.

Nine chapters, 52 pages, are devoted to Spelter and Tin Plate Coating, Zinc, Copper, Lead, and Tin in Ores, Analysis of Refined Copper, and Refined Lead, Analyses of Spelter, Brass and Bronze. One chapter, 24 pages, on the Analysis of Coal and Coke. One chapter, 31 pages, on the Analysis of Gases. One chapter, 14 pages, on Clay and other Silicates. One chapter, 5 pages, on Softening of Water for Boiler Use. One chapter, 22 pages, Calculation of Normal Solutions and Tables.

This book is well written. The methods are clear and well defined. It is a pleasure to recommend this book for the purposes as set forth in the caption.

William Brady

Review of the Examination of Water and Water Supplies. By John C. Thresh, D.Sc., M.D., D.P.H. Second edition. P. Blakiston Sons & Company. Philadelphia, Pa. Printed in Great Britain.

This book chiefly aims to be useful in forming an opinion as to the suitability of water supplies for drinking and other domestic purposes. It should not only be helpful to chemists, but to engineers, health officers and others who may be called upon to express an opinion as to the purity of water supplies.

The examination of the waters of rivers, lakes and harbors to determine their capacity for absorbing sewage, the ways in which researches into the purification of water are carried out and field methods of analysis, all questions of considerable importance in America, are scarcely dealt with or are omitted altogether.

Dr. Thresh, who is a practical analyst and medical officer of health of the Essex County Council, England, has written his book from an essentially English standpoint. Where references are made to American and continental practice, they are usually employed by way of illustration and there is little evidence that the procedures employed and recommended have been materially modified by foreign experience. To some analysts in the United States this may prove disappointing, but it is not as a compendium of dry rules of procedure that the book will be most useful.

Dr. Thresh's 600 pages cover a much larger field than do most works on water supplies and to the worker who is conscious of the restrictions which a close observance of American routine imposes, its breadth, liberality of treatment and comprehensiveness should prove inspiring.

The first part of the book describes methods of examining the sources from which water is derived, based on geological and topographical considerations and gives much useful information concerning the environmental study of springs, wells, rivers and watersheds. The second part describes the objects of analytical methods, physical, chemical, microscopical and bacterioscopic and their interpretation. The third part deals with the apparatus and reagents and the details to be followed in determining the ingredients of water which the author considers are of interest in connection with sanitary and industrial problems and describes methods of calculating and expressing the results. Tables of the results of numerous analyses of waters, typical of English supplies, are included in this part. The appendix describes the preparation of reagents and media.

Departures from present American custom appear in various parts of the book. For example, it is not usual in the United States to taste water which is being examined and, if tasted, it would not at all be likely to be described as mawkish. Nor will American analysts readily recognize the term sinter to indicate deposits. In the determination of free and albuminoid ammonia, American custom is not identical with Dr. Thresh's. The only method of determining nitrates is by reduction, the author giving as his reason for not including others that he has little confidence in them. The determination of the weight of suspended matter, regarded in the United States as of considerable importance in connection with many water supply problems, is not included as an important part of a sanitary analysis.

Notwithstanding its obvious defects which, it should be said, are by no means so important in England as in America, the book should prove a valuable contribution to the library of chemists, health officers and engineers. The author's comments on data and their interpretation are generally notable for their sound, common sense and a generous recognition of the limitations and difficulties of the subject. The book is well printed on good paper and contains numerous illustrations, including 36 plates showing the results of the microscopic examination of sediments. There is no other book in the English language dealing so comprehensively with the subject of the examination of drinking water supplies from the English standpoint.

George A. Soper

Chemical Technology and Analysis of Oils, Fats and Waxes. By J. Lewkowitsch. Fifth edition, Vol. I. Price, $6.50. Macmillan & Co., London, and The Macmillan Company, New York, 1913.

In view of the untimely death of Dr. Lewkowitsch at the age of fifty-six while this edition of his monumental work is still in press, a detailed and searching criticism of the present volume would hardly be seemly. Fortunately, there is little to criticize. The volume under review covers the same topics as the corresponding volume of the fourth edition while the size is increased about one-fourth, the present volume comprising 668 pages. This growth is in general the result of a real rewriting of the text as a whole and not merely the introduction of isolated paragraphs of new matter. It is true that in some cases new work is mentioned only very briefly and without substitution of the newer numerical data for the older data which were already tabulated in the earlier editions so that the reader who seeks the actual data of recent work must usually consult the original articles, but this is almost inevitable in so comprehensive a work. It is noticeable that the growth in bulk of the successive editions has not prevented the author from handling his material with that firmness of grasp and logical sequence which has always been a marked feature of this work.

The present volume has a detailed table of contents but no index, an index to the entire work being promised with Volume III. It is greatly to be hoped that, as stated in the technical press, the revision of the entire work will be found to have been completed before the author's death. This fifth edition of "Lewkowitsch" may well stand for many years both as the leading work of reference in its field and as a worthy monument to the professional attainments of its author.

H. C. Sherman

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian The Chemists' Club, New York

Analysis: Detection, Determination and Separation of the Chemical Elements. Vol. II. By A. Ruedisuele. 8vo. Price, $6.25. Berne, 1913.

Analysis, Industrial Organic. By P. S. Arup. 8vo., 318 pp. Price, $2.00. J. & A. Churchill, London.

Analysis, Quantitative. By Edward G. Mahin. 8vo. 511 pp. Price, $3.00. McGraw-Hill Book Co., New York.

Analysis, Quantitative, in Practice. By John Waddell. 8vo. 162 pp. Price, $1.25. J. & A. Churchill, London.

Analysis, Qualitative, from the Standpoint of the Ionic Theory. By Wilhelm Boettger. 3rd Ed. 8vo. 565 pp. Price, $3.00. W. Engelmann, Leipzig. (German.)

Analysis, Text-book of Quantitative Chemical. By A. C. Cummings and S. A. Kay. 8vo. 374 pp. Price, $2.00. Gurney & Jackson, London.

Bloxam's Chemistry, Inorganic and Organic. By A. G. Bloxam and Samuel J. Lewis. 10th Ed. 8vo. 878 pp. Price, $5.50. P. Blakiston's Son & Co., Philadelphia.

Chemistry. By E. von Meyer. 8vo. 663 pp. Price, $4.50. B. Teubner, Leipzig. (German.)

Chemical, Annual, Van Nostrand's, for 1913. By John C. Olsen. 3rd Ed. 8vo. 638 pp. Price, $2.00. D. Van Nostrand Co., New York.

Chemical Constitution and Physical Properties. By S. Smiles. 8vo. 650 pp. Price, $5.00. Th. Steinkopff, Dresden. (Translation in German.)

Chemistry in Our Own Times, The Progress of Scientific. By William A. Tilden. 2nd Ed. 8vo. 366 pp. Price, $2.00. Longmans, Green & Co., New York.

Chemische Apparatur (Chemical Machinery and Apparatus). New Journal. Editor, A. J. Kieser. 4to. Price, $4.00 per year. Otto Spamer, Leipzig.

Coal Tar Distillation. By Arthur R. Warnes. 8vo. 200 pp. Price, $2.00. Gas World, London.

Essential Oils: Scientific and Industrial Bulletin of Roure Bertrand Fils, Ser. 3, No. 8. Sm. 8vo. 158 pp. Roure-Bertrand Fils, Grasse.

Glycerin, Its Production, Use and Determination. By S. W. Koppe. 8vo. 196 pp. Price, $1.25. A. Hartleben, Vienna. (German.)

Graphite Deposits of Pennsylvania. By Benjamin L. Miller. 8vo. 147 pp. Topographic and Geologic Survey of Pennsylvania, Report No. 6.

Loeb, Morris, Scientific Work of. Edited by Theodore W. Richards. 8vo. 349 pp. Harvard University Press, Cambridge. Privately printed.

Metallography. Part II. By W. Guertler. 8vo. 650 pp. Price, $8.00. Gebrueder Borntraeger, Berlin. (German.)

Metals, The Microscopic Analyses of. By Floris Osmond. 3 vols. 2nd Ed. 8vo. 313 pp. Price, $2.25. Chas. Griffin & Co., London.

Molybdenum, Vanadium and Tungsten, The Quantitative Methods of Examination of. By H. Mennicke. L. 8vo. 231 pp. Price, $2.25. M. Krayn, Berlin. (German.)

Oils and Fats, Examination of Hydrocarbon. By D. Holde. 8vo. 596 pp. Price, $6.25. Julius Springer, Berlin. (German.)

Organic Chemistry. Vol. II. By Julius B. Cohen. 8vo. 427 pp. Price, $4.00. Edward Arnold, London.

Quantitative Analysis. By Frank Clowes and J. Bernard Coleman. 10th Ed. 8vo. 565 pp. Price, $3.50. P. Blakiston's Son & Co., Philadelphia.

Rubber and Rubber Planting. By R. H. Lock. 8vo. Price, $1.25. Cambridge University Press, London.

Sugar Analysis. By Ferdinand G. Wiechmann. 3rd Ed. 8vo. 303 pp. Price, $3.00. John Wiley & Sons, New York.

Sugar Manufacture. By Siegmund Teitler. 8vo. Price, $1.00. Alfred Hoelder, Vienna. (German.)

Tanning Materials, The. By J. Dekker. 8vo. 610 pp. Price, $5.25. Gebrueder Borntraeger, Berlin. (German.)

Textiles: Organic and Inorganic Chemistry with Special Consideration of Bleaching, Dyeing and Finishing Processes. By M. Reimann. 4th Ed. 8vo. 374 pp. M. Koch, Leipzig. (German.)

Water, Clean, and How to Get it. By Allen Hazen. Sm. 8vo. 210 pp. Price, $1.50. John Wiley & Sons, New York.

Zinc and Cadmium. By R. G. M. Liebig. 8vo. 598 pp. Price, $8.00. Otto Spamer, Leipzig. (German.)

RECENT JOURNAL ARTICLES.

Alloys and Minerals, The Fractionation of, in the Electric Microfurnace. By Arnold L. Fletcher. *Journal of the Chemical Society, Transactions,* Vol. 103, 1913, No. 614, pp. 2097–2108.

Arsenic in Sulfuric and Hydrochloric Acids, Rapid Method for the Determination of. By H. Koelsch. *Chemiker Zeitung,* Vol. 38, 1914, No. 1, pp. 5–6.

Asphalts, Examination of the. By Heinrich Loebell. *Chemiker Zeitung,* Vol. 38, 1914, No. 2, pp. 18–20.

Bleaching Methods, Modern Silk. By Herbert A. Carter. *Silk,* Vol. 6, 1913, No. 12, pp. 25–30.

Catalysis and its Industrial Applications. By E. Jobling. *Chemical World,* Vol. 3, 1914, No. 1, pp. 17–19.

Coal-tar, Naphthalene-free Carbon and the Fractionating Constants of. By E. C. Pailler. *Chemical Engineer,* Vol. 18, 1913, No. 6, pp. 221–222.

Copper Ores, Leaching Shannon. By Francis S. Schimerka. *Engineering and Mining Journal,* Vol. 96, 1913, No. 24, pp. 1107–1110.

Essential Oils, Natural and Synthetic (Perfumery). By John C. Umney. *Journal of the Royal Society of Arts,* Vol. 62, 1913, No. 3185, pp. 47–62.

Ferric Oxid, Some of the Physical Characteristics of. By W. H. Fulweiler and A. F. Kunberger. *American Gas Light Journal,* Vol. 99, 1913, No. 24, pp. 369–373.

Fertilizers, The Artificial, and their Significance in Economics. By Konrad Kubierschky. *Zeitschrift fuer angewandte Chemie, Aufsatzteil,* Vol. 26, 1913, No. 97, pp. 721–731.

Flue Dust, Utilization of Blast Furnace. By Eugene B. Clark. *Industrial World,* Vol. 47, 1913, No. 51, pp. 1522–1526.

Furnace, for High Temperatures, An Electric Vacuum. By Johannes Wolf and Erich Mueller. *Zeitschrift fuer Elektrochemie,* Vol. 20, 1914, No. 1, pp. 1–4.

Gas: Progress in Carbonization Methods. By J. H. Taussig, *et al. American Gas Light Journal,* Vol. 100, 1914, No. 1, pp. 2–7 and 10–13.

Gas: Report Presented by the Committee on Naphthalene Problem of To-day, American Gas Institute. By H. L. Underhill, *et al. American Gas Light Journal,* Vol. 100, 1914, No. 2, pp. 17–23.

Iron Blast Furnace, Handling the Raw Materials at the. By J. E. Johnson, Jr. *Metallurgical and Chemical Engineering,* Vol. 12, 1914, No. 1, pp. 44–53.

Metallurgical Practice, Use of Organic Compounds in. By Geo. Patchin. *Chemical World,* Vol. 3, 1914, No. 1, pp. 9–12.

Methylation Process, A New. By A. Koetz and E. Schaeffer. *Journal fuer praktische Chemie,* Vol. 88, 1913, No. 25, pp. 604–640.

Ore, Concentration of Complex Sulfid, from the Mary Murphy Mine. By H. C. Parmelee. *Metallurgical and Chemical Engineering,* Vol. 12, 1914, No. 1, pp. 21–26.

Ozonator Designs, Notes on Open Up. By A. Vosmaer. *Metallurgical and Chemical Engineering,* Vol. 12, 1914, No. 1, pp. 36–41.

Petroleum: Oxidizability of Mineral Oils. By H. Kantorowicz. *Chemiker Zeitung,* Vol. 37, 1913, No. 154/5, pp. 1594–1595.

Physical Chemistry, Report on the Progress of, in 1913. By W. Herz. *Chemiker Zeitung,* Vol. 38, 1914, No. 3, pp. 25–28.

Prussic Acid Production by the Dessau Process. The Decomposition of Betain by Caustic Soda. By Fr. Albus. *Chemiker Zeitung,* Vol. 37, 1913, No. 149, pp. 1533–1534.

Rare Earths and their Radioactive By-products; Incandescent Gas Light. By E. Stern. *Zeitschrift fuer angewandte Chemie, Aufsatzteil,* Vol. 26, 1913, No. 102/3, pp. 806–815.

Sodium Amalgam and Water, The Interaction of. By H. B. Baker and L. H. Parker. *Journal of the Chemical Society, Transactions,* Vol. 103, 1913, No. 614, pp. 2060–2073.

Tannins, Vegetable, Further Contributions to the Qualitative Differentiation of. By E. Stiasny. *Journal of the American Leather Chemists' Association,* Vol. 9, 1914, No. 1, pp. 19–25.

Textiles: The Decortication of Fibrous Plants. By H. R. Carter. *Journal of the Textile Institute,* Vol. 4, 1913, No. 2, pp. 231–265.

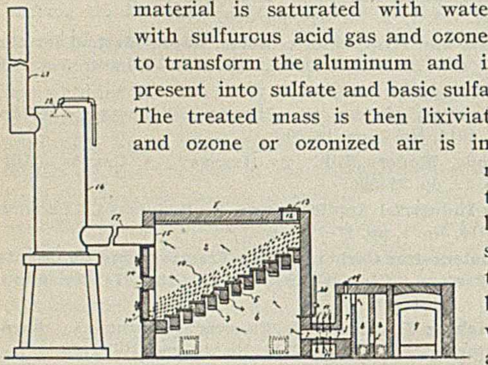
Wood, The Action of Chlorin on Pine. By Emil Heuser and Rudolf Sieber. *Zeitschrift fuer angewandte Chemie, Aufsatzteil,* Vol. 26, 1913, No. 102/3, pp. 801–806.

Wood Oil, Chinese, The Testing of. By E. W. Boughton. *Drugs, Oils and Paints,* Vol. 29, 1913, No. 7, pp. 252–256.

RECENT INVENTIONS

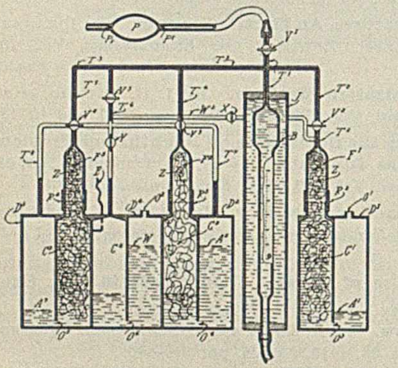
By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Preparing Aluminum Sulfate. H. F. D. Schwahn, Nov. 4, 1913. U. S. Pat. 1,077,309. Clay, shale or other aluminous material is saturated with water and treated with sulfurous acid gas and ozone or ozonized air to transform the aluminum and iron compounds present into sulfate and basic sulfate, respectively. The treated mass is then lixiviated with water, and ozone or ozonized air is injected into the resulting solution until the last trace of iron sulfate therein is transformed into basic ferric salt, which separates as a yellow mud. The iron-free solution of aluminum sulfate is then drawn off and evaporated.



Gas-Analyzing Apparatus. J. W. Hayes, Nov. 4, 1913. U. S. Pat. 1,077,342. This apparatus is designed for the rapid determination of the constituents of furnace gases, illuminating gas, producer gas and the like.

In the use of the apparatus the gas to be analyzed is forced by bulb *P* into measuring burette *B*, displacing liquid with which it has been previously filled by the use of leveling bottle *L* connected to the burette by tube *R'*. The bottle *L* is then raised until liquid therein reaches the zero mark in burette *B*, whereupon valve *V'* is closed. The gas will then have been measured at atmospheric pressure and at the temperature of the water which surrounds burette *B*. By the operation of the valves in the tubes connected with the neck of the burette the gas may then be forced upon raising the leveling bottle *L*, into the various absorption chambers which may be provided with suitable reagents for the absorption of carbon dioxid, oxygen, carbon monoxid, etc. Each absorption tube is connected at its bottom with a displacement vessel and its top with the neck of the burette.



Metallizing Ceramic and other Surfaces. Q. Marino, Nov. 4, 1913. U. S. Pat. 1,077,357. A solution of iron fluoride is applied to the surface to be covered and the iron reduced to a metallic state by applying a finely divided metal capable of reducing the iron.

Hydrogenizing Organic Compounds. H. Thorn, Nov. 4, 1913. U. S. Pat. 1,077,442. The substance to be hydrogenized is treated with formic acid and a colloidal solution of a metal of the platinum group.

Treatment of the Surface of Aluminum Articles. A. Lang, Nov. 4, 1913. U. S. Pat. 1,077,480. The aluminum surface is coated with a metal chloride and subjected to the action of the heat.

Boron Nitrid. R. Heyder, Nov. 4, 1913. U. S. Pat. 1,077,712. A mixture of boric anhydrid, magnesium and ammonium chlorid is heated to the reaction temperature and after the completion of the reaction, the resulting mixture is washed with a solvent of the by-products of the reaction and the boron nitrid is dried *in vacuo* at a temperature of about 60–70° C.

Devulcanizing Rubber. D. A. Cutler, Nov. 11, 1913. U. S. Pat. 1,078,086. The vulcanized rubber is subjected to the action of a bath containing zinc chlorid and oil of pine.

Hydrogenating Oil Mixtures, Etc. C. Ellis, Nov. 11, 1913. U. S. Pat. 1,078,136. An acid oil is diluted with a substantially neutral oil and the mixture hydrogenated.

Extracting Manganese from its Ores. F. Heusler, Nov. 11, 1913. U. S. Pat. 1,078,199. The manganese ore is first heated to a red heat to calcine a portion thereof. A quantity of the calcined ore is then mixed with a quantity of the crude, uncalcined ore and subjected to a reducing process in the presence of a flux and carbonaceous matter.

Aluminum Nitrid. O. Serpek, Nov. 11, 1913. U. S. Pat. 1,078,313. A mixture of carbon and aluminous material is heated to above 1300° C. in a current of nitrogen and hydrogen.

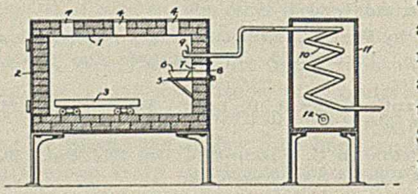
Recovering Alkalis from Silicate Rocks. S. Gelléri, Nov. 11, 1913. U. S. Pat. 1,078,495. The silicate rock, mixed with limestone and a sulfate, is heated and the heated mass subjected to the action of ammonium carbonate vapors under high pressure.

Double Superphosphate. Wilson and Haff, Nov. 18, 1913. U. S. Pat. 1,078,887. Pyrophosphoric acid is added to natural phosphate rock.

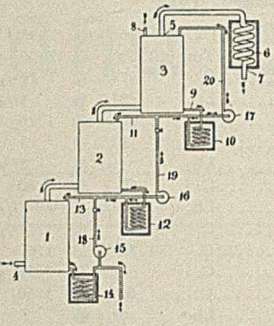
Metallic Magnesium. Wallace and Wassmer, Nov. 18, 1913. U. S. Pat. 1,079,079. Magnesium sulfid is gradually added to fused magnesium chlorid and the mixture subjected to electrolysis.

Sulfur from Hydrogen Sulfid and Sulfur Dioxid. W. Feld, Nov. 18. 1913. U. S. Pat. 1,079,291. Gases containing sulfuretted hydrogen and sulfurous acid are subjected to the action of a solution of thiosulfate of a metal the sulfid of which is soluble in water.

Treatment of Iron and Steel for a Permanent Black Finish. W. R. Swan, Nov. 25, 1913. U. S. Pat. 1,079,453. Articles of iron and steel are placed in the furnace 1 together with a quantity of copper sulfate, salammoniac or aluminum chlorid, tannin and glucose and heated to about 1050° F. Superheated steam is then injected for about thirty minutes. The iron, after being allowed to cool, is submerged in paraffin oil heated to about 150° F. The treatment gives the treated article a dead black rust-resisting coating.



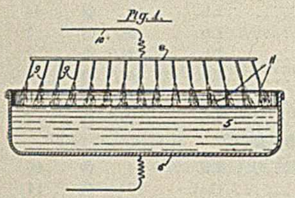
White Lead. E. Euston, Nov. 25, 1913. U. S. Pat. 1,079,481. A substantially neutral lead acetate solution in a tower is sprayed through a constantly renewed atmosphere of carbon dioxid and basic lead acetate solution is introduced at a rate proportional to the precipitation of white lead so as to maintain the lead acetate solution in a substantially neutral condition.

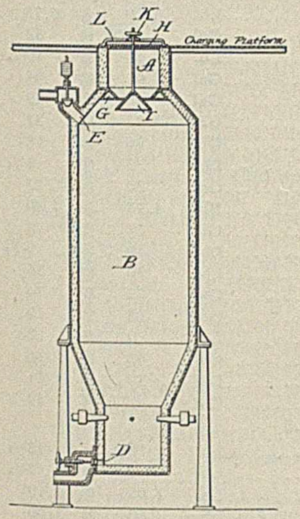


Concentrating Acid, by means of a Drying Agent. E. Collett, Nov. 25, 1913. U. S. Pat. 1,079,541. The acid vapors, such as nitric acid vapors, are introduced through inlet 4 and passed against a counter-current of sulfuric acid, successively through drying columns 1, 2 and 3, escaping into a condenser, 6, from which the concentrated acid is drawn off through pipe 7.

The sulfuric acid is withdrawn from each of the drying columns 1, 2 and 3 and cooled before being introduced into another drying column.

Bleaching and Thickening Oils and Fats. O. Scherieble, Nov. 25, 1913. U. S. Pat. 1,079,727. The material to be bleached and thickened is placed in the pan 6, the bottom of which forms one electrode of a high potential current. The other electrode 8, in the form of a lattice with downwardly extending points 9, is arranged above the material which is thus subjected to the action of a silent or brush discharge. The use of a current from 50,000 to 100,000 volts is recommended.





Zinc Compounds. E. B. Cutten, Dec. 2, 1913. U. S. Pat. 1,080,102. Zinc oxid free from slag-forming materials is mixed with coal or coke and heated in a cupola or low blast furnace under a pressure of from 20 to 60 pounds per sq. in. or higher. The heating is effected by means of liquid or gaseous fuel admitted under high pressure to the bottom of the charge. The resulting temperature is sufficient to vaporize the zinc at atmospheric pressure but the pressure maintained in the reducing chamber is sufficient to prevent such vaporization, the zinc being collected as molten metallic zinc.

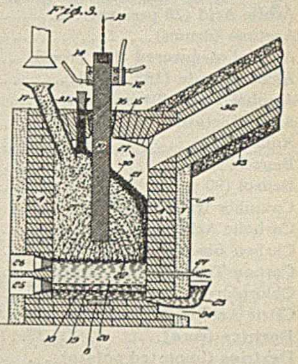
Hydrogenation of Organic Compounds, Especially the Fatty Acids, Etc. K. H. Wimmer, Dec. 9, 1913. U. S. Pat. 1,081,182. Fatty acids and their glycerids are hydrogenated by subjecting them to the action of an organic metal salt and hydrogen.

Electrolytic Manufacture of Perborates. K. Arndt, Dec. 9, 1913. U. S. Pat. 1,081,191. The perborates are produced by electrolyzing an aqueous solution of borax and sodium carbonate.

Tungsten and its Alloys. F. M. Becket, Dec. 16, 1913. U. S. Pat. 1,081,568. Crude ferrotungsten is subjected to an oxidizing roast and the resulting oxids are reduced without substantial fusion of the reduced products. The iron and phosphorus in the reduced product are then removed by an acid treatment.

Clarifying Wines. A. Ornstein, Dec. 16, 1913. U. S. Pat. 1,081,623. The flour of ground soya beans (*Soga hispida*), from which the fatty matter has been extracted, is added to the wine to be clarified.

Electrically Smelting Volatile Metals. W. M. Johnson, Dec. 9, 1913. U. S. Pat. 1,080,912. This process is primarily intended for reducing and separating zinc from its ores and compounds by a volatilizing process in an electric furnace.



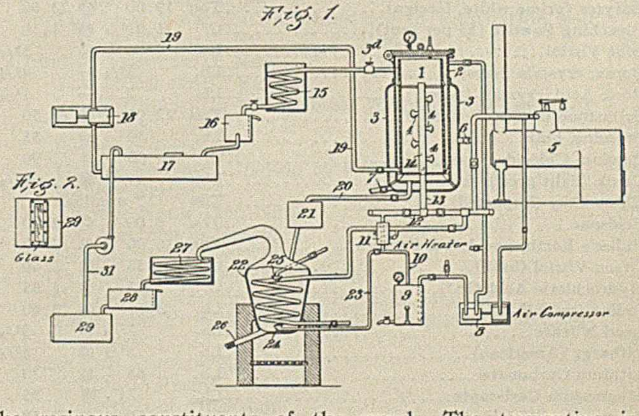
In smelting zinc ores a charge proportioned to yield a fusible slag is superposed upon a molten electrode which may be molten lead, and an electric current passed through the molten electrode, the charge and the evolved zinc vapors. The reduction is carried out in the absence of extraneous air and the volatile reaction products are conducted through the charge and into contact with a portion of such charge heated to the temperature of the maximum reductivity of carbon. The zinc vapors are finally condensed apart from the charge.

Acetic Acid. N. Grünstein, Dec. 23, 1913. U. S. Pat. 1,081,959. Acetic acid is produced from acetaldehyde by the action of oxygen in the presence of acetic acid.

Waterproof Mortar. A. Markus, Dec. 23, 1913. U. S. Pat. 1,082,035. A mixture of pulverized soluble soap, pulverized soluble aluminate, lime hydrate and clay is added to the mortar to be waterproofed.

Vulcanized Glycerol Resin. W. C. Arsem, Dec. 23, 1913. U. S. Pat. 1,082,106. This is a rubber-like infusible composition comprising a compound of sulfur and the glycerol ester of phthalic and oleic acids.

Rosin and Turpentine from Wood. C. Howard, Dec. 30, 1913. U. S. Pat. 1,082,526. Chips of coniferous wood are treated with turpentine under pressure to obtain a solution of the resinous constituents of the wood. The turpentine is agitated during this treatment and the pressure within the treating chamber is caused to alternately rise and fall.



Fertilizer. W. E. Carson, Dec. 23, 1913. U. S. Pat, 1,082,108. This is a mixture of pulverized natural limestone and pulverized hydrated caustic magnesium lime.

Protecting Iron from Rust. A. Lang, Dec. 23, 1913. U. S. Pat. 1,082,161. A layer of iron oxid is first artificially produced on the surface to be treated and this layer is then chemically combined with an anilin dyeing agent.

Bituminous Putty. W. A. Levering, Dec. 30, 1913. U. S. Pat. 1,082,640. The material consists of a major portion of lime dust and a minor portion of air-blown petroleum residuum.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JANUARY, 1914

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	1.62½	@	1.77½
Acetone (drums)	Lb.	13	@	14
Alcohol, denatured (180 proof)	Gal.	33	@	36
Alcohol, grain (188 proof)	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent)	Gal.	46	@	48
Amyl Acetate	Gal.	1.75	to	1.80
Aniline Oil	Lb.	10	@	10⅛
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	23	to	25
Camphor (refined in bulk)	Lb.	40	@	42½
Carbolic Acid (drums)	Lb.	8	@	10
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7⅜	@	7⅞
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	51	@	52
Dextrine (corn)	C.	2.92	@	3.13
Dextrine (imported potato)	Lb.	5	to	6
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19	@	19½
Oxalic Acid	Lb.	7¼	@	7½
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	25	@	30
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	2.24	@	2.90
Starch (potato)	Lb.	4⅛	—	4¾
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	34	—	35
Tartaric Acid, crystals	Lb.	31½	@	31¾

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¼	—	7¾
Acetate of Lime (gray)	C.	2.00	@	2.05
Alum (lump)	C.	1.75	@	2.00
Aluminum Sulfate (high-grade)	C.	1.25	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8½
Ammonium Chloride, gray	Lb.	5⅞	@	6⅛
Aqua Ammonia (drums) 16°	Lb.	2¼	@	2½
Arsenic, white	Lb.	3	@	4
Barium Chloride	C.	1.60	@	1.75
Barium Nitrate	Lb.	5	to	5¼
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.22½	@	1.30
Blue Vitriol	Lb.	5	@	5¼
Borax, crystals (bags)	Lb.	3¾	—	4½
Boric Acid, crystals (powd.)	Lb.	7	—	7¾
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	60	@	90
Chalk (light precipitated)	Lb.	4	@	4½
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16.00	@	17.00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1.15	@	1.55
Iodine (resublimed)	Lb.	3.55	@	3.60
Lead Nitrate	Lb.	7⅞	@	8⅛
Litharge (American)	Lb.	5½	@	5¾
Lithium Carbonate	Lb.	65	@	70
Magnesium Carbonate	Lb.	21	@	35
Magnesite "Calcined"	Ton	28.50	@	29.50
Nitric Acid, 36°	Lb.	3⅞	@	4¼
Phosphoric Acid (sp. gr. 1.75)	Lb.	21½	@	25½
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°	Lb.	6¾	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3.25	@	3.30
Potassium Chlorate, crystals	Lb.	7¼	@	7½
Potassium Cyanide (bulk), 98–99%	Lb.	16	@	18
Potassium Hydroxide	C.	4.00	@	4.25
Potassium Iodide (bulk)	Lb.	2.95	@	3.00
Potassium Nitrate (crude)	Lb.	4½	@	5
Potassium Permanganate (bulk)	Lb.	8¾	@	10
Quicksilver, Flask (75 lbs.)		38.00	@	——
Red Lead (American)	Lb.	6	@	6¼
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	36½	@	38^1/
Soapstone in bags	Ton	10.00	@	12.00
Soda Ash (48 per cent)	C.	67½	@	72½
Sodium Acetate	Lb.	3¾	@	4⅛
Sodium Bicarbonate (domestic)	C.	1.00	@	1.10
Sodium Bicarbonate (English)	Lb.	2¾	@	3
Sodium Bichromate	Lb.	4⅝	@	5⅛
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	7¼	@	7½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	—	@	2.22½
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6¾	@	7
Sulfur, Flowers (sublimed)	C.	2.20	@	2.60
Sulfur, Roll	C.	1.85	@	2.15
Sulfuric Acid, 60° B	C.	85	@	1.00
Talc (American)	Ton	15.00	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	12½	@	13½
Tin Oxide	Lb.	42	@	44
White Lead (American, dry)	Lb.	5¼	@	5^1/
Zinc Carbonate	Lb.	8½	@	9
Zinc Chloride (granulated)	Lb.	4½	@	5
Zinc Oxide (American process)	Lb.	5⅜	@	6⅜
Zinc Sulfate	Lb.	2½	@	3

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	44	@	46
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8¼	@	8½
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.80	@	6.85
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	45
Cottonseed Oil (p. s. y.)	Lb.	6.70	@	6.75
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	10¼	@	10¾
Lard Oil (prime winter)	Gal.	92	@	94
Linseed Oil (raw)	Gal.	48	@	49
Menhaden Oil (crude)	Gal.	33	@	37
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3½	@	3¾
Paraffine Oil (high viscosity)	Gal.	26	@	27
Rosin ("F" grade) (280 lbs.)	Bbl.	4.25	@	4.40
Rosin Oil (first run)	Gal.	27	@	28
Shellac, T. N.	Lb.	19	@	19½
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	9	@	12
Tallow (acidless)	Gal.	65	@	66
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	47½	@	49

METALS

Aluminum (No. 1 ingots)	Lb.	18¼	@	18¾
Antimony (Hallet's)	Lb.	7	@	7⅜
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	14¼	@	14½
Copper (lake)	Lb.	14⅝	@	14¾
Lead, N. Y.	Lb.	3.95	@	4.07½
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	57	@	——
Tin	C.	37.00	@	——
Zinc	C.	5.15	@	5.20

FERTILIZER MATERIALS

Ammonium Sulfate	C.	2.85	@	2.97^1/
Blood, dried	Unit	3.20	@	—
Bone, 4½ and 50, ground, raw	Ton	27.25	@	28.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.10
Castor meal	Unit	nominal		
Fish Scrap, domestic, dried	Unit	nominal		
Mowrah meal	Ton	nominal		
Phosphate, acid, 16 per cent bulk	Ton	—	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 70–80 per cent	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	39.07	@	—
Pyrites, furnace size, imported	Unit	0.13¼		
Tankage, high-grade	Unit	3.25 & 10		