The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V NOVEMBER, 1913 No. 11

Published monthly. Subscription price to non-members of the American Chemical Society, $6.00 yearly.
Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City
Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

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EDITORIALS

THE MINING CONGRESS

Two notable addresses presented at the recent meeting of the American Mining Congress at Philadelphia are published in this issue of THIS JOURNAL.

An address on "Our Radium Resources," by Charles L. Parsons, of the Bureau of Mines, brings out many valuable facts in connection with this most interesting development. He again calls attention to the American carnotite deposits as a new source of radium and the possibility of the production of this material in America. His address includes a discussion of the methods for the extraction of radium, its present market value, and a warning to the medical profession and the public against the activity of impostors. He calls attention to the fact that the United States Bureau of Standards is preparing radium standards by means of which it will be possible for physicians to protect themselves against frauds.

Dr. Parsons announces a new policy in the administration of the Bureau of Mines which is of far-reaching importance in industrial developments of great public interest in the following statement: "I am authorized by the Director of the Bureau of Mines to announce that a coöperative agreement has been entered into with the newly organized National Radium Institute whereby the Bureau obtains the opportunity of scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, uranium and vanadium therefrom with a view to increased efficiency of production and the prevention of waste." The coöperation of the government in the solution of the radium problem will meet the hearty approval of the medical profession and the general public who are so intimately concerned in the eradication of cancer.

It is also proposed to carry on investigations regarding the physical characteristics of the radium rays in the hope that some or all of the results may be duplicated by physical means.

Reference is made to the forthcoming announcement of remarkable cures effected by the use of radium and meso-thorium, and in view of the sensational announcements in the public press, authoritative statements in this field will be awaited with breathless interest.

The address by President Van Hise, a full abstract of which is published in this issue, will be read with keen interest by those concerned in the problem of scientific conservation. A careful analysis of these problems has led President Van Hise to point out in the most forcible language the obligations of the government and the public in furthering the interests of legitimate conservation, and the address will be exceedingly suggestive reading not only to the people immediately connected with industrial development, but also to those responsible for our legislative and administrative policies.

It is our belief that this address will serve to emphasize the need of a coöperative policy and legislation calculated to develop conservation instead of the obstructive policy now in general favor.

OZONE

A striking example of the danger of commercializing a popular notion without first subjecting it to proper tests is brought out in two articles in the *Journal of the American Medical Association* for Sept. 27, on the Purification of Air with Ozone. We were taught in our "Prep" school chemistry that it was the "ozone of the country air" which was responsible for the health and longevity of the rural population; and of course the healthful effect of ozone we inferred was due to its value as a disinfectant. Furthermore, ozone is an energetic oxidizing agent; so is hydrogen peroxide; hydrogen peroxide is a valuable germicide; so, we thought, was ozone.

Ohlmüller's experiments, twenty years ago, together with those of several investigators since, discrediting its germicidal action, did not shake the popular faith in ozone. Public officials have readily accepted claims such as the following: (1) Ozone is a necessity for the destruction of infectious germs, for the sterilization of air in operating rooms, for the purification of air in homes of persons suffering from contagious diseases, and for giving to offices and homes the invigorating air of country, seashore and mountain. (2) Ozone cannot exist except momentarily in air containing organic matter, and therefore the presence of ozone is an indication that the air is sterile and devoid of organic matter. (3) Ozone is unique as a germicide by reason of the fact that it has no deleterious effect on the higher forms of animal life, owing to the low percentage of carbon in their structure.

In the first of the two articles mentioned, "Ozone: Its Bactericidal, Physiologic and Deodorizing Action," by E. O. Jordan, M.D., and A. J. Carlson, M.D., of Chicago, the authors describe an extensive series of experiments undertaken by them at the suggestion of, and under a grant from *The Journal of the American Medical Association.* Their investigation was complete and exhaustive and their data fully justify their conclusions and summary which we quote:

> "So far as the destruction of bacteria is concerned, ozone has little or no value. Some bacteria are undoubtedly killed by ozone, especially if they are in a moist condition and are in contact for several hours with a current of ozone coming direct from the generator. In practice, however, the fact is of slight importance. Human beings are injuriously affected by amounts of ozone far less than are necessary to produce even this slight bactericidal effect, and there is no evidence for supposing that a quantity of ozone that can be tolerated by man has the least germicidal action. If disinfection of a closed room without inmates is desired, this can be much more effectively carried out by the use of formaldehyde or some other familiar gaseous disinfectant than by ozone. Ozone has no place in practical room disinfection.
>
> "Ozone is not an actual 'deodorizer' in concentrations that can obtain in practical ventilation. In very great concentra-

tions ozone seems capable of oxidizing some odorous substances so that the odors are diminished or changed, but the change may be in the direction of increasing the disagreeableness of the odor. In very great concentrations ozone 'masks' most odors by its own intensive odor, and possibly by fatigue or anaesthesia of the olfactory epithelium. Certain odors are masked by ozone even in weak concentrations. Is such masking of odors desirable and generally advantageous? We think not. It is probable that the injury to the respiratory tract by ozone in sufficient concentration to act as an effective mask is of greater moment than the deleterious action of most odors. Except in special industrial processes, the unpleasant odor of the inspired air in shops, offices or living rooms is usually a sign that the air needs to be renewed or changed. Why should we put out of commission the sense organ which aids us in determining whether or not the air is fit to breathe? It seems to us that this is wrong in principle, and that ozone is being used and will be used as a crutch to bolster up poor ventilating systems. Ozone does not make 'pure air' any more than strong spices make pure food.

"In concentrations that appreciably affect man and animals, ozone appears to have uniformly an injurious action. This injurious action is primarily on the respiratory passages—irritation of the sensory nerve endings, and irritation, corrosion and depression of the epithelial cells. The depression of the alveolar epithelium leads to changes in the gaseous exchange in the lungs, and secondarily to changes in the blood, and ozone headache, depression and drowsiness are produced.

"Hill and Flack [*Proc. Roy. Soc.*, **82**, 404 (1911); *Jour. Roy. Soc. Arts.*, **60**, 344 (1912)] point out that ozone gives a certain 'tang' to the air, and thus relieves the impurity (temperature and moisture) which is apt to obtain in offices and assembly rooms. This tang is a combined effect of ozone odor and the ozone irritation of the sensory nerves in the respiratory tract. We have seen that this acts (reflexly) on the vascular mechanism and it may temporarily 'whip up' a fagged brain. But is this ozone tang any more beneficial or any more physiologic than a whiff of smelling-salts or a puff of the cigarette? We recognize that a certain amount of variation in the rate of movement and in the temperature of the air about us aids in maintaining the tonus of the brain, but our ventilation engineers must reproduce the variability of outdoors by actual variations in the air and in the rate of movement of the air in the ventilating systems, and not by adding a poisonous gas to the air. Nor can we accept the suggestion of Hill and Flack that small amounts of ozone may be of therapeutic value in certain diseases of the respiratory tract by reason of the hyperemia following the ozone irritation. The cells injured by ozone are probably more readily invaded by bacteria, and have less than normal power of growth and healing despite the hyperemia. And all bacteria so far studied are much more resistant to ozone than are the cells of the respiratory tract of man and experimental animals. The physiology of ozone points to the conclusion that the use of this poisonous gas as a therapeutic agent is either valueless or injurious."

The second article, "The Alleged Purification of Air by the Ozone Machine," by W. A. Sawyer, M.D., Director of the Hygienic Laboratory of the California State Board of Health, and his co-workers, Beckwith and Skolfield, though not as extensive, is no less convincing than the first. The conclusions of these authors are quoted also:

"The gaseous products of the two well-known ozone machines examined are irritating to the respiratory tract and, in considerable concentration, they will produce edema of the lungs and death in guinea pigs.

"A concentration of the gaseous products sufficiently high to kill typhoid bacilli, staphylococci and streptococci, dried on glass rods, in the course of several hours, will kill guinea pigs in a shorter time. Therefore these products have no value as bactericides in breathable air.

"Because the products of the ozone machines are irritating to the mucous membranes and are probably injurious in other ways, the machines should not be allowed in schools, offices or other places in which people remain for considerable periods of time.

"The ozone machines produce gases which mask disagreeable odors of moderate strength. In this way the machines can conceal faults in ventilation while not correcting them. Because the ozone machine covers unhygienic conditions in the air and at the same time produces new injurious substances, it cannot properly be classed as a hygienic device."

It is to be hoped that the results of these investigators will receive sufficient publicity to correct popular ideas on the germicidal action of ozone and that the work will not have to be repeated as it has been so many times within the last twenty years.

A. M. BUSWELL

BUREAU OF MINES COAL ANALYSES

Government purchasing agents, designing and operating engineers, and the fuel departments of industrial concerns, dealers in large quantities of coal, and persons interested in the distribution and character of the different coals in the United States will find valuable information in a report just issued by the United States Bureau of Mines as *Bulletin* **22**, entitled "Analyses of Coals in the United States, with Descriptions of Mine and Field Samples Collected between July 1, 1904, and June 30, 1910." This report contains the analyses of 5,000 samples of coal taken from 1,500 coal mines and prospects situated in the various coal fields of the United States. Not only all of the important fields are represented, but practically all of the more important mining districts.

The purpose of the Bureau in compiling and publishing this information is to present reliable information regarding the chemical composition and heating value of the coals. The samples of coals were collected by experienced men according to a definite and uniform system, and were analyzed under carefully controlled conditions, so that there might be no question as to the relative merits of the different coals so far as this can be determined by chemical analyses and determinations of heating values.

An increasing proportion of the coal consumed in the power stations and the larger manufacturing plants of the country is now being purchased under specifications based on chemical analyses and calorimetric determinations of heat units. In the purchase of fuels many matters formerly left to chance are now carefully investigated. It is the aim of mechanical engineers to construct furnaces and to arrange the heat-absorbing surface in a furnace with reference to the peculiar character of the fuel which is to be burned. Noting the composition of the fuel and constructing the furnace with reference to it, he can assure efficient and smokeless combustion. Moreover, in any particular market, the choice of coal is limited generally by its quality and by freight rates to one or two fields in which the character of the coal beds is comparatively uniform. Having on hand a representative analysis of the coal from a given bed in any particular district, the engineer can determine whether the coal he receives comes from the bed and the district stated, and whether it is being prepared for market as carefully as it should be. Wide variations in the compositions and heating values of the coals from different districts and from different beds make comparable analyses almost indispensable to engineers having to install boiler or gas-producer plants in different cities, as well as to railroads and steamboat companies, and to the engineers and purchasing agents of the various departments of the United States Government.

The Bureau of Mines report is in two parts: one gives the methods used in collecting and analyzing the samples and the results of the analyses; the other gives the exact location from which each sample of coal was taken, together with a description of the characteristic features of the coal bed at the point of sampling, the nominal capacity of the mine and such notes on the preparation of the coal as might be useful to consumers. The data contained in these two volumes are not equalled in scope and detail and in value for comparative purposes by the figures that have been published by any other coal-producing country in the world. The Governments of some of these countries have published analyses of coals from different mines and from different districts but, with few exceptions, the samples of coal were not collected and analyzed under a uniform system that would make the results comparable in all respects.

ORIGINAL PAPERS

COPPER COVERED OR COPPER CLAD STEEL[1]

THE MANUFACTURE, PROPERTIES AND USES OF COMPOSITE METAL MADE BY ALLOYING OR WELDING COPPER AND STEEL

By James Otis Handy

Of the metals in common use, copper is the only one which occurs naturally in large quantities in the metallic state. The great native copper deposits of Michigan are the best illustration which could be found of the extraordinary resistance of copper to corrosion.

The metals zinc, tin, and lead, which are commonly used as protective coatings for iron and steel, do not occur in the native state and do not approach copper in durability under atmospheric conditions. Their use is comparatively modern and in the case of tin (now selling at 41 cents per pound) is commercially possible only because of the exceedingly thin coat which may be put on (2 lbs. per box means a 0.00012 inch tin coating).

The necessity of protecting iron from corrosion and the desirability of strengthening copper alloys used for primitive tools and weapons led, at a very early period, to the use of a combination of an iron core and a bronze covering. Such articles have been found in the ruins of Nimroud, an ancient Assyrian city, and among the remains of the Swiss Lake Dwellers (Friend: "Corrosion of Iron and Steel," page 8).

For similar reasons, the union of iron or steel with copper in such a manner as to obtain a composite metal retaining unimpaired the good qualities of both metals has long been a desideratum.

Many inventors have given their attention to the difficult problem of securely uniting iron or steel with copper, and the patent literature of the United States and of European countries contains many illustrations, chiefly of unworkable or imperfect processes.

The earliest patent we have found was one issued to Poole, of England, in the year 1821. Copper or brass was melted in a shallow cast iron pan (British Patent 4598 of 1821).

The commercial electro-deposition or electroplating of copper on iron or steel seems to have started before 1840, in England. This process has been used chiefly for the production of thin coatings, but processes have been developed by Elmore and others for making, by electro-deposition, copper tubes of considerable thickness.

Such a process was undoubtedly used commercially by the manufacturers who, in the year 1883, supplied to the Postal Telegraph Cable Company bimetallic wire consisting of a hard steel core wire 0.120 inch in diameter surrounded by a seamless, electro-plated, closely-fitting copper tube having approximately 0.042 inch walls. The ratio of steel to copper by weight was about 1 : 3 (Figs. 1 and 2).

The same company used also a compound wire consisting of a steel core wire surrounded first by a thin electro-deposited copper sheath 0.008 inch thick and then by a wrapping of heavier copper with walls 0.044 inch thick (Figs. 3 and 4).

In neither type of wire was there a bond between copper and steel other than a close conformation. The workmanship was so excellent, however, that samples taken down after 28 years' exposure in the line from New York to Chicago showed absolutely no corrosion of the steel core. The copper sheaths retained the dimensions given above.

Desire to solve the problem of uniting copper with iron or steel would naturally lead to attempts to make a weld by processes analogous to the one successful with iron or mild steel. When, however, heating and hammering iron and copper together failed, even with the use of various fluxes, to produce a weld, it became apparent that the problem was a difficult one.

Inventors tried to follow established methods for coating one metal with a more fusible one, *e. g.*, the coating of iron or steel with zinc, tin, or tin-lead alloy by passing the former metals, properly cleaned, through baths of the melted, fusible metals. The high melting point of copper and its strong tendency to oxidize when melted, offered great obstacles. Coatings made by dipping steel into melted copper are always thin if the steel is hot, and are usually imperfectly adherent.

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[1] Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8–12, 1913.

The ideas of casting melted copper in considerable amount against an iron or steel base or around a steel core, or of casting iron or steel inside a copper tube, were conceived and tried by the following inventors:

"Rollers for Printing Fabrics," British Pat. 1924 of 1856; Tytherleigh. *Method.*—Dipping iron in melted copper; then heating and casting more copper around it.

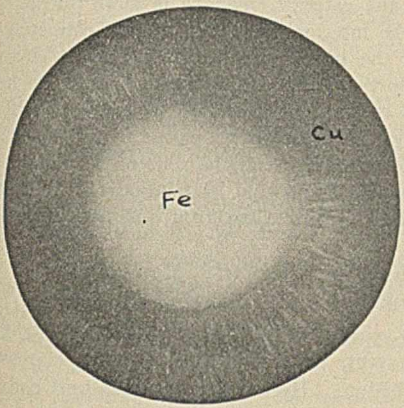

Fig. 1 × 11
"Postal Telegraph" Wire with Steel Core and Entirely Electrodeposited Copper Covering

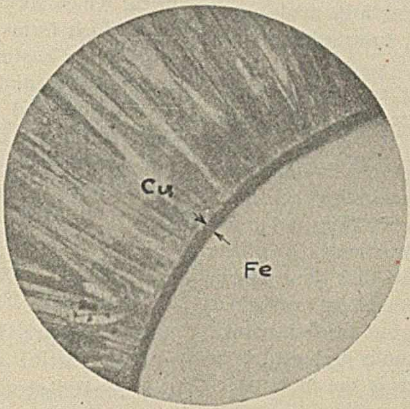

Fig. 2 × 44
"Postal Telegraph" Wire with Steel Core and Entirely Electrodeposited Copper Covering

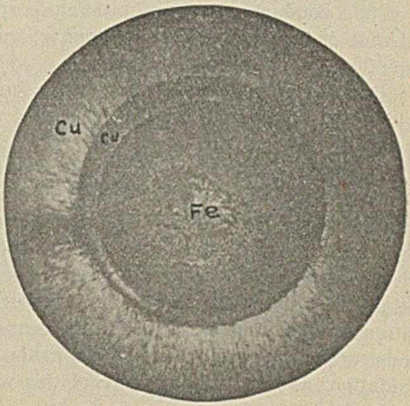

Fig. 3 × 11
"Postal Telegraph" Wire with Steel Core, Electrodeposited Tube, and Folded—on Copper Cover

Specification.—"In carrying my invention into effect, I take a hollow iron cylinder, of somewhat less diameter than the roller or cylinder to be manufactured. I prefer to perforate the said cylinder with holes. I clean the said iron cylinder by acids or otherwise. I afterwards cover the said iron cylinder with borax or other suitable flux, and heat it sufficiently to fuse the flux thereon. In another furnace I heat a pan or vessel (made of a material capable of bearing the requisite heat), the said pan or vessel containing copper, brass, or other alloy of copper. When the copper or alloy is fused, I put the iron cylinder therein and turn it, so as to *coat* it with the metal. I take the cylinder from the said pan or vessel, and while hot I put it in a hollow cylinder or mould, closed at bottom with clay or other suitable material. I place a core or axis in the iron cylinder, and adjust it, by screws or otherwise, in the axis of the mould. I put the whole into a furnace, and when the coating on the iron cylinder begins to melt I *pour fused copper or copper alloy* into the mould, and I maintain the heat until the copper or alloy is thoroughly incorporated with the coating on the iron cylinder; the fire is then slackened, and the whole allowed to cool. The roller or cylinder is afterwards finished by the process of turning."

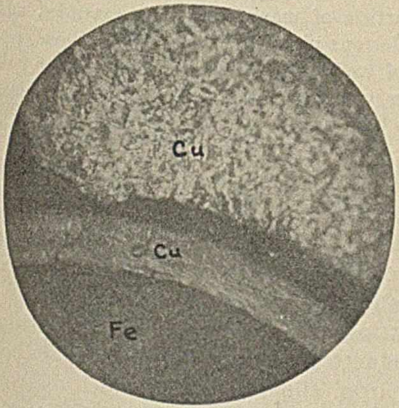

Fig. 4 × 44
"Postal Telegraph" Wire with Steel Core, Electrodeposited Tube, and Folded—on Copper Cover

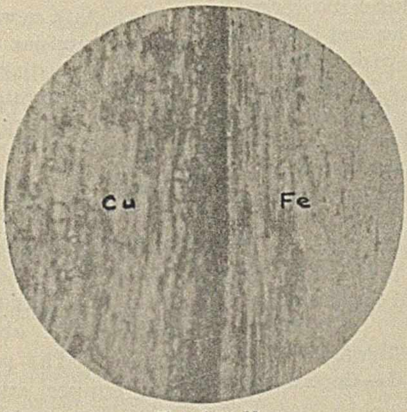

Fig. 5 × 50
Commercial Alloy Union of Copper and Iron. Longitudinal Section of "Monnot-Duplex" Wire

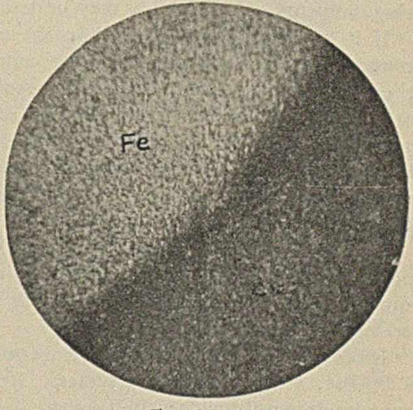

Fig. 6 × 44
Commercial Alloy Union of Copper and Iron. Cross Section of "Duplex Copper-Clad" Wire

"Improvement in Coating Metals," U. S. Pat. 21,797 of 1858; Hiler. *Method.*—Casting iron or steel in a copper mold and completing the union by rolling.

Specification.—"I have discovered that the best union of the iron or steel with its coating metal can be made by heating the *iron or steel* until it is *fused* and bringing it while in that condition in contact with the coating metal, and keeping it so in contact until both metals have become cooled to a proper temperature.". . . . ."*On the melted iron being poured into the mold in contact with the coating metal the latter becomes fused by the heat of the former;* but before it is so fused the iron has parted with so much of its heat as to be sufficiently chilled to prevent the coating metal from mixing with the iron, and also to prevent the said coating metal from sinking down and occupying the bottom of the mold."

Claim.—"What I claim as my invention, and desire to secure by Letters Patent, is: The coating iron or steel with copper, silver, or brass, or alloys where silver or copper is used, by bringing the iron or steel, while in a melted state, into contact with the coating metal, and allowing them to so remain until the two metals have become hard by cooling, substantially as specified."

Suggested Uses of Hiler Product.—Stair rods, trunk nails and bands, buttons, etc.

"Improvement in Line-Wires for Telegraph," U. S. Pat. 47,940 of 1865; Farmer and Milliken. *Method.*—Casting copper around an iron bar; then rolling and drawing into wire. This seems to be the pioneer patent on telegraph wire composed of copper with a steel core.

Specification.—"In the construction of aerial telegraph lines the general practice, as is well known, is to use iron wire for transmission of the electric current, this wire being galvanized or covered with a thin coating of zinc to prevent oxidation. In the earlier constructions of lines it was sometimes attempted to use copper wire, but for want of tensile strength in such wire its use had to be abandoned. Yet the employment of copper wire is a desideratum on account of its great superiority over iron as a conductor, and could its tensile strength be made equal to that of iron it would, to a great extent, supersede the iron wire."

"Our invention, therefore, consists in a copper telegraph wire cored or covered, for the purpose of strength, with iron or steel."

"In carrying out the invention or constructing this compound wire we prefer to core the copper with iron, first casting the copper around an iron bar and then by the processes of *rolling* and drawing attenuating the same into wire by the well-known methods of wire-drawing. It will be obvious, however, that the iron can be placed around the copper and the resultant bar drawn out into a wire, leaving the copper in the center; but the first-named construction we consider preferable, as the iron is protected from oxidation, and the manufacture of this wire is the more practicable."

Claim.—"As a new article of manufacture, a telegraph wire reënforced, for the purpose of strength, with a core or cover of iron or steel, the wire being made by drawing a compound bar of the two metals."

"Improvement in Combining Copper with Cast Steel," U. S. Pat. 73,375 of 1868; Park. *Method.*—Casting steel in a hollow copper ingot, previously heated.

Specification.—"A combination or union of copper with some harder and stronger metal has been long needed for many purposes in the arts and manufactures, such as locomotive fire-box sheets, wire for ships' rigging, rods, bolts, spikes, and various other articles for which copper alone cannot be employed, owing to its softness and want of strength."

"My invention consists of combining copper with cast steel, by casting the molten steel on or around the copper, which is previously heated, thus forming an ingot which may be hammered, rolled, or otherwise worked into any desired shape, the steel being tempered or hardened as may be desired after it is worked."

"If it is desired to have steel in the center and copper all around it, as is required for making copper-coated steel wire, or copper-coated spikes or rods, I prepare a hollow ingot of copper, into the center or cavity of which, after it has been heated to a good red heat, I teem or pour the molten cast steel. In this case no mould would be necessary, but may be used if preferred. Such ingot may be drawn out into wire, or worked into other articles, such as bolts, spikes, etc."

Claim.—"Combining copper and cast steel by heating the copper to a good red heat, and teeming or pouring thereupon liquid molten cast steel, substantially as and for the purposes hereinbefore described."

"Process of Manufacturing Compound Telegraph Wire," U. S. Pat. 310,995 of 1885; Farmer. *Method.*—Copper plated iron wire drawn through melted copper.

Claim.—"1. The method herein described, of manufacturing compound telegraph wire, which consists in electroplating a steel or iron wire with a thin film of copper, then drawing the same through molten copper and shaping the coating in substantially the manner set forth."

"Improvements in the Manufacture of Wires, French Pat. 168,133 of 1885; Martin. *Method.*—(*a*) Casting copper in iron tube. (*b*) Casting copper around medial part of iron bar and then reheating and rolling, etc."

In an 1888 supplement to the above patent he described casting copper around the medial part of a steel bar. He then rolled and drew it. Martin seems to have introduced bimetallic wire very extensively in France and elsewhere in Europe. His work appears to be the commercial development of the ideas of Farmer and Milliken.

Claim.—"I claim in this supplement to my principal patent my perfected method of making bimetallic wires in which the metal which forms the exterior envelope is more ductile than that which forms the interior core, this method consisting essentially in casting the metal intended to form the envelope around the medial portion of the rod which must form the heart of the wire, and in extending the rod so partially covered by the metal of the envelope by alternate passes first in one direction and then in the other between the rolls of a rolling mill."

"Process of Producing Compound Metal Bodies," U. S. Pat. 853,716 of 1907; and "Copper Clad Iron and Steel," 893,932 of 1908; Monnot.

Monnot develops further the plan suggested by Tytherleigh, Farmer and Milliken, and Martin. He uses supermolten, *i. e.*, very hot melted copper to give a thin initial coating and then casts copper around the coated steel billet. He finally reheats and rolls.

Specification.—(U. S. Pat. 853,716.) "When at the supermolten temperature many metals are very sensitive to flame, gases and other bodies, readily becoming impure; and there is reason to believe that at such temperatures *such metals have a solvent action* on other solid metals placed in them.

"By applying only a thin film coating by the action of supermolten metal, and then applying the main coating by means of metal nearer its point of solidification, *there is less probability of reduction of quality of the coating metal. However, the main coating may be and frequently is formed entirely from supermolten metal, this method having the important advantages of requiring less manipulation and fewer baths of molten metal.*"

Claims.—(U. S. Pat. 893,932.) "*1st.* As a new article of manufacture, a ferrous metal base, having a welded-on, continuous, poreless, dense coating of copper united thereto by a union resisting temperature changes, cutting tools, and mechanical stresses, said coating *having the properties of metal set from a liquid state.*

"*2nd.* As a new article of manufacture, an extended metal article comprising a ferrous metal base and a continuous, poreless, dense coating of copper weld-united thereto, by a union resisting temperature changes, cutting tools, and mechanical stresses; said ferrous base and copper coating having been extended together."

In all of the above processes except those of Tytherleigh and Monnot, heating and rolling are essential to complete the union between the two metals. The unions are more or less perfect according to whether the operator reads into the patents effective means of keeping the abutting surfaces clean at the critical instant. The products of most of these processes contain copper and iron alloys because steel dissolves readily in melted copper and melted steel dissolves copper with great speed. Copper in steel or iron in copper are disadvantageous electrically because they harden the principal metal and diminish the conductivity of composite wire. Copper in steel retards its corrosion (Buck, THIS JOURNAL, 5, 447).

It is possible by skilful regulation of temperatures of casting and by proportioning correctly the amounts of melted metal and of the solid metal core or tube, to avoid alloy formation, except in the Tytherleigh, Park, and Monnot procedures. In the latter, an alloy is intentionally made, and the fact is considered an important mechanical advantage, counterbalancing, in the inventor's opinion, the higher electrical resistance.

There have been a number of attempts to utilize hydraulic pressure and means other than rolling pressure to weld cast copper while still hot to steel. As examples of these are the following:

"New Process of Manufacturing Bimetallic Plates and Wires," Belgian Pat. 171,442 of 1903, *Martin*.

Claim.—"A process of making bimetallic plates and wire, which consists in applying on the inside walls of a conical ingot mold, widened at the bottom, a lining or sheet of copper, of silver, of brass, etc., covering all or a part of the surface of the ingot mold, then running the steel into the mold, and (finally) forcing out the ingot through the small end of the mold by the use of a hydraulic press whose piston presses against the large end of the ingot, in such a way as to weld the two metals and to suppress all flaws between them."

"Process of Making Bimetallic Products," U. S. Pat. 853,932 of 1907, *Monnot and Martin*.

The chief feature of these patents, which both cover the same processes, is the forcing of a cast, composite ingot through a die, or the use of hydraulic pressure on properly heated, flat slabs, in order in both cases to get a weld before further working. This practice, even if successful, seems expensive and is superfluous if heating and rolling are to follow.

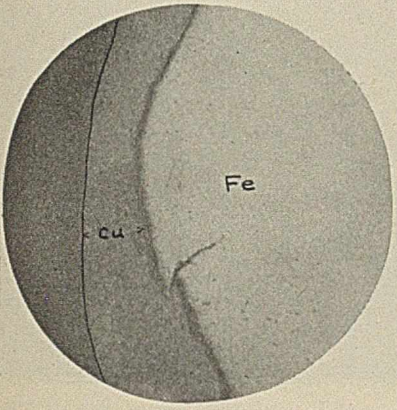

Fig. 7 × 44
Commercial Alloy Union.
Defective Steel
Core

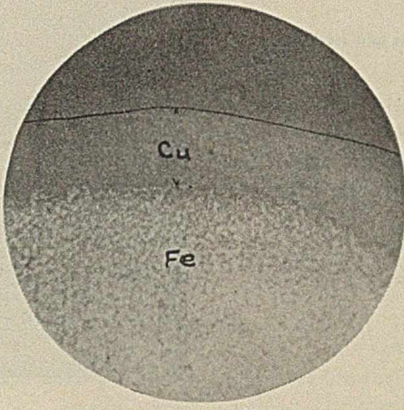

Fig. 8 × 44
Commercial Weld Union of Copper and Iron.
Cross Section of "Standard
C. C. C." Wire

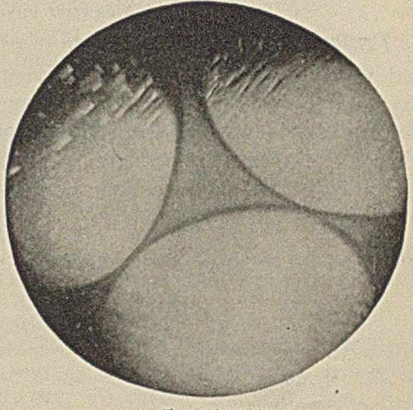

Fig. 11 × 11
Alloy Union of Copper
and Iron at
1130° C.

In the process of *Griffith* (U. S. Pat. 580,344 of 1897) for "Uniting or Welding Metal," there was a return to the original idea of welding without first melting either copper or iron.

Specification.—"To this end the invention consists in the process hereinafter described, in which the plate, bar or other article of iron or steel is first cleansed from scale or oxid; its surface or surfaces then covered with a coating or deposit of copper or an alloy of copper or any other suitable metal or alloy thereof capable of being deposited by chemical or electrical deposition or otherwise, in this instance by the action of a bath of a solution of the salts of copper; is then placed face to face with a sheet or plate of copper or an alloy thereof; is then heated to the proper degree, and, finally, is passed through rolls or is subjected to pressure requisite to effect the perfect and intimate welding of the metals."

Claim.—"The herein described process of uniting or welding plates of metal of different kinds, which consists in cleansing one of the plates from scale, oxid, or other impurities, then coating or covering one or more faces of this plate with a metal or an alloy thereof having a lower fusing point, then applying to this coated surface a plate of metal or an alloy of the same character as the coating, but free from any coating, then applying heat to the two plates, and finally uniting by pressure, substantially as described."

The new methods introduced by Griffith were the plating of the iron with copper, either by chemical or electrical deposition, and then placing copper and copper-coated iron in close contact, heating them up and rolling them together at the proper temperature. The copper-plating of the iron prevents its oxidation and keeps its surface in condition to unite firmly with the copper when the two metals receive a proper rolling pressure at the right temperature. The temperature recommended by Griffith was about 1700° F. The writer has observed that at 950° C. (1742° F.) welding of copper to copper-plated iron, rolled as composite cylindrical billets, was complete after the first few passes. Welding by rolling pressure is the most effective method. Forcing through a die or otherwise using hydraulic pressure are very cumbersome methods.

German Pat. 152,042 of 1903, Wachwitz.

This inventor uses aluminum as intermediary in effecting a union of copper and iron. He rolls clean aluminum and copper sheets together at about 800° F. He rubs metallic aluminum into the surface of clean iron. His first operation in sheet manufacture is to bind the copper-aluminum sheet to the iron-aluminum slab and heat and roll. These complicated operations are said to produce a secure weld.

U. S. Pat. 1,065,727 of 1913, Rockey and Eldridge.

This is an attempt to make copper-clad steel by dipping into successive baths of melted copper covered with melted boric anhydride. It is mentioned only to show that efforts are still being made along the lines indicated.

It has been noted that welded composite metal made by the Griffith process contains little or no copper-iron alloy. Spring, in 1878, by pressure alone (without heat), produced alloys of certain mixed metal filings (Law, "Alloys," page 3). It has also been asserted that solid metals may be united in thin layers at the point of contact by the use of heavy pressure and that the union is an alloy. It might naturally be expected that when forced together at 950° C., copper and iron might superficially alloy. The fact remains, however, that copper-clad steel wire made by the "Colonial" and "Standard" developments of the Griffith process, has a conductivity almost the same as the sum of the conductivities of the iron and copper composing it. This is not true of copper alloyed with iron nor of the products of other processes with which the writer is familiar.

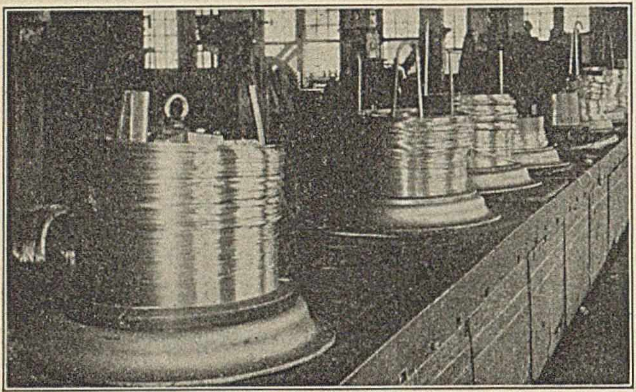

FIG. 9—WIRE-DRAWING BENCH
The Dies are at the Left of Each Reel. Each Die and Reel Form an Independent Unit

TABLE I—CONDUCTIVITIES BASED ON PERCENTAGES BY VOLUME, CONDUCTIVITY OF COPPER BEING ASSUMED AS 100 AND OF SOFT STEEL AS 13.5

B % steel	Conductivity of the steel	A % copper	C Conductivity total	Ratio A : C
0	0	100	100.0	1 : 1
10	1.35	90	91.35	1 : 1.015
20	2.70	80	82.70	1 : 1.034
30	4.05	70	74.05	1 : 1.058
40	5.40	60	65.40	1 : 1.090
50	6.75	50	56.75	1 : 1.135
55	7.43	45	52.43	1 : 1.165
60	8.10	40	48.10	1 : 1.202
65	8.78	35	43.78	1 : 1.251
70	9.45	30	39.45	1 : 1.315
77	10.40	23	33.40	1 : 1.452
80	10.80	20	30.80	1 : 1.540
90	12.15	10	22.15	1 : 2.215
100	13.5	0	13.5	.....

The accompanying tables show how remarkably uniform the "welded" copper-clad wire is and how closely the actual and the calculated conductivities correspond. In the "alloyed" type occasional samples show close agreement, but in general there is a noticeable deficiency and in several cases the *low actual conductivities* are remarkable.

The better showing of the "welded" type is undoubtedly due to the high purity of the copper coating, which is free from iron alloy or oxide of copper.

In this connection it is of interest to endeavor to define "weld" and to compare welded with alloyed copper-clad steel.

TABLE II—CONDUCTIVITIES BASED ON PERCENTAGES BY WEIGHT, CONDUCTIVITY OF COPPER BEING ASSUMED AS 100 AND OF SOFT STEEL AS 14.3

B % steel	Conductivity of the steel	A % copper	C Conductivity total	Ratio A : C
0	0	100	100.0	1 : 1
10	1.43	90	91.43	1 : 1.016
20	2.86	80	82.86	1 : 1.036
30	4.29	70	74.29	1 : 1.060
40	5.72	60	65.72	1 : 1.095
50	7.15	50	57.15	1 : 1.143
55	7.87	45	52.87	1 : 1.175
60	8.58	40	48.58	1 : 1.215
65	9.30	35	44.30	1 : 1.266
70	10.01	30	40.01	1 : 1.333
77	11.00	23	34.00	1 : 1.478
80	11.44	20	31.44	1 : 1.570
90	12.87	10	22.87	1 : 2.287
100	14.3	0	14.3	.....

TABLE III—CONDUCTIVITY OF SOFT STEEL WIRES CONTAINED IN COPPER-CLAD STEEL

		Maximum	Minimum	Average
"Welded" type..........	12 samples	14.41%	14.04%	14.28%
"Alloyed" type..........	9 samples	14.02%	13.44%	13.74%

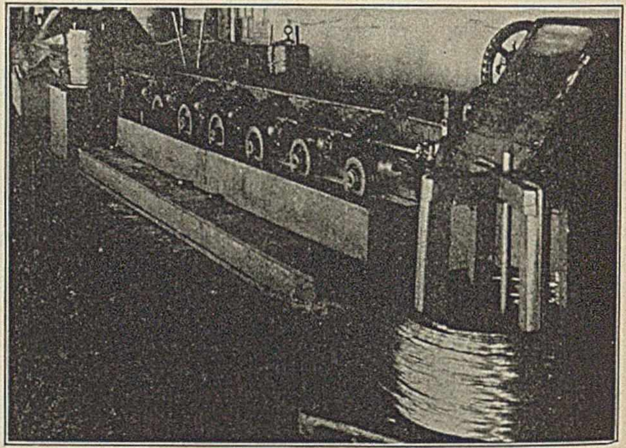

FIG. 10—CONTINUOUS WIRE-DRAWING MACHINE
Six Size Reductions in One Operation

TABLE IV—ACTUAL CONDUCTIVITY OF COPPER-CLAD WIRE SAMPLES COMPARED WITH CALCULATED CONDUCTIVITY

		Conductivity	
	Copper	Actual	Calculated
"Welded" type............	22.8 %	35.20%	34.60%
"Welded" type............	24.06	35.80	35.68
"Welded" type............	20.15	32.24	32.37
"Welded" type............	23.44	35.25	35.28
"Welded" type............	23.42	35.45	
"Welded" type............	23.65	35.11	
"Welded" type............	23.06	35.43	
"Welded" type............	23.66	35.13	
"Welded" type............	24.32	36.12	
"Welded" type............	23.59	35.42	
"Alloyed" type............	44.00	34.00	52.57
"Alloyed" type............	43.50	45.72	52.15
"Alloyed" type............	34.20	43.80	44.27
"Alloyed" type............	22.53	33.92	34.38
"Alloyed" type............	33.65	41.57	43.80
"Alloyed" type............	41.20	47.42	50.20
"Alloyed" type............	22.75	33.52	34.57
"Alloyed" type............	31.90	38.49	42.32
"Alloyed" type............	38.86	46.81	48.21
"Alloyed" type............	40.35	48.91	49.48
"Alloyed" type............	35.20	43.52	45.11
"Alloyed" type............	35.10	45.47	45.03
"Alloyed" type............	38.80	45.06	48.16

A weld, until the advent of electric and oxy-acetylene methods of uniting metals, meant simply the joining securely by pressure of two pieces of heated, plastic metal. Usually both pieces of metal were of iron or mild steel, but it has been found that the process may be applied to other metals which pass through a plastic state before fusion. Copper is such a metal and platinum is said to be similar. It is therefore quite proper to speak of unions between plastic copper and plastic iron as welds in the original sense of the term.

Unions made by fusing two metal surfaces together are more analogous to soldered joints than to welds as commonly understood.

Nevertheless, it is held by Prof. Sauveur that there is no "true" weld between dissimilar metals (he considers iron and copper dissimilar) unless there is a "crystalline interlocking" at and across the junction, and this structure is not produced unless one of the metals is in a fused condition and therefore capable of alloying with the other metal. Prof. Sauveur therefore classifies copper-iron alloy welds (Figs. 5, 6 and 7) as true welds, and unions such as he believes the Griffith-Colonial-Standard process gives (Fig. 8), as only adhesions, not really welds.

Be the definition what it may, the union of copper and iron in the Griffith process is so secure that it resists the remarkably severe stripping action to which it is subjected in wire drawing (Figs. 9 and 10). The composite metal extends evenly in rolling and drawing so that 0.004 inch wire (No. 40 B. & S.), hair-like in fineness, still carries practically the original percentage of copper coating. Some variation occurs, as would be expected, even though there is no stripping. Sample "J. O. H. No. 13" (regular "welded" copper-clad wire) contained at No. 40 gauge (0.004 inch) 21.2 per cent of copper as against 23.06 per cent in the same wire at No. 10 size. It is not believed that this represents loss of copper, but merely slight unevenness in coating. Larger samples would probably correspond more closely. There is, of course, some loss of copper during the manufacturing processes which precede wire drawing.

CONDITIONS UNDER WHICH MELTED COPPER WILL UNITE WITH STEEL

The difficulty in effecting a union between heavy steel objects and melted copper is the chilling effect of the solid mass upon the melted metal. It is doubtless for this reason that Monnot recommends the use of "supermolten" copper (above 2550° F.) and also prescribes heating the steel billet to redness.

When, however, steel and copper are at the same temperature and are clean, they unite instantly, as soon as the copper melts (1085° C., 1987° F.).

The following experiment proves the statement just made:

Several clean steel wire nails were made into a bundle with an equal number of pieces of copper wire disposed symmetrically. The bundle was secured by two bands of copper wire and was dropped into melted borax sufficient to completely cover it. The temperature was gradually raised until the copper melted, when it ran like solder over the surface of the steel nails, cementing them firmly together (Figs. 11 and 12).

The effect of either prolonged contact of melted copper and solid steel or of higher temperature than 1100° C. in promoting the formation of copper-iron alloy is shown by the following experiment:

Pieces of copper-clad wire of equal length were exposed, under melted borax, in separate crucibles, to various temperatures. The amounts of steel dissolved by the melted copper globules indicate the vigor with which the action proceeds.

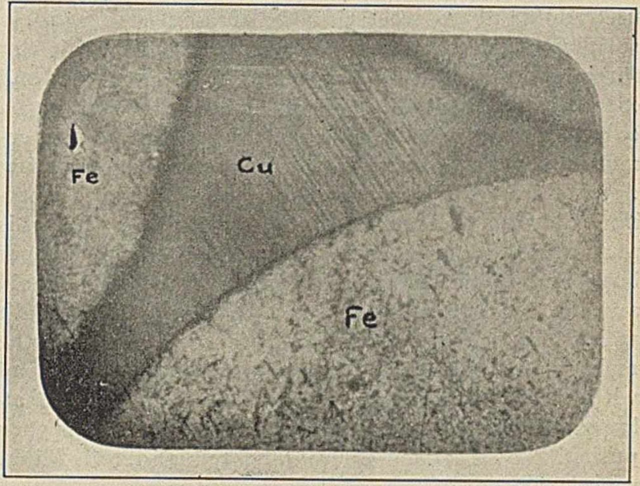

Fig. 12 × 50
Alloy Union of Coppe r and Iron at 1200° C.

Temperature	Time	Iron in copper button
1200–1250° C.	5 minutes	3.18%
1300–1320° C.	3 minutes	4.20
1330–1400° C.	2 minutes	5.12
1400–1450° C.	4 minutes	8.53

A second experiment showed that, when left at 1420° C. (2588° F.) for 15 minutes, melted copper dissolved nearly all of an $^{11}/_{16}$ inch steel rod which was vertically immersed in it. The copper finally contained from 8.7 per cent to 14.35 per cent of iron in top and bottom, respectively.

In a third experiment, which was intended to give some light as to the effect of very brief contact of copper and steel at 1420° C., it was found that even when the crucible in which melted copper and iron had been brought together (at 1420° C.) was removed from the furnace in 30 seconds, the copper had alloyed with 2.85 per cent of its weight of iron.

At 1200° C. a parallel experiment gave iron 1.85 per cent in the copper.

These experiments show how quickly iron and melted copper unite when both are at the same temperature. This is a detriment if the product is to be used for electrical purposes. For other uses, where the product cannot be reheated or worked, it is a matter of interest to know just how the metals may be united.

METHODS OF MANUFACTURE

There are two types of copper-clad steel which are manufactured and used: (1) the type which depends on a copper-iron alloy for the bond; and (2) the type which consists of copper welded to steel by proper methods without melting the copper.

(1) The method of manufacture of the first type of

copper-clad steel is described by Tassin.[1] It consists essentially in preparing round steel billets approximately 5 inches in diameter and 26 inches long, which are cleaned by pickling and then heated up in molds which serve the double purpose of excluding the air at first and finally of receiving the annular copper jacket which is cast around the steel core. Producer gas is run through the mold to hinder oxidation of the steel and copper. The heated billet and mold are lowered into a bath of what is called by Monnot, the inventor, "super-molten copper" having a temperature approximating 2550° F., for the purpose of forming a film of copper-iron alloy on the surface of the steel billet. For this purpose the mold is opened after it enters the copper bath and is closed again as it leaves it. The mold and billet are then lowered into a second copper bath which has a very much lower temperature and the mold is this time filled with copper and is closed and withdrawn from the bath in that condition and allowed to cool. The copper-covered steel billet is then pushed out of the mold and heated and rolled into rods which are afterwards drawn into wire.

The object in having the first copper bath at so high a temperature is stated to be the hastening of the formation of a film of adherent copper-iron alloy. The reason for casting the greater part of the copper at the ordinary casting temperature, which is about 200° above its melting point, is that it is then possible to keep the copper from rapid oxidation and also, which is more important, to prevent the speedy contamination of the bath with copper and iron alloy. Numerous experiments made by the writer have shown that copper at 2550° F. dissolves solid steel, or alloys with it, with remarkable rapidity, thus making the copper unfit for use as a part of an electrical conductor.

(2) The welding process of uniting copper and steel is carried out as follows: Soft steel billets, approximately $3^1/_4$ inches in diameter by 72 inches long, are carefully freed from scale and are electro-plated with copper. They are then enclosed in neatly fitted cast copper tubes having walls of such thickness as to furnish approximately 25 per cent of copper in the composite blank, the total weight of each blank being approximately 200 pounds. The use of copper tubes gives a uniform product not otherwise obtainable. In order to exclude the air the blanks are coated at the ends with a fire-resistant paste. They are then heated to a temperature approximating 950° C. (1742° F.), this being sufficient to render both metals plastic. Each blank is then rolled in such a way that it is given a strong and uniform rolling pressure at all points, while the metals still retain a large part of their original heat. It has been found that the welding operation is completed within 50 seconds from the time the composite blank leaves the heating furnace and that the original 6 foot billet is extended in $1^3/_4$ minutes to a 25 foot wire bar $1^3/_4$ inches square. During the first few passes there is a slight extrusion of copper from the ends of the composite blank; the remainder, however, is securely welded and the small extruded portions are sheared off from the finished wire bar.

These wire bars are reheated and rolled into coils of $^3/_8$ inch wire rods. These are freed from oxide by pickling and are subsequently drawn cold into wires of any desired fineness (Fig. 13).

FIG. 13—IN STORE-ROOM AT WIRE MILL
Copper-Clad Wire Bars in Foreground. Coils of Copper-Clad Wire and Cable

It is remarkable that the copper after it is welded to the steel by the preliminary rolling process adheres firmly to it and extends evenly with it through the various processes of hot rolling, cold drawing, annealing, etc. There is a strong stripping force in wire drawing which would instantly remove the copper jacket if it were not securely united to the steel. The writer had the opportunity of observing the drawing of copper-clad wire of many sizes, from 0.30 inch in diameter to 0.003 inch, the latter being as fine as hair (samples shown). No stripping took place in any case and the finest wire showed by chemical analysis that the copper covering still maintained nearly the same ratio to the steel core which existed in the original wire bar. Wire drawing may be likened in stripping tendency to the drawing of a lead pencil through a hole of the size of the graphite core only.

Supplementing this evidence of secure union of the two metals by the "welding" process is the fact that numerous heating, quenching, and twisting tests of welded copper-clad wire of all sizes produced no separation of copper from steel.

PROPERTIES AND USES OF COPPER-CLAD STEEL

The principal use of copper-clad steel at the present time is for electrical conductor wire of which over 10,000,000 pounds have been made by one manufacturer. It is used under conditions where a combination of high tensile strength and elasticity with sufficient conductivity is needed. This is particularly the case with uninsulated line wires for telegraph, signal, and telephone service, and with insulated "drop wires" running from poles to subscribers' houses in telephone practice. Even hard-drawn copper wire has not sufficient mechanical strength for such uses unless it is employed in larger sizes than can well be afforded. Iron or steel conductors have been used, but they rapidly deteriorate when in contact with the air, whereas copper-clad steel is as durable as the copper itself.

The elastic limit or point at which permanent stretching begins in the case of pure copper wire is so low that wind strains cause a sagging which must be taken up

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[1] THIS JOURNAL, 1, 670.

and which eventually causes breakage. The most rapid destruction occurs, however, when copper wires are exposed to snow and ice in winter. Great losses occur through breakage of the wires and interruption of communication. (Sagging and breaking of copper-clad wire shown by slides.)

The judicious substitution of copper-clad steel wires for copper wires has done away with much of the trouble formerly experienced in the maintenance of telegraph, telephone, signal, power, and lighting wire circuits.

The grade of copper-clad wire most used has a conductivity averaging 30 per cent of the conductivity of pure copper wire; at the same time its tensile strength is 70 per cent greater and it is possible to apply 150 per cent greater tension before permanent stretching occurs. Its weight is 10 per cent less than that of copper wire of the same size and it has 100 per cent greater conductivity than either steel or iron (Table V).

Table V—Properties of Standard Colonial Copper-Clad Wire and Hard-Drawn Copper Wire

Bare, hard drawn

Size B. and S. G.	Average resistance at 60° F. in ohms per M. ft.		Weight per M. ft. in lbs.		Average breaking weight in lbs.	
	C. C. C.	H. D. Copper	C. C. C.	H. D. Copper	C. C. C.	H. D. Copper
0000	0.1603	0.04906	584	641	9805	7914
000	0.2021	0.06189	463	509	8250	6533
00	0.2549	0.07803	366	403	6830	5365
0	0.3214	0.09831	291	320	5680	4386
1	0.4052	0.1241	230	253	4800	3565
2	0.5110	0.1565	184	202	3900	2892
3	0.6443	0.1972	145	159	3200	2338
4	0.8124	0.2488	114.5	126	2630	1890
5	1.025	0.3138	91.0	100	2160	1520
6	1.292	0.3955	72.0	79	1770	1221
7	1.629	0.4986	57.7	64	1450	984
8	2.054	0.6288	45.5	50	1180	788
9	2.590	0.7934	35.5	39	965	630
10	3.267	0.9996	29.0	32	790	506
11	4.118	1.262	22.8	23.5	645	403
12	5.195	1.591	18.2	20.0	525	318
13	6.548	2.003	14.3	16.5	430	257
14	8.258	2.527	11.3	12.4	350	202
15	10.41	3.185	9.0	10.0	280	165
16	13.13	4.022	7.2	7.9	230	128
17	16.56	5.059	5.6	6.2	185	102
18	20.88	6.392	4.4	4.8	150	83
19	26.33	8.057	3.5	3.9	120	64
20	33.22	10.14	2.82	3.1	100	51

The tensile strength of copper-clad wire varies from 60,000 pounds per square inch in 0000 wire (0.46 inch in diameter) to 98,000 pounds per square inch in the case of No. 10 wire (0.102 inch in diameter), the actual breaking weights in the two cases being 9,805 pounds and 790 pounds, respectively. It is an interesting thing to know that the average breaking weight of copper-clad wire is from 3 to 6 times as great as the weight of a mile of the same wire, and the elastic limit is sufficiently high so that if wind and ice were not to be allowed for, there could be spans of a mile and more in length in the case of river crossings, etc. Tables VI and VII show relative costs for equal strengths and relative strengths for equal size.

Copper-clad wire is also used for trolley wire, springs, anchor bolts, pump rods, cotter pins, etc. Copper-clad wire (bare) has been successfully used for field work in military, telephone, and telegraph service.

Its use has been suggested for small angle irons in skylights and other windows. It has not yet been extensively applied in building construction, but its great durability entitles it to wider use, especially for roofs, cornices, rain-water conductors, etc. The results of exposure tests of copper-clad sheet steel in the Pittsburgh atmosphere have been most encouraging.

WEATHER RESISTANCE OF COPPER AND COPPER-CLAD SHEET STEEL

Samples of sheet of copper and of steel coated with

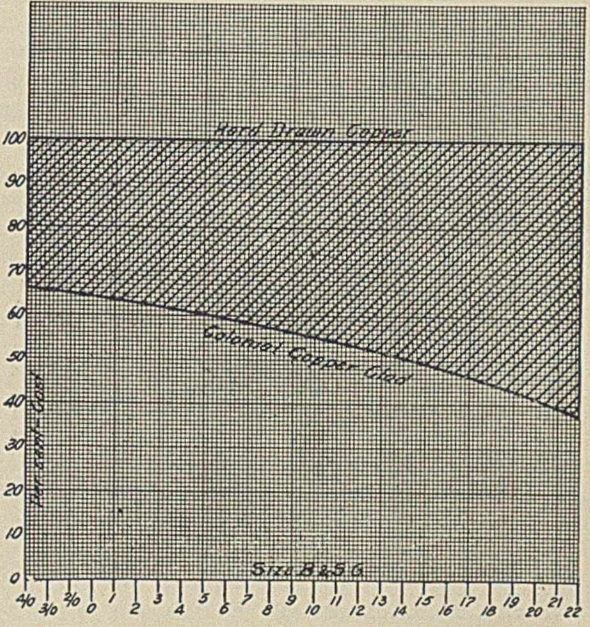

Table VI—Comparison of Costs for Equal Strength (Bare Wire—Hard Drawn)

For equal strength values, this diagram gives the approximate relative costs per mile of the two materials, in bare form, hard drawn

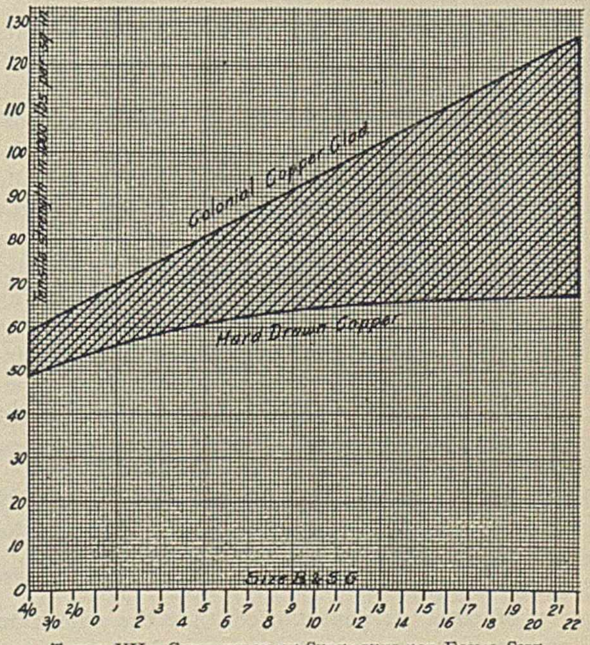

Table VII—Comparison of Strengths for Equal Size (Bare Wire—Hard Drawn)

For equal sizes, this diagram gives the actual strengths of the two materials, in bare form, hard drawn the same grade of sheet copper by the Griffith process, and a sample of sheet made from a Colonial copper-covered wire bar were exposed on the roof of the Pittsburgh Testing Laboratory building from November 21st, 1911, to August 12th, 1913. The sheets were held in a flat position on a wooden base by means of screw hooks. This arrangement permitted the retention of moisture under the sheets and favored the starting of decay of the wood at those points. The sheets were in no case held so tightly that dust was excluded and slag dust from the roof coating blew in and cemented itself to the sheets in some cases.

The sheets were measured and weighed before exposure. The samples exposed were as follows:

A. Copper-clad, one side. 1st lot Griffith.
B. Copper-clad, both sides. 1st lot Griffith.
C. "Lake" copper sheet used for welding to steel in making A, B, D, and F.
D. Copper-clad, one side. 2nd lot Griffith.
E. Copper-clad sheet made from one and three-fourths inch wire bar C-17.
F. Duplicate of A, but exposed with steel side up.

WEIGHT AND SIZES

	Weight Grams	Thickness, inch Iron	Thickness, inch Copper	Size, feet	Area Square inches
A.......	3730.6	0.060	0.005	2.97 × 1.09	466.56
B.......	5317.7	0.071	0.006	2.42 × 1.525	531.36
C.......	274.58	...	0.04	1.09 × 0.31	48.66
D.......	2853.8	0.026	?	4.59 × 0.92	680.11
E.......	1067.42	0.060	(incl. Cu)	2.05 × 0.49	144.65
F.......	3773.1	0.059	0.004	3.0 × 1.1	475.2

LOSS OF WEIGHT DURING EXPOSURE OF 21 MONTHS AND 20 DAYS

	Original weight Grams	Final weight Grams	Loss in weight Grams
A....................	3730.6	3317.0	413.6
B....................	5317.7	5277.0	40.7
C....................	274.58	274.3	0.28
D....................	2853.8	2038.0	815.8
E....................	1067.42	1067.0	0.42
F....................	3773.1	3355.0	418.1

These results show the remarkable durability of copper and of copper-clad steel. (Specimens shown.)

Sample *E* is the only one which really represents the protecting efficiency of copper at the edges as well as on both surfaces. The long edges were copper clad but the ends were sheared. There was no extraordinary penetration of iron rust at the sheared ends. The only defects were some blisters developed by the crude way of working the wire bar into sheets. Slight rusting occurred at those exposed points but nowhere else, and the total amount of rusting was very insignificant. No tendency was observed for the rusting to penetrate under the copper and push it up. The same was true as to the places where the steel was exposed in drilling holes for holding the sheet in position. The total loss in weight in two years was insignificant, amounting to only a fraction of a gram, or less than 0.05 per cent.

The durability of Sample *C*, the copper sheet, is especially remarkable considering the acidity of the Pittsburgh atmosphere. The loss amounted to only 0.28 gram, approximately 0.1 per cent. The determination of total oxygen showed that the oxidation had penetrated less than 0.0002 inch or 0.5 per cent of the thickness of the sheet.

Samples *A* and *F* represented rather imperfectly made specimens of copper-clad steel made by the Griffith process, *A* being intentionally left with exposed steel projecting at edges and ends in order to show the manner in which the steel corroded at and near the contact of copper and steel.

The loss of weight of both sheets was practically the same although *A* was exposed with the copper side up, and *F* with the steel side up. This seems to show that moist air rather than rain controlled corrosion of both steel surfaces. No perforation took place at any point of the copper surfaces on *A* or *F*. There was no special grooving to indicate electrolytic corrosion such as would be expected if the copper were not securely welded to the steel. The large losses in weight were due to the rusting away of the exposed steel (Fig. 14).

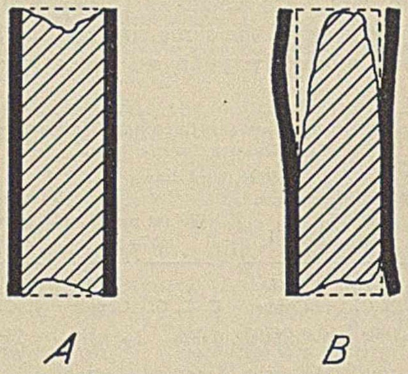

FIG. 14.—DIFFERENCE IN CORROSIONS OF STEEL SHEETS, COPPER-CLAD *vs.* COPPER-CASED

(*A*) Cross-section Showing Corrosion of Steel at Edges Only—Copper Well Joined to Steel
(*B*) Cross-section Showing Corrosion of Steel on Sides —Copper Separated from Steel

Sample *B* was coated with copper on both sides by the Griffith process, the short ends being sheared, but the steel extended 0.4 inch beyond the copper on one of the long sides. There were no perforations of the copper, and the loss in weight was caused by the rusting of the exposed steel at the edge.

Sample *D*.—During the first part of the exposure of this sheet a number of pin holes in the copper near one end were observed. Instead of extending by electrolytic action, these pin holes apparently were soon sealed up and were not observable at all, either as blisters or pits at the end of the period of exposure. This is quite contrary to what might have been predicted by one who considered the union between the copper and the steel a purely mechanical one.

While these experiments were in a way quite crude, they show conclusively the remarkably efficient protecting power of copper for steel to which it is welded. It is all the more remarkable when it is considered that the exposures were made in the moist and acid Pittsburgh atmosphere. Attention is called in this connection to the absence of electrolytic corrosion phenomena when copper and iron were securely welded.

The method of manufacturing these steel sheets was the Griffith process of welding copper to steel, slabs of soft steel being cleaned and electro-plated with copper and fastened securely to copper sheets of the desired thickness, the combined metals being then heated up to a proper welding temperature and united by rolling to the required dimensions. Such sheets, of course, can be given any finish which is desired. They may either have a high polish and considerable stiffness or they may be made soft and pliable. If used for flat roofing sheets a higher temperature will be required for brazing together than is required for soldering either terne or tin plate. If used as corrugated sheets no brazing would be required.

There is no good reason, we believe, why a process of coating sheets with copper should not be developed along the lines of the present processes of tinning and galvanizing, and such copper-clad sheets could be more cheaply manufactured, but it would be naturally expected that as the coating would consist almost entirely of copper-iron alloy, it would be less durable than the pure copper coating made by the process of welding without melting.

POTASSIUM CYANIDE SOLUTION AS AN ETCHING MEDIUM AND SOLVENT FOR THE COPPER ON COPPER-CLAD STEEL

A boiling 25 per cent solution of potassium cyanide in distilled water was found to be a fairly rapid solvent for copper and its action upon steel is negligible.

It was accordingly used by the writer for investigating differences in coatings of copper-clad steel wires. The purest coatings dissolved most slowly and most uniformly, remaining bright. Impure coatings dissolved rapidly, developed a grooved structure, and if iron was present in material amount, the coating turned grayish black. In the case of coatings high in iron (12 per cent), the iron separated as a felt-like substance when the copper dissolved. (Samples of wire stripped of Cu by KCN were shown.)

The following experiments illustrate the solubility of iron and copper in dilute potassium cyanide solution:

SUBSTANCE	Weight Gram	Time boiled Minutes	Weight dissolved Gram	SOLVENT
Sheet steel........	0.7400	30	0.0006	50 cc. 10% KCN
Copper foil.......	0.0950	30	0.0106	50 cc. 10% KCN
Copper foil in contact with steel.	0.0854	Cu 30	0.0782	50 cc. 10% KCN
	0.7080	Fe 30	0.0006	50 cc. 10% KCN

The more rapid solution when iron was in contact with copper was very striking.

The fact that an impure copper coating dissolves more rapidly is shown by the following comparison of two copper-clad wires.

		COPPER DISSOLVED				
	Weight Grams	1st boil Grams	2nd boil Grams	3rd boil Grams	4th boil Grams	5th boil Grams
"Welded".......	299.0	9.0	11.0	14.0	15.5	14.5
"Alloyed".......	302.0	11.0	17.0	16.0	18.0	23.0

As an etching medium, potassium cyanide solution at ordinary temperature developed differences in copper coatings with and without iron, but it was particularly successful in bringing out the coarse structure produced in cast copper by the presence of arsenic. In the following comparison No. 3 showed a fine grain and bright color when etched, No. 1 a distinct coarse and slightly darker one, and No. 2, with 0.41 per cent arsenic, was very dark and very coarsely crystalline:

	1	2	3
Copper.................	99.76 %	99.48 %	99.90 %
Arsenic.................	0.062	0.412	0.005
Oxygen.................	0.085	0.024	0.065
Electrical conductivity.....	82.75	44.75	97.9

For these analyses and the specimens of cast copper, the writer is indebted to Mr. G. L. Heath, Chief Chemist of the Calumet and Hecla Copper Company.

SUMMARY

Copper may be united to steel by alloying or welding. In the former method the copper is melted. In the latter it is plastic only: 950° C. is a favorable temperature for welding. Both methods, if properly carried out, give mechanically secure unions. The welding process is most satisfactory for the manufacture of copper-clad wire because the conductivity is not diminished by the presence of copper and iron alloys. Melted copper dissolves iron very rapidly. The resultant alloys are poor conductors of electricity. Iron and copper form an alloy if heated together in a non-oxidizing atmosphere to a point just above the melting point of copper. If heated hotter, alloy formation proceeds more rapidly.

Copper is extraordinarily resistant to atmospheric corroding influences. Tests of copper-clad sheet steel in Pittsburgh showed very little effect on the copper in twenty-two months. Copper is more expensive than zinc but costs only 40 per cent as much as tin. It is more durable than either. Combinations of copper and steel should be more widely used. Steel welded to copper does not corrode more rapidly than does the same steel entirely out of contact with copper.

Potassium cyanide in 25 per cent aqueous solution dissolves copper and barely attacks iron. It is useful as a solvent and as an etching medium for copper-clad steels and as an etching medium for cast copper containing arsenic.

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THE CONDENSATION OF GASOLINE FROM NATURAL GAS[1]

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In this paper are given some results of work performed by the Bureau of Mines having to do with the condensation of gasoline from natural gas.

CHEMISTRY OF NATURAL GAS

With the growth of the natural gas gasoline industry natural gases have been classified into two divisions so called "wet" and "dry" gases, depending upon whether or not gasoline can be commercially condensed from them. The classification is exceedingly loose because natural gas mixtures may range from those containing only methane as the combustible constituent (a gas difficult to liquefy) to those in which the hydrocarbon vapors predominate and which liquefy easily. Between the two extremes there are natural gases containing the different constituents, methane, ethane, propane, butanes, pentanes, etc., in many different combinations. ,Some of these may not contain enough of the desirable gasoline constituents for commercial purposes, others may.

Natural gases not found intimately associated with oil are the so-called "dry" gases. Those found in the same strata with oil and in intimate contact with the same are those from which gasoline is obtained in the natural gas gasoline industry. The Bureau of Mines finds as the result of many analyses that natural gases are mixtures in which hydrocarbons of the paraffin series predominate and that small quantities of nitrogen, carbon dioxide and water vapor are present. Hydrogen sulfide is sometimes present; perhaps other sulfur compounds too. F. C. Phillips found natural gases of Western Pennsylvania, which he worked with, to contain paraffin hydrocarbons, carbon dioxide and nitrogen. Other investigators invariably report at least small proportions of carbon monoxide, hydrogen and ethylene. Experimental errors in the work easily accounts for these errors. The authors of this paper believe the work of S. A. Ford as showing very large percentages of hydrogen to be in error. His analyses have been quoted many times in different text books. They were made in 1885. The authors of this paper in looking over the analyses made by them of thirty natural gas samples collected from different parts of the country find the heating value ranging from 685 B. t. u. to 1577 B. t. u. per cubic foot at 60° F. and 760 mm. pressure. These analyses will be incorporated with many others in a government publication. These gases range from marsh gas issuing from the marsh beds, and containing only methane as the combustible gas to casing head gases that are used for lighting and heating towns. Only two of the gases, those of the highest heating value, are probably adapted for gasoline condensation. One sample contained (as shown by combustion analysis) in addition to methane, carbon dioxide and nitrogen, 75.16 per cent of ethane. The natural gas of Pittsburgh has a gross heating value of about 1177 B. t. u. per cubic foot at 0° C. and 760 mm. pressure.

SIGNIFICANCE OF ORDINARY ANALYTICAL RESULTS

In the analysis of natural gases by the slow combustion method, the data obtained admit of the calculation of only two of the chief constituents. The mixture, however, may contain all of the gaseous paraffins and considerable quantities of the vapors of the liquid hydrocarbons. When the lower members of the paraffin hydrocarbons predominate, the results obtained are more accurate than when the higher members predominate. Natural gases from which gasoline can be extracted contain appreciable quantities of the liquid hydrocarbon vapors. In the analyses of these mixtures the ordinary slow combustion analysis will give only approximate results for several reasons.

First—The gas mixture often contains more than two combustible constituents.

Second—Some of the gases and vapors deviate considerably from the gas laws and their true molecular volumes[1] are unknown.

Third—So small an amount of the mixture must be used in some cases that experimental errors are greatly magnified in calculating to a percentage basis.

Typical analyses of two different natural gases follow which contain small amounts of methane and larger amounts of ethane, propane and butane with the vapors of the liquid hydrocarbons pentane, hexane, etc. These analyses serve to show how approximate a com-

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[1] Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8-12, 1913. Published by permission of the Director of the Bureau of Mines.

[1] A government publication by the authors which covers this question is in press.

bustion analysis may be even when the analysis is carefully performed.

In the analysis of gases of this type the explosion method is entirely out of the question. The analyses were made by the method of slow combustion. Duplicate analyses were made of each sample.

SAMPLE NO. 1

	I Cc.	II Cc.
Volume of sample taken	20.00	19.95
Oxygen added	95.70	95.30
Total volume	115.70	115.25
Volume after burning	64.10	64.00
Contraction due to burning	51.60	51.25
Volume after CO_2 absorption	22.10	22.60
Carbon dioxide produced by burning	42.00	41.40
RESULTS OF ANALYSES	PER CENT	
Ethane	96.00	98.75
Propane	6.00	3.33
Total paraffins	102.00	102.08

SAMPLE NO. 2

	III Cc.	IV Cc.
Volume of sample taken	20.35	23.50
Oxygen added	96.15	126.75
Total volume	116.50	150.25
Volume after burning	60.10	85.30
Contraction	56.40	64.95
Volume after CO_2 absorption	10.40	28.20
Carbon dioxide produced by burning	49.70	57.10
RESULTS OF ANALYSES	PER CENT	
Ethane	65.85	66.80
Propane	37.50	36.50
Total paraffins	103.35	103.30

The foregoing analyses show how a small difference in the contraction due to combustion and the carbon dioxide produced will, when calculated to the same basis, affect the distribution of the paraffins and also the total paraffin content. The fact that the gases total over 100 per cent is because the correct molecular volumes of all the gases present in the mixtures are not known. For example, in the case of analyses I and II (duplicate analyses) the contraction in I is 51.60 cc. from 20.00 cc. of the original sample while the contraction in II is 51.25 cc. This latter result, when calculated to 20.00 cc. of sample, gives a difference of 0.22 cc. from the first, which is the experimental error.

The carbon dioxide produced in I from 20.00 cc. of sample is 42.00 while that produced from II when calculated to 20.00 cc. sample is 41.50 cc. or a difference of 0.5 cc., the experimental error.

The combined difference in the contractions and carbon dioxide change the paraffin distribution by 98.75 — 96.00 or 2.75 per cent in the case of ethane and 6.00 — 3.33 or 2.67 in the case of propane. The total paraffin hydrocarbon content is changed only by 102.08 — 102.00 or 0.08 per cent.

In a like manner in the case of analyses III and IV (duplicate analyses) the contraction produced in III by the combustion is 56.40 cc. with 20.35 of sample while the contraction produced in IV calculated to 20.35 cc. of sample is 56.25 cc. or a difference of 56.40 cc. — 56.25 cc. or 0.15 cc., the experimental error.

The carbon dioxide from 20.35 cc. of sample is 49.70 cc. in III while the carbon dioxide in IV is 49.44 cc. when calculated to 20.35 cc. of sample. This is a difference of 0.26 cc., the experimental error. Here the combined difference of the contractions and the carbon dioxide change the paraffin distribution by 66.80 — 65.85 or 0.95 per cent in the case of ethane and 37.50 — 36.50 or 1.00 per cent in the case of propane. The total paraffin content is changed only by 103.35 — 103.30 or 0.05 per cent.

Although combustion analysis shows only approximately the quantity of paraffin hydrocarbons present, the total paraffin hydrocarbons are correct or nearly correct. The same can be said of the heating value and specific gravity as calculated from the analyses. The ascertaining of the different hydrocarbons that may be found in natural gases has long been a stumbling block to gas analysts. The ordinary eudiometer analysis offers nothing in the way of a complete separation. The total paraffin hydrocarbon content with only an approximation of the individual paraffin has been the only end attained. The authors in working on the problem succeeded in making a separation of a natural gas into its individual paraffin hydrocarbons by means of fractional distillation at low temperatures. Natural gas was first liquefied by means of liquid air and then by means of a Töpler pump, the methane was removed. The vapor pressure of liquid ethane (boiling point —93° C.) is so small at the temperature of liquid air (—190° C.) that two fractionations sufficed to remove the methane, which was measured and analyzed. The residual gas was then subjected to a temperature of —130° C. and as much gas as could be removed was withdrawn with the pump. The mixture withdrawn proved to be ethane and propane. At —130° C. all the ethane (boiling point —93° C.) and part of the propane (boiling point —45° C.) is removed. This fraction was measured and analyzed. The residual liquid was then allowed to volatilize and was found to be propane. The proportions were then found by simple calculations. Butane was not found within the experimental error of the manipulation which was perhaps 0.2 or 0.3 per cent. Traces of butane exist in the gas, however, also of pentane and hexane. The complete analysis including the quantity of each paraffin hydrocarbon found by the above method follows. For comparison the ordinary eudiometric analysis of the natural gas is given. The natural gas is that used in Pittsburgh.

	By liquefaction and fractionation Per cent	By eudiometric analysis Per cent
CH_4	86.8	79.2
C_2H_6	5.7	19.6
C_3H_8	6.2	...
N_2	1.3	1.2
Total	100.0	100.0

The carbon dioxide in the Pittsburgh natural gas amounts to a trace (0.03 per cent). The gas cannot be used for the commercial production of gasoline although it contains sufficient of the hydrocarbon vapors to produce some condensate (drip) in the pipe lines. This is because of the immense volume of gas passing. The gas comes from W. Va. and is typical in composition of gases from that field that are supplying many towns. The natural gas from the Hogshooter Pool of Oklahoma, some of which goes to Kansas City, contains only methane (95.4 per cent) as the combustible constituent. The rest is nitrogen and carbon dioxide (dry basis). The Bureau has the composition of the natural gases that are supplying many towns. Further work is being done by the authors on the fractionation of natural gases. More difficulty is experienced in making a separation when all of the gaseous paraffins and vapors of the liquid ones are present.

OCCURRENCE OF GASOLINE IN NATURAL GAS

The yield of gasoline from natural gas is determined largely by the quantity of the liquid paraffin vapors in the permanent gases. Temperature and pressure conditions in the well, gasoline content of the oil, and intimateness of contact between oil and gas, all affect the yield. Such rapid expansion of a gas from a casing head may occur as to cause a heavy condensation of vapors at the casing head.

Methane (critical temperature —95.5° C., critical pressure 735 pounds per square inch) is always in a well in the gaseous condition. Ethane (critical temperature 35° C., critical pressure 664 pounds per square inch) exists in some wells as a gas, in others, probably as a liquid. Propane and the butane are even more easily liquefied than ethane. In gases used for gasoline production they are present as gases. In such cases reduced pressures are usually applied to the wells. The gasoline vapors are mixed with these permanent gases in the same manner that moisture exists with air.

In gasoline plant operation, the pressure applied to condense the vapors must, of course, depend on the partial pressures of the vapors in the natural gas mixture. If butane (boiling point 1° C.) for instance constitutes twenty per cent of the mixture, there would be needed a total pressure of seventy-five pounds per square inch in order to have 15 pounds on the butane vapor, and cause condensation of the vapor to begin. For this reason one gas may produce condensate with 75 pounds, while another gas will need 200 to 300 pounds. In the standard type of cooling and pressure arrangement as used to-day, methane and ethane are not liquefied but some propane and butane are. In addition the final mixture as received at the collecting tank, will contain condensed gasoline vapors, *i. e.*, pentanes, hexanes, etc. There will also be found a portion of the gases methane and ethane dissolved in the liquids. In other words several changes will have taken place. One has to do with the condensation of vapor, another with the liquefaction of gas and another with the solubility of the permanent gases in the liquid produced. The three changes mentioned are so intimately connected with each other that one factor cannot be disturbed without affecting the others. For instance such a temperature and pressure could be employed as to increase the condensation of the desirable constituents (the gasoline vapors) but with increasing pressure and lowered temperature more of the undesirable gaseous constituents would liquefy. These when exposed to atmospheric conditions of temperature and pressure would immediately volatilize, carrying with them some of the gasoline constituents. At increasing pressures more ethane and methane would be dissolved. With release of pressure they too would escape.

TESTING NATURAL GAS FOR GASOLINE VAPORS

Before plant installations are made for the purpose of extracting gasoline from natural gas an investigation of the several factors should be made. These include (1) quality of gas, (2) quantity of the gas, (3) disposal of product.

QUALITY OF GAS

Laboratory methods in use at the present time consist chiefly of combustion tests, solubility tests and specific-gravity tests. The combustion analysis gives only a rough approximation. The specific-gravity test is much used. Natural gases may range in specific gravity from about 0.56 to 1.50, compared to air. Some gases are used for condensing gasoline that have as low a specific gravity as 0.80. All gases of this specific gravity are not adapted, however. If the carbon dioxide or nitrogen content of a natural gas is high and not known, the specific gravity test may be misleading.

Alcohol, claroline oil, olive oil, kerosene oil, etc., all have been used for determining the solubility of natural gases. The higher members of the paraffin series are more soluble in these solvents than are the lower members. The authors have used tests that consist in shaking 100 cc. of the natural gas in 50 cc. of alcohol or 35 cc. of claroline oil, and noting the loss in gas volume. The test is arbitrary. Under these conditions it was found that natural gases soluble to the extent of from 30 to 86 per cent of their volume were used for condensing gasoline. In all these tests inconsistencies have been noted, so that especially as regards the minimum specific-gravity tests and solubility numbers herein given one would not feel sure about the feasibility of plant installation.

Natural gases differ much in composition. The so-called wet gases, for instance, might contain a very large proportion of methane, with but little ethane, propane and butane, but enough of the gasoline vapors to warrant plant installation. Another gas with the same specific gravity might contain a comparatively small proportion of methane and ethane, a large proportion of butane and propane but not enough of the gasoline constituents to warrant plant installation. The safest recourse is to be had to some type of laboratory compressor or better still to a portable outfit consisting of gas meter, gas engine, compressor, cooling coils and receiver. Such an outfit can be hauled from well to well on a wagon. Tests conducted by such a method must also be in the hands of competent persons.

QUANTITY OF THE GAS

Many plants are in operation working on as little as 125,000 cubic feet of gas per 24 hours. Some are working on as little as 40,000 cubic feet. These latter are largely experimental. A fair sized plant to handle 125,000 cubic feet costs about $10,000. There are probably 200 plants in the United States making gasoline from natural gas.

VALUE OF RESIDUAL GASES

Residual gases left after plant operation are of high heating value, unless contaminated with air. Air may leak into the pipes due to reduced pressure on the pipe lines (as much as 25 inches of mercury). In one case the authors found that a residual gas had a heating value almost twice as high as the heating value of the Pittsburgh natural gas. According to the facts already presented the residual gas is bound to be a rich gas, because the methane and the ethane are not liquefied, and only a portion of the propane and butane. Neither are all the gasoline vapors condensed. Air may appreciably lower the value of the gas, however. Some residual gases contain 40 to 50 per cent of air.

Table I

Lab. No.	Kind of gas	Gross heating value 60° F. and 760 mm. Calculated	Specific gravity Air = 1	Per cent absorbed by 35 cc. claroline oil	Composition, Per cent							
					Air calculated from O_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2	Total
2281	Natural gas from Follansbee, W. Va....	2339	1.41	83.6	....	....	21.4	78.2	....	0.4	(a)	100.0
2284	Residual gas after 50 lbs. compression. Product has been removed...........	2295	1.38	82.0	....	....	26.6	72.8	....	0.6	(a)	100.0
2286	Residual gas after 250 lbs. compression. Product has been removed...........	1913	1.15	63.6	....	....	77.3	22.0	....	0.7	(a)	100.0

(a) Trace of CO_2 present. Gas is from 75 producing wells and is withdrawn under a reduced pressure of 20 inches of mercury. The gasoline is blended with low-grade refinery naphtha and then marketed.

DEPLETION OF THE RESIDUAL GAS AS REGARDS QUANTITY

To give exact figures for the quantity of gas and vapor that disappear from the raw gas in plant operations is impossible. If four gallons of condensate are produced from each 1,000 cubic feet of natural gas, about 140 cubic feet of gas per 1000 may disappear. This figure is based upon the equivalent of liquid butane, pentane, etc., in cubic feet of gas.

Table II

Lab. No.	Kind of gas	Gross heating value 60° F. and 760 mm.	Sp. gr. Air = 1	Per cent absorbed by 35 cc. claroline oil	Composition, Per cent							
					Air calculated from O_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	N_2	Total
2809(b)	Natural gas, McDonald, Pa......	1719	1.01	38.5	....	2.7	96.1	....	....	1.0	0.2	100.0
		1204(b)	..	27.0	30.1	1.9	67.3	....	....	0.6	0.1	100.0
2807	Residual gas after 20 lbs. compression product has been removed..	1233	..	30.1	29.0	0.7	69.6	....	....	0.6	0.1	100.0
2809	Residual gas after 80 lbs. compression, product has been removed..	1164	..	25.0	30.0	7.2	62.0	....	....	0.7	0.1	100.0

(a) This analysis calculated air-free to show the composition of the crude gas. (b) Actual composition of gas delivered to the compressor.

The following tables show the laboratory tests conducted on gases from two plants at various stages of plant operation. The Bureau has many more.

Table I gives the results of the analysis of the natural gas used by a plant near Follansbee, W. Va. The analysis, specific gravity and claroline absorption show this to be a rich gas. It will be seen that but little difference exists between the composition of the crude gas before and after it has been compressed to 50 pounds per square inch. It is only after compression to 250 pounds per square inch and cooling, that the composition of the gas mixture changes appreciably. The high heating value of the residual gas is apparent.

Table II shows the results obtained from a small plant near McDonald, Pa. This is not a very "wet" gas. Its claroline absorption number is rather low. It is probably near the lower limit of a gas adapted for the condensation of gasoline. The composition of the gas does not change to a very marked degree after it has been compressed to 80 pounds per square inch.

NOTE

The foregoing is abstracted from a bulletin covering in greater detail the condensation of gasoline from natural gas. This bulletin is in press. It treats of the waste of natural gas, status of the natural gas gasoline industry, future of it, utilization of casing head gas, occurrence of gas and oil, use of gas from flow tanks, value of plant equipment, chemistry of natural gas, occurrence of gasoline in casing head gas, gasoline plant operation, testing natural gas for gasoline, value of residual gas, air in the gas, life of wells, handling and blending the condensate, and the marketing of the product.

Bureau of Mines
Pittsburgh

SOME TESTS OF PAINTS FOR STEEL, SUBJECTED TO ALTERNATE EXPOSURE TO AIR AND FRESH WATER[1]

By Percy H. Walker[2] and S. S. Voorhees[3]

The following joint investigation was planned by the Geological Survey, Department of the Interior, and the Bureau of Chemistry, Department of Agriculture, in response to general requests for definite information regarding effective paint coatings for the protection of structural steel, especially when subjected to intermittent water immersion. Before the work could be started, however, certain general investigations, including protective coatings, were transferred from the Geological Survey to the Bureau of Standards, so that the present investigation was conducted under the joint direction of the Bureau of Chemistry and the Bureau of Standards.

The general investigation considered the protection afforded by paint coatings to both wood and steel structures under varying conditions of service. Such a program naturally resolved itself into a theoretical consideration of the agencies which cause corrosion and decay and means to prevent this action, and such theoretical conclusions had to be confirmed by an extended series of service tests before they could be accepted. A number of investigations and tests have been made on most of the phases of this general problem, but, owing to the difficulty of controlling the factors with sufficient exactness to obtain truly comparable results, the progress has been slow.

Composition of Pigments and Constants of the Linseed Oil

White Lead, Contract No. 8072:	
Spec. gravity (15.6° C./15.6° C.)	6.46
Total lead as PbO (per cent)	85.8
Carbon dioxid (CO_2) (per cent)	12.7
Loss on ignition less CO_2 (per cent)	1.6

The above analysis indicates the following composition:

Lead carbonate ($PbCO_3$) (per cent)	76.9
Lead hydroxid [$Pb(OH)_2$] (per cent)	23.1

Zinc White, American, Contract No. 2958:	
Specific gravity (15.6° C./15.6° C.)	5.56
Moisture (per cent)	0.2
Insoluble in HCl (per cent)	0.1
Lead	trace
Zinc oxid (ZnO) (per cent)	99.4

Lampblack, Contract No. 8128:	
Specific gravity (15.6° C./15.6° C.)	1.72
Moisture (per cent)	1.1
Ash (per cent)	0.07

Slag Pigment, Contract No. 10436:	
Specific gravity (15.6° C./15.6° C.)	3.51
Moisture (per cent)	0.2
Ferrous oxid (FeO) (per cent)	15.1
Ferric oxid (Fe_2O_3) (per cent)	3.4
Alumina (Al_2O_3) (per cent)	6.1
Manganese oxid (MnO) (per cent)	5.3
Silica (SiO_2) (per cent)	13.0
Calcium sulphid (CaS) (per cent)	1.1
Lime (CaO) (per cent)	41.4
Magnesia (MgO) (per cent)	9.1
Phosphoric anhydrid (P_2O_5) (per cent)	4.4

Flake Graphite, Contract No. 8129:	
Specific gravity (15.6° C./15.6° C.)	2.20
Moisture (per cent)	0.07
Ash (per cent)	6.8

Artificial Graphite, Contract No. 8123:	
Specific gravity (15.6° C./15.6° C.)	2.17
Moisture (per cent)	0.06
Ash (per cent)	7.2

Indian Red, Contract No. 8124:	
Specific gravity (15.6° C./15.6° C.)	5.12
Insoluble siliceous matter (per cent)	0.8
Alumina (Al_2O_3) (per cent)	2.6
Ferric oxid (Fe_2O_3) (per cent)	96.6

Chromium Oxid Green, Contract No. 8126:	
Specific gravity (15.6° C./15.6° C.)	5.02
Insoluble siliceous matter (per cent)	1.7
Ferric oxid (Fe_2O_3) (per cent)	0.1
Chromium oxid (Cr_2O_3) (per cent)	98.3

Chrome Yellow, Contract No. 8127:	
Specific gravity (15.6° C./15.6° C.)	5.75
Loss at 110° C. (per cent)	0.3
Total lead as PbO (per cent)	69.5
Chromic anhydrid (CrO_3) (per cent)	28.8
Sulfuric anhydrid (SO_3) (per cent)	0.7
Sodium oxid (Na_2O) (per cent)	0.3

Zinc Yellow, Contract No. 8125:	
Specific gravity (15.6° C./15.6° C.)	3.50
Loss at 110° C. (per cent)	0.2
Total loss on ignition (per cent)	13.8
Insoluble in acetic acid ($BaCrO_4$) (per cent)	1.6
Potassium oxid (K_2O) (per cent)	10.2
Zinc oxid (ZnO) (per cent)	38.2
Chromic anhydrid (CrO_3) (per cent)	41.6
Sulfuric anhydrid (SO_3) (per cent)	2.5

Red Lead, Contract No. 10368:	
Specific gravity (15.6° C./15.6° C.)	8.63
Insoluble in HCl (per cent)	0.3
Total lead (Pb) (per cent)	91.4
Lead peroxid (PbO_2) (per cent)	23.7

Kaolin, Contract No. 10357:	
Specific gravity (15.6° C./15.6° C.)	2.41
Silica (SiO_2) (per cent)	30.3
Alumina and Oxid of Iron ($Al_2O_3 + Fe_2O_3$) (per cent)	18.6
Lime (CaO) (per cent)	15.9
Sulfuric anhydrid (SO_3) (per cent)	21.7
Moisture and undetermined, by difference (per cent)	13.5

Magnetic Black, Contract No. 8066:	
Specific gravity (15.6° C./15.6° C.)	4.42
Loss at 110° C. (per cent)	0.6
Total loss on ignition (per cent)	5.2
Total iron calculated as Fe_2O_3 (per cent)	93.2
Ferrous oxid (FeO) (per cent)	29.9
Carbon dioxid (per cent)	8.0
Sodium	present
Calcium	trace

This material is, therefore, not pure Fe_3O_4 but has approximately the following composition:

Magnetic oxid of iron (Fe_3O_4) (per cent)	60.4
Ferric oxid (Fe_2O_3) (per cent)	18.3
Ferrous carbonate ($FeCO_3$) (per cent)	18.0
Sodium carbonate (Na_2CO_3) (per cent)	2.8
Moisture (per cent)	0.5

American Vermilion (Scarlet Lead Chromate), Contract No. 10518:	
Specific gravity (15.6° C./15.6° C.)	6.79
Total lead as PbO (per cent)	80.9
Chromic anhydrid (CrO_3) (per cent)	17.2
Sulfuric anhydrid (SO_3) (per cent)	1.1
Loss on ignition (below red heat) (per cent)	0.8

Linseed Oil, Contract No. 8067:	
Color	golden brown
Odor	normal
Specific gravity (15.6° C./15.6° C.)	0.9335
Acid number	1.7
Saponification number	193.6
Iodin number	179.6
Ash (per cent)	0.15

One of the national technical societies is engaged in this general research, but as no definite information was available on the protection of structural steel subject to intermittent immersion, in the present

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[1] Results of coöperative investigations carried on by the Bureau of Chemistry and the Bureau of Standards. Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8–12, 1913.

[2] Chief, Contracts Laboratory, Bureau of Chemistry.

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investigation the effect of fresh water immersion was studied. Fifteen paints were tested in this series, including twelve standard single pigments, two mixed pigments, and one experimental pigment. As the test was confined to a comparison of pigments the same oil and drier were used throughout the test. All the pigments except the experimental one were standard commercial products purchased in the open market, and analyzed in the usual manner in the Contracts Laboratory, Bureau of Chemistry.

While those tested do not include all the paint materials recommended for the protection of steel structures, they do include the standard types used for this purpose and these tests should be considered as only preliminary to aid in developing a more extended investigation at some later date.

PREPARATION OF DRIER

The drier was made in the laboratory by saponifying with caustic alkali the linseed oil used in the test, dissolving the resulting soap in water and precipitating the lead and manganese linoleates by adding lead acetate and manganous sulfate, respectively. The washed and dried lead and manganese linoleates were dissolved in pure spirits of turpentine so that the resulting solution contained 3.92 per cent lead and 0.79 per cent manganese.

PREPARATION OF PAINTS

Preliminary tests were made with the selected pigments to determine the amount of oil necessary to give a paint of a viscosity, as determined by the Stormer viscosimeter, of about 50 seconds (a paint of this viscosity having been found to have a good consistency for spreading) and to determine the amount of drier to cause the paint to dry in about twelve hours. In the actual preparation of the paints the pigments were ground in an improved No. 2 Harris mill with sufficient oil to form a paste. The pastes were then reground with the remaining oil as calculated from the preliminary tests, the drier was added, and the whole paint again run through the mill. Table I shows the actual composition and viscosities of the finished paints. The specific gravity of each paint was determined by the weight of 100 cc. at 21.1° C. (70° F.).

METAL USED

Plates of basic open hearth steel, one-eighth inch thick, 24 inches long, and 18 inches wide were used for all tests. Analysis of a sample taken from one of the plates gave the following results:

STEEL, CONTRACT NO. 15576

Determination	Bureau of Chemistry Per cent	Bureau of Standards Per cent
Silicon (Si)	0.019	0.019
Sulfur (S)	0.062	0.062
Phosphorus (P)	0.009	0.011
Manganese (Mn)	0.39	0.39
Carbon (C)	0.13	0.11
Copper (Cu)	0.011	0.013

MARKING PLATES

Each plate was marked by the position of one-eighth inch holes drilled 1 centimeter from the long upper edge of the plate. The distance in centimeters of each hole from the left hand short edge was the same as the number of the paint. As each paint was tested in triplicate, individual plates in each set were distinguished by one, two, or three one-eighth inch holes drilled 1 centimeter from the left-hand short edge and about 20 centimeters down that edge from the upper left-hand corner of the plate (see Fig. 1).

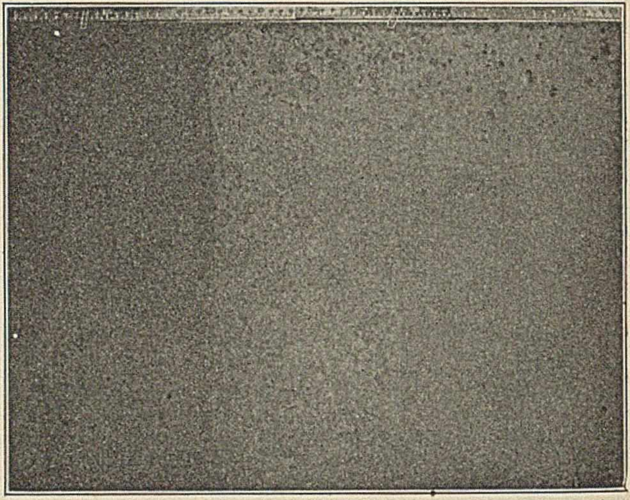

FIG. 1—MARKING PLATES (PAINT NO. 5, SET 1)

CLEANING PLATES

Any method of pickling to clean metal for paint tests is open to the objection that it is exceedingly difficult to insure complete removal of all the acid or salts from the pickled surface. Sand blasting is by far the best method; no corrosive acids are brought into contact with the metal and the sand-blasted surface is an ideal one for the application of paint.

The plates were thoroughly cleansed from all mill scale, dust, grease, etc., by sand blasting until a uniform surface of clean metal was exposed, and were painted while still bright. All were in perfect condition when painted except two, Plate 3 of Paint 1 and Plate 3 of Paint 5, which were somewhat rusted in tiny, deep spots extending rather uniformly over the surfaces. Since there was no appreciable difference between the three plates on these two tests it is evident that these small rust spots had no marked influence.

SPREADING RATE

It was intended to apply all paints at a uniform spreading rate of 900 square feet per gallon. The specific gravities were determined by weighing 100 cc. of the well mixed paint at 21.1° C. (70° F.). (The specific gravity multiplied by 3785.4 gives the weight in grams per gallon, and the product divided by 900 gives the number of grams of paint to be applied to each square foot.) Owing to the difficulty of thoroughly mixing the paints, the specific-gravity determinations are not always correct, and it would probably have been better to have made the calculations from the determined values for the various ingredients of each paint. As some errors were made in calculating, from the determined specific gravities, the weights of paint to be applied, the spreading rates were not all exactly 900 square feet to the gallon. They do not, however, differ very greatly from this figure and in Table I the spreading rates, calculated from the weight used and the determined specific gravities, are given in column 9, and from the calculated specific gravities, in column 10.

BRUSHES USED IN PAINTING

The brushes used in all the painting in this series of tests were flat chisel-edge flowing varnish brushes of good quality, the length of bristles outside of ferrule being between $2^1/_4$ and $2^1/_2$ inches. A new brush was used for each paint and after use it was cleaned in turpentine, then in benzine, allowed to dry, and kept free from dust until used again for a subsequent coat of the same paint.

APPLICATION OF PAINT

Each cleaned plate was supported over a table by four wooden pins which held it at points one-half inch from the edges (see Fig. 2). A suitable quantity of the well mixed paint in a casserole with the brush was weighed on a balance accurate to 10 mg. The paint was applied to the full surface of the plate, brushing backward and forward, and the casserole, paint, and brush were weighed from time to time until the decrease in weight showed that the required amount of paint had been applied. The plates were then lifted by the edges, turned over, and after the other sides were painted in a similar manner, were placed in a rack where they were supported by four points. Any abrasions were retouched, and allowed to dry thoroughly before applying the next coat (see Fig. 3). The second coat was applied to the full width and two-thirds of the length of the plate and the third coat to the full width and one-third of the length. All tests were conducted in triplicate and by the method of painting each plate represented first, second, and third coat work.

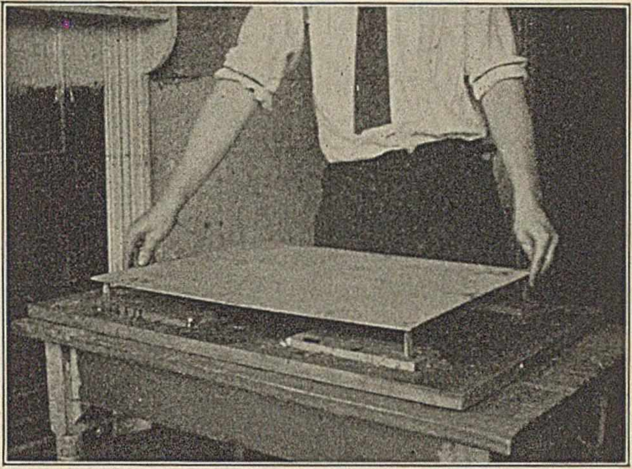

Fig. 2—Method of Supporting Plate for Painting

Table I—Data on Composition and Properties of Paints Used in Tests of Paints for Steel

1	2	3	4	5	6	7	8	9	10	11		
		Specific gravity				Weight per gallon (Sp. gr. × 3785.4)		Spreading rate (sq. ft. per gal.) calculated from		Date of painting		
Paint No.	Composition of Paint	Determined	Calculated	Viscosity (water = 6.2)	Paint applied per sq. ft. Grams	From determined sp. gr. Grams	From calculated sp. gr. Grams	6 and 7	6 and 8	Coat 1	Coat 2	Coat 3
1(a)	2270 grams white lead, 947 cc. linseed oil, 30 cc. drier	2.45	2.39	53	10.32	9274.2	9047.1	899	877	1910 Aug. 1	1910 Aug. 29	1910 Sept. 16
2	1435 grams zinc white, 2400 cc. linseed oil, 40 cc. drier	1.35	1.37	48	5.69	5110.3	5186.0	898	911	"	"	"
3	646 grams white lead, 556 grams zinc white, 825 cc. linseed oil, 40 cc. drier	1.78	1.87	46	7.47	6738.0	7078.7	902	948	"	"	"
4	235 grams lampblack, 1300 cc. linseed oil, 40 cc. drier	1.00	1.08	47	4.20	3785.4	4088.2	901	973	"	"	"
5(a)	1075 grams special slag pigment, 650 cc. linseed oil, no drier	1.83	1.76	46	7.33	6927.3	6662.3	945	903	"	"	"
6	780 grams flake graphite, 1300 cc. linseed oil, 40 cc. drier	1.18	1.20	48	4.95	4466.8	4542.5	903	918	Aug. 2	"	"
7	762 grams artificial graphite, 1150 cc. linseed oil, 45 cc. drier	1.21	1.21	47	5.07	4580.3	4580.3	903	903	"	"	"
8	1024 grams Indian red, 482 grams kaolin, 1300 cc. linseed oil, 40 cc. drier	1.60	1.59	50	6.71	6056.6	6018.8	903	897	"	Aug. 30	"
9	1799 grams Indian red, 1900 cc. linseed oil, 30 cc. drier	1.57	1.58	48	6.60	5943.1	5980.9	900	906	"	"	"
10(b)	1764 grams chromium oxid green, 1800 cc. linseed oil, 35 cc. drier	1.63	1.59	48	6.88	6170.2	6018.8	897	875	Aug. 3	"	"
11	1400 grams chrome yellow, 2960 cc. linseed oil, 40 cc. drier	1.21	1.26	49	5.07	4580.3	4769.6	903	941	"	"	"
12	1230 grams zinc yellow, 1600 cc. linseed oil, 35 cc. drier	1.36	1.39	48	5.74	5148.1	5261.7	897	917	"	"	"
13	1553 grams magnetic oxid black, 1950 cc. linseed oil, 40 cc. drier	1.48	1.44	50	6.22	5602.4	5451.0	901	876	"	"	"
14	500 grams red lead, 220 cc. linseed oil, no drier	2.39	2.54	50	10.04	9047.1	9614.9	901	958	Aug. 4	Aug. 15	Aug. 30
15	900 grams American vermilion, 300 cc. linseed oil, no drier	2.88	2.72	50	12.10	10902.0	10296.3	901	851	Aug. 30	Sept. 16	Oct. 12

(a) Plate 3 somewhat rusted in tiny deep spots over practically whole surface.

(b) Second coat did not dry at all for a long time. Was still sticky when third coat was applied.

PRECAUTIONS BEFORE EXPOSING PLATES

The preparation of the paints and the painting were done in a room free from laboratory fumes. The plates

TABLE II.—INSPECTION OF TESTS OF PAINTS FOR STEEL. Inspected by Walker and Schmidt, March 1, 1911—All plates in good condition

Paint No.	Inspection by P. H. Walker and G. C. Schmidt, May 1, 1911	Inspection by F. W. Smither and G. C. Schmidt, June 2, 1911	Inspection by S. S. Voorhees and P. H. Walker, July 3, 1911	Inspection by S. S. Voorhees and P. H. Walker, August 3, 1911	Inspection by P. H. Walker and G. C. Schmidt, Sept. 5, 1911	Inspection by F. W. Smither and G. C. Schmidt, October 13, 1911	Inspection by P. H. Walker and G. C. Schmidt, December 2, 1911	Inspection by S. S. Voorhees, W. A. Doying, and P. H. Walker, March 1, 1912.
1	Good condition.	Good condition.	Good condition; some rust near edges and in few small spots; no apparent difference between coats or different plates.	Plate 1, serious rusting of small area around abrasion(?) on bottom of coat 1; slight rusting on bottom of coats 2 and 3. Plate 2, slight rusting near bottom of coat 1; coats 2 and 3 in good condition. Plate 3, like Plate 2, except much more pronounced rusting on side next to wood of frame. (Plates shifted so as not to touch wood.)	Serious rusting on coat 1, Plates 1 and 2; otherwise like last inspection.	No material change since last inspection.	Considerable rusting. Plate 3 worse than other 2 plates.	Serious breaking through on all coats. Most marked on coat 1. Should have been repainted before.
2	Plate 1 somewhat blistered at bottom of coats 2 and 3; Plates 2 and 3 in good condition. Good protection.	No change since last inspection.	Good; some rust on coat 1; most pronounced on Plate 1 which also shows some blisters at lower edge of coat 3.	All show slight rusting on coat 1. No rust on coats 2 and 3. On Plate 2, coat 3, bright metal observed under loose blister 1/4 in. in diameter.	Little change since last inspection.	Slight blistering on coat 2, decided blistering on coat 3. Bright metal under blisters.	Some rust showing; more pronounced on Plate 1. Blisters more pronounced than on last inspection.	Serious corrosion on lower part of plates. Blistering on coats 1 and 2 with bright metal underneath. Paint has lost life on coats 1 and 2. Should have been repainted before.
3	Plate 1 considerably blistered at bottom of coats 2 and 3. Some blistering on Plates 2 and 3. Good protection.	Plate 1, considerable blistering at bottom of coat 3. A little at bottom of coat 2. Some blistering on Plates 2 and 3. Good protection.	Good; some rust showing on coat 1. Most pronounced on Plate 1 which shows blisters at lower edge of coat 3.	Same as Paint 2, except bright metal observed under blisters on all plates.	Little change since last inspection.	No material change since last inspection.	Decided blisters on coat 3, Plates 2 and 3; slight blisters coat 2, Plate 2; otherwise like last inspection.	Very slight rusting in body of paint; slight blistering with bright metal underneath, especially on coat 3. Needs repainting.
4	Plate 1 slightly blistered; Plates 2 and 3 good; good protection.	No change since last inspection.	Good; some rust on coat 1, Plate 1; very little on Plates 2 and 3.	No rust observed on any of the plates, but peculiar white spots were observed (growth of some kind).	Some rust on coat 1, Plate 1; otherwise like last inspection.	Little change since last inspection.	Decided rust on coat 3, Plate 3 being worse than other two. Some rust on coats 1 and 2, but not so pronounced as on coat 3.	Breaking through in fine rust spots which have spread on surface. Needs repainting but is better than Paint 3.
5	Some rust on all 3 plates.	Plates 1 and 2, considerable rust on coat 1; less on coat 2, still less on coat 3. Plate 3, very little rust.	Coat 1, rusting all over on all 3 plates. Considerable rust on coats 2 and 3.	Coat 1 very badly rusted. Coat 2 considerable rust. Coat 3 some rust. Paint failing.	All 3 plates need repainting; removed from tank and exposed on roof.			
6	Slight rust on coat 1, Plate 1. Plates 2 and 3 in good condition.	No change since last inspection.	Coat 1, peeling on all 3 plates; coats 2 and 3 in good condition.	Coat 1 slightly rusted. Coats 2 and 3 practically perfect.	More rust on coat 1. Otherwise like last inspection.	About same as last inspection.	Considerable rust on coat 3 and some on coat 2, Plate 2. Otherwise like last inspection.	Some breaking through on all coats, Plates 1 and 2, but not so much as Paint 4. Needs repainting.

7	Good condition except some scratched places.	No change since last inspection.	Good condition.	Coat 1 slightly rusted. Coats 2 and 3 practically perfect.	Same as last inspection.	About same as last inspection.	Some rust on coat 3, Plate 1; more pronounced on Plate 2; practically none on Plate 3.	Similar to Paint 6 but perhaps slightly more corroded. Needs repainting.
8	Good condition except some scratched places.	No change since last inspection.	Very slight rusting on coat 1. Good condition.	Possible indication of very slight corrosion on coat 1. Coats 2 and 3 perfect.	Same as last inspection.	Coat 1 same as last inspection. Coat 2, Plates 2 and 3 show indication of rust. Coat 3, more rust.	Same as last inspection.	Coat 1 badly corroded. Coats 2 and 3 breaking through worse than Paints 6 and 7. Needs repainting.
9	Practically perfect.	Practically perfect.	Good condition.	Possible indication of very slight corrosion on coat 1. Coats 2 and 3 practically perfect; corrosion on coat 1 less than in Paint 8.	More corrosion on coat 1 than in Paint 8. Otherwise like last inspection.	About same as last inspection.	About same as last inspection.	Similar to Paint 8. Needs repainting.
10	Little rust on coat 1, Plates 1 and 2. Plate 3 good.	Plate 1, rust on coats 2 and 3. Plate 2, a little rust on coat 1. Plate 3 good.	Coat 1, decided rusting on 3 plates.	Considerable rusting over whole of coat 1. Few spots of rust on coat 2. Coat 3 good.	Same as last inspection.	About same as last inspection.	Same as last inspection.	Coat 1 breaking through badly. Coats 2 and 3 in fair condition. These probably do not need repainting.
11	Good condition except one or two scratches.	No change since last inspection.	Coat 1, some rust; most pronounced on Plate 2.	Some rust on coat 1. No rust on coats 2 and 3.	Coat 1 badly rusted on Plates 1 and 2; slightly rusted on Plate 3. Coats 2 and 3, no change.	About same as last inspection.	Coat 1 considerably rusted; most pronounced on Plate 1; least on Plate 3.	Similar to Paint 10, except that coat 3, Plate 2, is breaking through.
12	Good condition except one or two scratches.	Plates 1 and 2 in good condition except one or two scratches. Plate 3 a little rust on coat 1.	Good condition.	Somewhat less rust on coat 1 than on Paint 11. No rust on coats 2 and 3.	Some rust on coat 1 on all plates; coats 2 and 3 good.	About same as last inspection.	Same as last inspection.	Best plates yet; some breaking through on coat 1; coats 2 and 3 in good condition. Do not need repainting.
13	Good condition.	A little rust on coat 1, on all plates.	Coat 1 failed. Coats 2 and 3 in good condition.	Coat 1 badly rusted. Coats 2 and 3 in good condition.	Coats 2 and 3 show some rust; most pronounced on Plate 3.	Coat 1 badly rusted. Coats 2 and 3 about same as last inspection.	Coat 1 considerably rusted; some rust on coat 2.	Coat 1 badly corroded; coat 2 somewhat corroded; coat 3 in good condition. Coats 1 and 2 need repainting.
14	Practically perfect.	Practically perfect.	Practically perfect.	Perfect, best yet.	Perfect.	Perfect.	Practically perfect.	Coat 1 gives fair protection, slight corrosion; coats 2 and 3 in excellent condition; best so far.
15	Practically perfect.	Practically perfect.	Excellent. A few spots on coats 1 and 2 of Plates 1 and 2, apparently abrasions.	Practically perfect. Equal to Paint 14.	Perfect.	Perfect.	Practically perfect. Peculiar growth, most pronounced on coat 3, Plate 2.	On coat 3, Plates 2 and 3, some discoloration which may be under paint. In other respects like Paint 14.

were dried in this room and kept there until the exposure tests were begun.

EXPOSURE OF PLATES

Three rectangular tanks large enough to hold 25 plates 18 by 24 inches were used for the exposure test. Tanks 1 and 2 were of wood and unlined, and tank 3 was lined with sheet lead. It was soon found, however, that tank 1 leaked so badly that it was necessary to line it. This was done with sheet zinc, so the actual exposures were made in a zinc-lined tank, an unlined wooden tank and a lead-lined tank. The plates were held in a vertical position by a wooden framework so that they were in contact with wood only and were separated from one another by a space of about 1 inch.

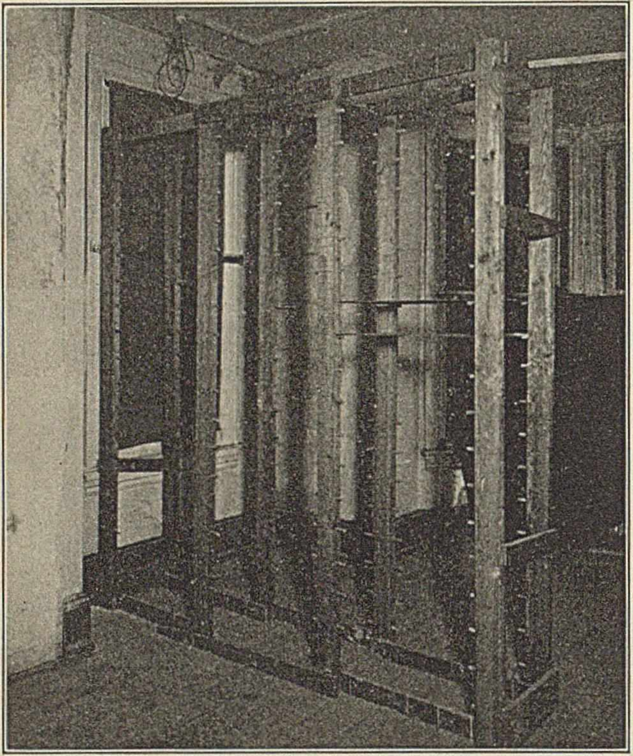

FIG. 3—FRAME FOR DRYING PLATES

The tests proper were started on February 1, 1911, when one plate of each test was placed in each of the tanks mentioned, these tanks being filled with water every afternoon at 4 o'clock and emptied the next morning at 9 o'clock. This filling and emptying was done each working day, except when the water was frozen from February 21 to 23, on March 16, and December 28, 1911, and from January 5 to 22, 1912. On the last named date the plugs were removed from the tanks and the water allowed to drain off as soon as the ice melted. The plates were kept in the empty tanks from that time. Table I gives data on the composition and properties of the paints used, spreading rates, dates of painting, and notes made while applying the paints; Table II gives results of nine inspections of these tests.

DISCUSSION OF FORMULAS USED

Paints 1, 2, 3, and 4 are standard formulas and require no comment. Paint 5, special slag pigment, is not a commercial pigment but is a material furnished by the Office of Public Roads, United States Department of Agriculture, as a material which, owing to its rust-inhibiting properties in aqueous solution, might be of service as a pigment. The analysis, however, shows the material to be highly basic in character and it was obviously impossible for it to produce a durable paint with linseed oil.

Paints 6 and 7 require no comment.

Paint 8, Indian red and kaolin, was intended to approximate in composition some of the native iron oxid pigments and at first China clay was secured to dilute the Indian red, but this was rejected since it was found to be largely adulterated with calcium sulfate. Kaolin, passing the United States Pharmacopoeia tests, was then used and the paint made and applied, but on making the analysis later this kaolin also was found to contain a large amount of calcium sulfate. An examination of the tests for kaolin in the Pharmacopoeia shows that these tests will not secure pure kaolin; the tests for this material should be thoroughly revised in the next edition of the Pharmacopoeia.

Paint 9 requires no comment.

Paint 10 is a little used and expensive pigment, but as its color is probably more permanent than that of any green made by mixing blue and yellow and as it has been used with good results in painting the cages at the National Zoölogical Park, Washington, D. C., it was deemed advisable to include it in the tests. The very peculiar behavior of this paint on drying is worthy of note. The first coat dried in less than twelve hours, but the second coat was not even tacky at the end of several days and was exactly like a mixture of pigment in a non-drying oil. It was at first thought that either some mistake had been made in the paint or that some unusual weather condition caused this peculiarity, but on painting a fresh piece of steel with the same paint, it was found to dry well as a first coat, but failed to dry as a second coat. The authors have no explanation to offer of this phenomenon.

Paint 11 requires no comment.

Paint 12, zinc yellow, is an expensive pigment, but has been highly recommended by some authorities as an inhibitor of rust.

Paint 13, magnetic oxid black, is a comparatively new pigment. It is worthy of note that the analysis shows the material not to be pure Fe_3O_4.

Paint 14 requires no comment.

Paint 15, American vermilion or scarlet lead chromate, is an expensive pigment, but one which from its excellent record in other tests should be included in any set of pigment tests.

CONCLUSIONS

The results of inspections given in Table II require very little comment. There are some inconsistencies in the reports, but as these inspections are merely results of general opinions on the condition of the plates inspected, such inconsistencies are to be expected. The notes are given essentially as taken down by the inspectors at the time of inspection.

The authors realize that no sweeping conclusions can be drawn from any one series of tests, and while they feel that more care has been taken to eliminate all variables except the pigments than has been taken in any previously published service tests, they think that results which are not in accordance with previous tests and experience should be taken with caution. The excellent showing, however, of Paints 14 and 15 are wholly in accordance with investigations by others and with the experience of users of paint for steel. Red lead and linseed oil and American vermilion (scarlet lead chromate) and linseed oil are undoubtedly among the very best for the protection of iron. The suggestion is therefore offered that future tests be made by adopting such a formula as Paint 14 as a standard and painting half of each plate tested with the standard and the other half with the paint to be tested. If the plates are cleaned by sand blasting instead of pickling it can safely be assumed that the only variable is the paint and much better conclusions may be drawn than when possible variations in the metal must also be considered.

Bureau of Chemistry and Bureau of Standards
Washington

THE CORROSION OF METALS BY WATER

By A. T. Stuart

Received June 17, 1913

Part I—Relative Corrosivity of "Mechanically Filtered" and "Raw" Water

Conditions in each of the following series of experiments were quite uniform so that comparisons within that set are possible. The metals used were employed in the form of wires, cut in equal lengths. These were coiled and suspended in bottles containing 400 cc. of the water to be examined. The measure of corrosion was obtained by wiping the wires with a cloth and finding the loss in weight.

In order to ascertain the effect on corrosion of unlike metals in contact, two common metals of greatest difference in potential were chosen. The wires were wound around each other, then coiled and suspended as before.

These tests were not allowed to last longer than seven days, for it was felt that in that time actual conditions in any civic supply were already exaggerated, contact surfaces considered. At the end of that time considerably larger amounts of iron were capable of being transported by the water than could ever be tolerated in practice.

The following waters were tested:

1. From Watertown, N. Y., "mechanically filtered," Sample "A."
2. From Watertown, N. Y., "mechanically filtered," Sample "B."
3. From Watertown, N. Y., "raw," Sample "C."
4. From Ottawa, Ont., "mechanically filtered," Sample "D."
5. From Ottawa, Ont., "raw," Sample "E."
6. From Ottawa, Ont., "chlorinated" (only), Sample "F."
7. From Ottawa, Ont., MgO used as precipitant, Sample "G."

Experiment 1A showed that waters "A," "B," and "C" were equally corrosive.

It is evident from these figures that no appreciable differences exist in the action on iron of raw or treated waters (mechanical filtration) in so far as they may be revealed by losses in weight of the metals. It is significant that the results obtained are the same for all samples of water except sample "G."

Although these figures are practically identical, there are extreme and important differences in the character of the water. Thus, it was found that raw waters, although corroding iron to the same extent, do not coat the iron with as much flocculent material nor do they allow it to settle out, as is the case with treated waters, but retain a large proportion in solution, which may perhaps be of a colloidal nature. Treated waters, at ordinary temperatures, became very murky and opaque and, when hot, large amounts of brownish red rust appeared. This is popularly known as the "red water trouble." However, it must be noted that our figures indicate that the actual amounts of iron corroded were the same for treated or raw waters.

Losses in Weight (Grams) of Various Metals Due to Corrosion by Water

Exp. 1—Iron Wire "A" Alone

Water	"F"		"A"		"B"	
At 22° C.	0.0269	0.0274	0.0280	0.0284	0.0282	0.0271
At 60° C.	0.0394	0.0317	0.0324	0.0316	0.0300	0.0258

Exp. 2—Iron Wire "A" Alone

Water	"E"	"D"	"G"
At 22° C.	0.0277	0.0261	0.0203
At 50° C.	0.0540	0.0529	0.0185

Exp. 3—Metals in Contact (Iron Wire "B")

	Water "E" Raw		Water "D" filt	
Iron and copper	Iron	Copper	Iron	Copper
At 22° C.	0.0369	0.0000	0.0375	0.0000
At 50° C.	0.0743	0.0000	0.0592	0.0000
Iron and aluminum	Iron	Aluminum	Iron	Aluminum
At 22° C.	0.0248	0.0000	0.0225	0.0000
At 50° C.	0.0315	0.0023	0.0260	0.0028
Iron alone	Iron		Iron	
At 22° C.	0.0317		0.0328	
At 50° C.	....		...	
Lead & aluminum	Lead	Aluminum	Lead	Aluminum
At 22° C.	0.0016	0.0003	0.0067(?)	0.0000
At 50° C.	0.0023	0.0003	0.0013	0.0014
Lead alone	Lead		Lead	
At 22° C.	0.0012		0.0007	
At 50° C.	0.0011		0.0014	

(Water "F" used in All Cases. Iron Wire "B")

	At 22° C.		At 50° C.	
Iron alone				
Iron.........	0.0289	0.0292	0.0589	0.0578
Iron & aluminum				
Iron.........	0.0220	0.0211	0.0125	0.0168
Aluminum.....	0.0000	0.0000	0.0034	0.0026
Iron & copper				
Iron..........	0.0318	0.0314	0.0623	0.0603
Copper......	0.0000	0.0000	0.0000	0.0000
Lead alone				
Lead..........	0.0016	0.0020	0.0045	0.0034
Lead & aluminum				
Lead..........	0.0014	0.0031	0.0032	0.0032
Aluminum......	0.0005	0.0000	0.0010	0.0004
Lead & copper				
Lead..........	0.0336	0.0436	0.1203	0.1192
Copper......	0.0000	0.0000	0.0000	0.0000
Copper & aluminum				
Copper.......	0.0000	0.0000	0.0000	0.0000
Aluminum.....	0.0084	0.0089	0.0036	0.0035

Part II—Effect of Water on Metals in Contact

Apparently the state assumed by the iron corroded from the metal is a much more important question from the standpoint of a city supply than the actual amounts. The conclusion in this connection is that the so-called mechanical treatment of waters of these types is very liable to bring about this troublesome discoloration.

It may be noted here that both these waters examined were of low mineral content and highly colored by peaty matter. It would be of interest to follow this matter further with various other types.

These figures are in excellent accord with the electrolytic theory of corrosion and illustrate an easy means for investigating this subject. A graphic representation could be presented with the aid of further figures which would be very interesting.

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SOME EXPERIMENTS ON THE CONVERSION OF LONGLEAF PINE TO PAPER PULP BY THE SODA AND SULFATE PROCESSES[1]

By Sidney D. Wells

INTRODUCTION

During 1912 the Forest Service in coöperation with the University of Wisconsin undertook a series of experiments on longleaf pine, *Pinus palustris*, with the following objects:

1. To study what influence the variable cooking conditions have in the sulfate process of pulp-making.
2. To determine the suitability of longleaf pine for paper pulp.
3. To compare the sulfate process with the soda process.

This work has been only partially completed but since there is urgent demand for information on the adaptability of longleaf pine, or southern pine as it is more commonly called, for the manufacture of paper pulp, it has been thought advisable to give what indications our work has so far made manifest.

Longleaf pine was chosen on account of the large quantities of this wood that are being wasted in the lumber operations of the southern states and also because many logs are at present being sawed into lumber at little or no profit on account of their small diameter which would be of admirable size for pulpwood. Furthermore, the large amount of resinous matter in this wood made it desirable as an extreme test of a cooking process and the long, thick-walled fibers of the wood assured a strong pulp if it could be produced without a too drastic treatment.

EXPERIMENTAL PROCEDURE

The cooking operations in this work were conducted in two forms of digesters. The first form consisted of a small rotary autoclave of about 2-gallon capacity which was heated with Bunsen burners. The other form was a vertical digester of 60-gallon capacity, heated by direct steam. The greater portion of the work was accomplished in the former and in all 145 cooks made. The data obtained in these cooks were used in determining the conditions for the larger digester in which 19 cooks were made to obtain conditions more nearly comparable with those used in commercial practice.

The wood used was procured in Louisiana and Mississippi, and was fairly average in rate of growth, size, and content of resinous matter. It was freed from bark and reduced to chips five-eighths of an inch long with the grain. These chips were allowed to become air-dry and were thoroughly mixed and sifted to remove any dirt and small pieces.

The cooking liquors were made up by dissolving the required amounts of commercial caustic soda, sodium sulfide, Glauber's salt, and soda ash to produce solutions of the desired concentration of each of these chemicals.

In studying the influence of the variable factors entering into the cooking operation the small autoclave was used. The effect that any one variable condition exerted was determined by a series of cooks made varying the condition under observation, and maintaining the other conditions as nearly identical as possible in each cook. The effects were ascertained by determining the yield of pulp and carefully treating the pulp in a hollander beating engine to develop a stuff capable of producing as strong a sheet as possible when made into paper. The quality and color of the pulps were judged by inspection, feel, amount of beater treatment necessary, and the strength and wearing qualities of the paper produced.

THE EFFECTS OF VARYING THE AMOUNTS OF CHEMICALS

The effect of varying the caustic soda or sodium sulfide was a decrease in yield and a lighter colored pulp with an increase in either one or both of the chemicals. Caustic soda was found to be about twice as drastic in its action as sodium sulfide and with the same yield the pulp produced by the former was lighter than that produced by the latter. The yields, however, do not decrease directly in proportion to the amounts of chemical used, and between 30 and 50 pounds of caustic per 100 pounds of chips the decrease in yield is much less for equal steps than below or above these amounts. The disagreeable odor caused by the production of mercaptans increased with the increase of the sodium sulfide, and was much more noticeable where the larger proportions of this chemical were used.

The sodium carbonate and sulfate present in the cooking liquor produced no very apparent effect except where the former was present in relatively large amounts when a retardation in the action of the other chemicals present was noticeable. Enough cooks were not made, however, to definitely establish this indication.

THE EFFECT OF VARYING THE PRESSURE, DURATION OF COOKING AND CONCENTRATIONS

The effect of increasing any one of these variables was to increase the severity of the cooking action attainable with the same quantity of cooking chemicals. With any combination of the above conditions there is a definite amount of chemical necessary to produce a pulp of the best quality and it is possible to use a wide range of conditions to produce approximately the same result.

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[1] Paper presented at the 48th Meeting of the A. C. S., Rochester, September 8-14, 1913.

SEMI-COMMERCIAL COOKS

In the cooks in the large digester the object sought was to obtain the best quality of pulp. It was found that easily-bleaching pulps could not be obtained without using a very drastic digestion with a high percentage of alkali, and that the pulps produced were very low in yield and extremely soft and weak. It was, therefore, decided to devote attention toward producing the strongest pulps possible, and treat these pulps in the beater to make the highest grade of "Kraft." Although the strength of the paper was constantly considered, the question of yield was also very important and the best cooks were determined with these two objects in view.

The best cooks secured were made under the following conditions:

Caustic soda charged per 100 pounds bone-dry chips, pounds	15.0
Sodium sulfide charged per 100 pounds bone-dry chips, pounds	7.5
Initial concentration caustic soda in cooking liquor, grams per liter	26.5
Initial volume liquor per pound of chips, gallon	0.68
Total duration of cook, hours	3.5
Duration of cook at maximum steam pressure, hours	3.0
Maximum steam pressure, pounds per square inch	100.0

The yields of crude pulp under these conditions were 49 per cent of the weight of the wood and the strength of the paper produced as determined on the Mullen tester was 9 pounds per thousandth of an inch of thickness. An average sheet of 0.005 of an inch tested 45 pounds and weighed 45 pounds per ream of 500 sheets 24 inches by 36 inches. Not only was the paper exceptionally strong but it was very resistant to wear and folding. The latter fact is apparent by some tests made on it in a Schopper Folding Tester in which it withstood 1200 double folds before breaking.

Cooking Conditions for Four Typical Semi-Commercial Cooks

									Beater treatment			
	Caustic soda charged per 100 lbs. bone-dry chips	Sodium sulfide charged per 100 lbs. bone-dry chips	Initial concentration of caustic soda in cooking liquor	Initial volume of cooking liquor per 100 lbs. bone-dry chips	Total duration of cook	Duration at maximum steam pressure	Maximum steam pressure	Yield of crude pulp	Duration of light brush	Period of lowering roll	Duration of stiff brush	Pop test per 0.001 inch of thickness
	Lbs.	Lbs.	Grams per liter	Gallons	Hours	Hours	Lbs. per sq. inch	Per cent	Hours	Hours	Hours	Lbs.
Large yield	15.0	7.5	26.5	68.0	3.0	2.8	90	61.2	1.5	0.5	2.0	7.0
Medium yield	15.0	7.5	26.5	68.0	3.5	3.0	100	49.0	4.0	0.5	2.5	9.0
Small yield	20.0	10.0	44.6	54.0	3.0	2.5	103	45.3	1.5	0.5	1.5	10.0
Soda cook	30.0	0.0	90.0	40.0	6.0	5.5	100	39.8	6.0	0.0	0.0	9.0

The pulps under these conditions were very chippy when blown but the chips were very soft, had no hard hearts and were readily broken up in the beater. An ordinary hollander with steel fly bars was used and the pulp was beaten two hours at light brush, four hours at stiff brush, and one-half hour was spent in lowering the roll from one stage to the other.

Stronger papers than these were produced but the yields fell off considerably. Yields up to 61 per cent were obtained but the strength fell off more than could be compensated by using proportionately heavier paper. It is very probable that with basalt lava beater rolls a stronger paper could have been produced with these pulps using the same or an even less consumption of power and in much less time.

SODA COOKS

To compare the soda process with the sulfate process in cooking longleaf pine several soda cooks were made. It was found that soda pulps could be made that would produce paper capable of resisting bursting pressure to the same degree as the best paper made from sulfate pulp but the wearing qualities were not nearly as good and the yields were from 5 to 10 per cent less. The unbeaten pulps were soft and fluffy for even slightly undercooked pulps, and although they could be hardened in the beater the treatment was longer, and much greater care had to be exercised to avoid cutting the fibers. Furthermore, although a fairly good grade of kraft can be made of sulfate pulp with a yield of 60 per cent, soda pulp produced with that yield would be so undercooked and brittle that only very poor wrapping could be produced. Moreover, it was found necessary to cook soda pulp at least 6 hours to secure good results while in the sulfate process $3^{1}/_{2}$ hours were found sufficient. Thus in the latter process the same digester capacity would produce two-thirds more pulp per day.

GENERAL CONCLUSIONS

Although the experiments performed in this investigation are only a portion of what are contemplated they seem to make apparent the following facts:

I. That longleaf pine is well adapted for the manufacture of natural-color kraft pulps and papers.

II. That the sulfate process when applied to this wood affords pulps of better quality and higher yields than the soda process.

III. That kraft paper can be made from longleaf pine equal or superior in quality to the imported or domestic kraft papers now procurable.

IV. The high specific gravity of the wood insures a greater yield per cord to this wood than is possessed by any other commercially important pulpwood.

The data of these experiments given in greater detail is contained in a report entitled "The Utilization of Longleaf Pine for Paper Pulp" by H. E. Surface and R. E. Cooper which is now in press at the Government Printing Office.

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INVESTIGATIONS WITH THE U. S. BUREAU OF MINES MODIFICATION OF THE ABEL-PENSKY AND PENSKY-MARTENS FLASH-POINT TESTERS[1]

By Irving C. Allen and A. S. Crossfield

In the handling of lamp oils, particularly in mines and in buildings where open lights are used, it is important that a relatively safe oil, *i. e.*, one with a high flash point, be employed. Equally important is the determination of the inflammability of all oils in common use. This paper, which is a brief of Technical Paper No. 49, published by the Bureau of Mines in the interest of greater safety at mining and metallurgical plants, does not aim to establish definite flash points for oils but describes the instruments and methods of testing that can be used as a basis on which to establish such flash points.

THE FLASH POINT

In the various methods used for determining the flash point of an oil the temperature at which its vapor flashes is not a definite factor but is dependent on a number of physical and chemical conditions not under the control of the operator. It is not an indication of the value of an oil for any particular purpose. It is an indication only of the temperature at which the oil gives off vapors in such proportions that they form an inflammable mixture with the air. If exposed to an electric light or a flame the mixture will ignite and the flame extend throughout the mixture, that is, an explosive mixture of vapor and air is formed.

THE FIRE HAZARD

The flash point, although probably the most important factor, will not, by itself, determine the fire hazard of any substance. The fire hazard of a substance is also affected by the volatility, the boiling point, the vapor pressure, the vapor density, the diffusibility and tendency of the vapors to travel and their explosive limits in air, its tendency to chemical change, the quantity of heat liberated per unit of time and unit of volume, the temperature of the flame, the corrosive action and toxic properties of the substance and of its products of combustion, its behavior toward water both before and after ignition, and the tendency of the substance to leak.

A requirement that an oil has the highest practicable flash point, tending thereby to reduce the fire hazard to a minimum, is praiseworthy and humane. To require too high a flash point may impair the burning qualities of a lamp oil and also work a hardship on the refiner. However, the immediate profits of the refiner should be deemed less important than the safety of the user and the protection of the public against possible loss of life and of property by fire.

The fire hazard of lubricating oils is of importance when the lubricants are used in rapidly running machinery, as in spinning mills, wood mills, etc., or in factories containing combustibles and in compressors for air, ammonia, or other gases.

Particular attention should always be given to the handling, storage, and inspection of all inflammable liquids.

The Bureau of Mines in Technical Paper No. 49 has recommended the adoption of a modified form of the Abel-Pensky and Pensky-Martens testers for the determinations of the flash points of oils flashing below 150° C. The reasons for the recommendations of these testers are clearly set forth in Technical Paper No. 49, a brief abstract of which includes (1) the reasons for the necessity of exact determination of flash points of oils to determine the fire hazard with their use; (2) the historical development of flash-point testing with descriptions of testers in use; (3) the different factors that influence the obtaining of exact and concordant results; (4) and directions for the use of the two testers recommended.

The modifications of the older forms of Abel-Pensky and Pensky-Martens testers consist of the following: each cup has been fitted with an annular overflow cup into which the excess of oil due to the expansion on heating flows through a small opening in the side of the cup on a level with the filling point. This assures the volume of the oil and the volume of the vapor mixture above the oil remaining constant. The Abel-Pensky tester is provided with a paddle-wheel stirrer identical with that of the Pensky-Martens, while the automatic slide of the Abel-Pensky tester has been fitted to the Pensky-Martens cup. However, in the last change it was found necessary to raise the clock work on posts above the hot bath as the intense heat drew the temper from the spring. The two testers as recommended are identical with the exception of the use of the water bath for the testing of low flash oils and the metal-air bath for those of high flash point. The cups, the automatic opening devices and the stirrers of the two testers are interchangeable. An investigation undertaken in these laboratories indicates that the Pensky-Martens tester can be used very satisfactorily for the testing of low flash-point oils though the temperature regulation is not as nice as with the water-jacketed Abel-Pensky tester. The same conclusion has been reached by other investigations.[1] Each tester is fitted with gas or oil ignition burners.

The present paper includes results of a brief investigation with the two testers. A degree of accuracy greater than 0.5° C. for oils flashing below 100° C. and 1.0° C. for oils flashing above 100° C. was not attempted and any fractions of degrees reported in subsequent tables are derived as averages of several tests or from thermometer, barometer or instrument corrections.

STANDARDIZATION OF INSTRUMENTS

To obtain comparable results the two instruments were compared with an Abel-Pensky tester standardized in 1908 by the Physikalische Technische Reichsanstalt, certificate No. S. & R. 3114. Determinations of flash points of three different oils were made on the three instruments. Results obtained are the averages of five tests agreeing within 0.5° C. and are shown in Table I.

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[1] Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-14, 1913, by permission of the Director of the U. S. Bureau of Mines.

[1] Dr. H. Wiebe, "Die Obere Brauchbarkeitsgrenze des Abel-Penskyschen Apparates and seine Vergleichung mit dem Penskyschen Flammpunktprüfer, *Petroleum*, **1913**, Band VIII, S. 1061.

Table I—Comparison of Bureau of Mines Testers with Abel-Pensky Tester S. & R. 3114

Average of five tests each

Sample	F. P. by Abel-Pensky S. & R. 3114	F. P. by B. of M. modification Abel-Pensky	Difference	F. P. by B. of M. modification Pensky-Martens	Difference
X	47.3°	48.0°	+0.7°	49.0°	+1.7°
No. 1086....	36.3°	37.0°	+0.7°	37.8°	+1.5°
No. 1087.....	44.5°	45.5°	+1.0°	46.2°	+1.7°
Average.......	...	...	0.8°	.	1.6°

In all results hereafter reported the above corrections have been made. The large corrections obtained make it advisable to have all instruments intended for exact work compared with some fixed standard.

USE OF GAS AND OIL IGNITION FLAMES

The use of gas or oil test flames is optional. Comparative tests made, using natural gas, colza oil and lard oil as ignition flames, gave results with a maximum difference of 0.3°, which is well within the error of manipulation. A petroleum distillate, "300° burning oil," on the other hand, gave a flash approximately 0.8° too high and the use of such an oil as an ignition flame is not recommended. The difference is probably accounted for by the fact that the latter flame was quite difficult to regulate, due to its rapid flow through the wick and that the combustion was incomplete as indicated by a bright luminous flame, which in itself may have obscured the first flash. For ease of manipulation a gas flame is most desirable.

Table II—Comparison of Flash Points with Gas and Oil Test Flames

Sample	Gas test flame	Lard oil test flame	Colza oil flame	Instrument used
1087..............	45.5	45.4	45.2	B. of M. modification
Kerosine X........	48.0	48.1	47 7	of Abel-Pensky

INFLUENCE OF STIRRER

The heat is applied to the oil from the bottom and sides of the cup with the result that there are convection currents set up within the oil with the general direction across the bottom of the cup, up the sides, across the top and down the center and past the thermometer bulb. Consequently, the oil as it passes the thermometer is slightly cooler than that at the circumference of the surface and a lower flash point will be recorded than is actually the case. This is clearly shown in Table III. Further, the greater the rate of heating the greater will be the convection currents and consequently the greater will be the difference between the temperature of the oil at the circumference and the temperature at the center of the cup. Also the higher the flash point the greater will be the temperature differences. The differences are almost entirely removed by the use of a stirrer and it has been found easier also to get concordant results in a stirred cup than in one that is without a stirrer.

Table III—Influence of Stirrer

Average of three tests each

Sample	F. P. B. of M. modified Pensky-Martens stirred	F. P. B. of M. modified Pensky-Martens unstirred	F. P. B. of M. modified Abel-Pensky stirred	F. P. B. of M. modified Abel-Pensky unstirred	Flash point Pensky-Martens stirred	Flash point Pensky-Martens unstirred
Kerosine X.......	...	...	..	..	46.2	45.7
1086.............	...	...	37.0	37.1	35.6	35.1
1087.............	46.2	45.4	45.5	45.2	44.3	45.8
1092.............	117.0	115.1	..	..	...	..
1095.............	184.7	183.0	..	..	...	..
1096.............	196.4	195.6	..	..	..	.

Different investigators (B. of M. Tech. Paper No. 49, p. 12) have found that a definite filling of the cup has a very appreciable influence on the determination of the flash point. Filling the cup above the point raises the flash point. The reasons for this are quite apparent. The oil as it is heated expands, the surface of the oil is brought nearer the test flame and a lower flash point results. Expansion of the oil reduces the volume of the gas mixture, an explosive mixture is formed at a lower temperature and consequently a lower flash point is recorded. An explosive mixture would be obtained at a lower temperature from a fixed weight of oil than from a fixed volume and a lower flash point would result. To do away with these sources of error the modified testers have been fitted with overflow cups so that as the oil is heated the increase in volume is run off and both volume of oil and volume of vapor mixture are kept constant. The above assumptions are borne out in Table IV.

Table IV—Comparison of Flash Point with Constant Weight and Constant Volume

Average of three tests

Sample	F. P. B. of M. modified Pensky-Martens constant vol.	F. P. B. of M. modified Pensky-Martens constant weight	Difference
1087	46.2	45.8	0.4
1092	117.0	115.1	1.9
1095	184.7	183.0	1.7
1096	196.4	195.3	1.3

The suggestion has been made that the overflow oil in the outer cup will be much hotter than the temperature indicated by the thermometer within the cup, that the vapors liberated will pass back into the cup and give a flash below the true flash of the oil, but it is believed that such conditions do not exist. In the first place the cup is so constructed that the bottom is directly exposed to the hot bath and if stirred the oil in the cup is at a temperature not appreciably lower than that in the overflow cup. The volume of the oil that overflows is small compared with that in the cup; and the quantity of vapors liberated from such a small volume even at a slightly higher temperature would have little effect on the flash point, particularly that fraction of the small volume which might pass back into the cup. Also, it is hardly to be assumed that the vapors would pass back into the cup rather than escape around the loose fitting ring of the overflow cup. The views above are borne out by the fact that in no case was the flash point of an oil determined in the cup with the overflow lower than that obtained when the overflow outlet was plugged. As further proof, comparisons were made of the flash point of an oil obtained in the usual way and of the flash obtained by placing a quantity of low flash oil in the overflow cup. The results are shown in Table V.

Table V

Test	Sample No. 1087	Sample No. 1087 with 5 cc. of No. 1086 (F. P. = 37°) in the overflow cup	Instrument used
No. 1	45.4	45.4	B. of M. modified
No. 2	45.3	45.4	Abel-Pensky
No. 3	45.8	45.4	
Average	45.5	45.4	

SUMMARY

The important factors to be considered in the construction and manipulation of an instrument to determine the flash point of an oil may be stated as follows:

(1) The conditions under which the test vapors are generated should be as like as possible to the conditions found in practice.

(2) Corrections should be made for variations from the normal barometric pressure.

(3) The size and dimensions of the cup.

(4) The size, shape, depth of immersion and exposed part of the thermometer should be definite and in every case the thermometer should be calibrated.

(5) The oil should never be exposed for any length of time at temperatures greatly higher or lower than the normal temperature.

(6) The rate of heating on testing should be constant and at a rate of about 1° C. for lamp oils and 3°–5° C. for high flash-point oils.

(7) The oil should be uniformly stirred during the test.

(8) The test flame should be of definite size, should be exposed at a fixed distance above the surface of the oil and exposed for a definite length of time.

(9) All water should be removed from the oil prior to testing.

(10) In general testing, so far as possible, the effect of the personality of the operators should be eliminated and the manipulation of the tester made entirely mechanical and automatic.

The most accurate tester and the tester that most nearly reproduces actual working conditions should be adopted for official tests. Considering all of the above factors, it is believed that these two testers, the Abel-Pensky and the Pensky-Martens, as modified by the Bureau of Mines, most nearly meet with the desired conditions.

The Bureau of Mines flash testers have been officially adopted by the National Fire Protection Association, the Independent Petroleum Marketers' Association of the United States and are now being considered for adoption by committees on tests of the National Petroleum Association, the American Chemical Society, the American Society for Testing Materials and the International Petroleum Commission.

Bureau of Mines
Pittsburgh

THE TITRATION OF CALCIUM AND MAGNESIUM IN THE SAME SOLUTION

By Paul J. Fox[1]

Received September 9, 1913

Few determinations are more frequently made in chemical laboratories than those of calcium and magnesium, and the writer was led into the following investigation with a view to lessening the labor required for these determinations: The titration of calcium as oxalate with permanganate is, of course, a well known and standard process, and the titration of magnesium as magnesium ammonium arsenate with sodium thiosulfate in acid solution after the addition of potassium iodide has been described by Meade[2] and by G. B. Frankforter and Lillian Cohen.[3]

It has occurred to the writer that it might be possible to combine these processes in one operation by first precipitating the calcium as oxalate, and then in the same solution and without filtering, precipitating the magnesium as magnesium ammonium arsenate, filtering off and washing the combined calcium oxalate and ammonium magnesium arsenate, dissolving in acid, titrating the calcium oxalate with potassium permangante and then the magnesium ammonium arsenate with sodium thiosulfate after the addition of potassium iodide. As will be shown in the sequel, this combined method is perfectly feasible, the two titrations not interfering with each other.

The titration of calcium as oxalate calls for no remark except to observe that the objection that the calcium sulfate formed prevents complete decomposition of the calcium oxalate is not, in the writer's experience, valid. With moderate skill in manipulation, it is always possible to obtain good results.

In the titration of the arsenate, however, certain irregularities were encountered. For example, following approximately the directions in the paper of Frankforter and Lillian Cohen, when 10 cc. portions of a certain solution of ammonium arsenate were acidified, and made up to 100 cc. so that 100 cc. contained about 15 cc. concentrated sulfuric acid, cooled, 5 grams potassium iodide added, and titrated after standing 5 minutes, 21.21, 21.52, and 20.78 cc. thiosulfate solution were required to decolorize the solution. All the portions were, of course, measured out by the same pipette and measured over the same portion of the burette. The figures given are selected from many and are representative of the magnitude of the variations. They were measured out and titrated at different times, a series titrated at the same time showing less variation. The end point was always certain and definite.

Many experiments were made to find the cause and remedy for the irregularities, but to cite the figures in detail would scarcely be profitable. The advantages of the improvements suggested are more or less self evident. The principal causes of irregularity—assuming of course that the iodide used is free from iodate or other substance capable of setting free iodine

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[2] R. K. Meade, *Jour. Am. Chem. Soc.*, **21**, 146 (1899).

[3] *Jour. Am. Chem. Soc.*, **29**, 1464 (1907).

in acid solution—are (1) the slowness with which pentavalent arsenic sets free iodine in acid solution; (2) in strong solutions, the escape of iodine before titration; (3) especially the effect of light on setting free iodine from hydriodic acid; and (4) the returning color at the end point.

The setting free of iodine from pentavalent arsenic may be represented by the equation

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2$$

This reaction proceeds from left to right rather slowly. Fine sand was tried as a catalyzer but with no appreciable accelerating effect. Heating to about 40° accelerated the reaction, but the temperature must be so closely managed to avoid a precipitation of yellow arsenic trisulfide, that it cannot be recommended: too many determinations are lost. Removing the reaction products on the right-hand side of the equation naturally suggested itself. It is not practicable to use sulfuric acid of sufficient strength to take up the water, but it was found distinctly advantageous to add the thiosulfate immediately after the potassium iodide, to a light straw color, and then to allow to stand, for 5 to 6 minutes, before titrating to the end point. This procedure also operates to prevent the escape of iodine before titration.

The principal cause of irregularity, however, was found to be light. Of course, titrations were not made in sunlight, but even the diffused daylight of Washington in summer is sufficient to set free considerable iodine. That the light and not the presence of iodates or other oxidizing bodies sets free the iodine was shown by dissolving five grams of the potassium iodide used in recently boiled acidified water, displacing the air in the flask by carbon dioxide, and allowing to stand for some time in the dark. No color was developed.

The returning color at the end point appears to be caused by the incomplete setting free of the iodine by the arsenic and by light. The reaction $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$ seems to have no tendency, even in the light, to go from right to left.

It was found possible to eliminate the effects of light, or rather to eliminate the irregularities, by placing the Erlenmeyer flask in which the titration was made in the dark during the time it was standing after having had the greater part of the thiosulfate added, and preparatory to completing the titration. Likewise, after bringing to an end point, the flask is allowed to stand in the dark one minute. If there is no return of color the end point has been reached. The darkness was conveniently provided by rolling a hollow cylinder out of black paper and placing it over the flask in which the titration had been made.

In spite of these precautions, however, it is necessary to make a correction for iodine set free otherwise than by arsenate. The correction has the effect of making the variation more nearly uniform. The improvement in results brought about by these precautions is shown by the following experiments: Ten cc. of a solution of ammonium arsenate was diluted to 100 cc. with water containing 15 cc. concentrated sulfuric acid, and 5 grams of potassium iodide added. Sodium thiosulfate (about tenth normal) was added to a light straw color, and the flask allowed to stand in the dark for about six minutes. The rule was observed to allow eight minutes to elapse between the adding of the potassium iodide and the completing of the titration. Then thiosulfate was slowly added to decolorization, and the flask placed in the black paper cylinder for one minute, and if a color returned, it was discharged. Commonly there was no return of color, if the last drops of thiosulfate had been added slowly. In three experiments, 20.85 cc., 20.82 cc., and 20.80 cc. thiosulfate solution were consumed. In general there was no difficulty in getting check results within one or two drops of tenth normal thiosulfate on titrations of about 20 cc. In this case no correction has been subtracted for light, as the procedure was merely being tested.

The most convenient means of finding the correction for iodine set free by light or by other means than pentavalent arsenic is by titrating with thiosulfate, as described above, two portions of ammonium arsenate solution (of which the exact concentration need not be known) one, say, of 10 cc., and the other of double the amount or 20 cc. If the 10 cc. arsenate required x cc. thiosulfate solution and the 20 cc. required y thiosulfate solution, then the correction is $(2x - y)$ cc. It may be 0.2 to 1.0 cc. Of course the correction may be found by titrating magnesium ammonium arsenate, but it is longer and not necessary. It is not possible to find the correction by making a blank in the ordinary manner, a correction found by such means coming out too low. The following figures show the results of the corrected method of titration of 10 and 20 cc. portions of an ammonium arsenate solution: (The arsenate solution is not the one previously referred to.)

ARSENATE Cc.	THIOSULFATE Cc.	MEAN Cc.
10	20.98	20.94
10	20.91	
20	40.83	40.92
20	41.02	

From which the correction proves to be $2 \times 20.94 - 40.92 = 0.96$ cc. This correction is unusually large. In general, it will amount to from 0.3 to 0.7 cc.

A solution of calcium chloride free from magnesium and iron was prepared by boiling a solution of calcium chloride with calcium oxide and acidifying the filtrate barely to acid reaction with hydrochloric acid. A solution of magnesium chloride free from iron and calcium was prepared by boiling magnesium chloride solution with magnesium oxide, filtering, evaporating the filtrate with a little ammonium oxalate, taking up with water and a little ammonia, filtering and slightly acidifying the filtrate. Portions of these were taken for analysis. In the case of the calcium chloride solution it was found gravimetrically, each experiment being in triplicate with unusual care, that 25 cc. yielded 0.1283 gram CaO, 50 cc. 0.2575 gram, 100 cc. 0.5158 gram CaO. Thus if we determine the CaO yield directly on 25 cc. $CaCl_2$ solution, we find that it amounts to 0.1283 gram. But if we take the difference, 50 cc. — 25 cc. = 0.2575 — 0.1283 gram = 0.1292 gram CaO. So also $^1/_3$ (100 — 25) cc. and $^1/_2$ (100 — 50) both equal 0.1292 gram after rounding off the tenth milligrams. Thus 25 cc. of the $CaCl_2$ solution is equivalent to 0.1292 gram CaO, or 10 cc. = 0.05167 CaO. In all the experiments the conditions of bulk of solution, temperature, and wash water were kept exactly alike, and the 0.9 mg. difference is evidently owing to the solubility of the calcium oxalate under the conditions of the experiment. This source of error is also mentioned by Hillebrand.[1] Strictly speaking, it is an absolute error which should be applied to each determination, but it will not be necessary to apply it if the permanganate is standardized by weighing out pure Iceland spar, especially if the bulk of permanganate used in standardization does not differ very greatly from that consumed in the analysis. In the case of the magnesium chloride solution, no such solubility error was found. By precipitation with ammonium phosphate, each determination being in duplicate:

10 cc. = 0.0391 MgO
20 cc. = 0.0780 MgO
30 cc. = 0.1173 MgO
Average for 10 cc. = 0.03907 MgO

No volumetric method for magnesium, so far as the author knows, can hope to yield so exact results. It must be remembered, however, that in the present case, the magnesium ammonium phosphate was precipitated under ideal conditions, there being present no other salts, and only slightly more than the calculated amount of ammonium phosphate necessary to precipitate the magnesium. Under working conditions this determination is well known to be subject to a serious plus error.[2] Under working conditions, probably the volumetric method will give as good results as the gravimetric unless special precautions and care are taken with the latter.

For the volumetric solutions the mean of all titrations showed each cc. of permanganate = 0.002816 CaO. For the thiosulfate each cc. = 0.002074 MgO.

METHOD FOR COMBINED DETERMINATION

The combined determination is made in the following manner: Precipitate the iron and alumina with ammonia or basic acetate in the usual manner.[3] There must always be sufficient ammonium salts present to prevent a precipitation of magnesia when the solution is made *slightly* alkaline. In the filtrate, precipitate the calcium hot with excess of oxalic acid[4] and dilute ammonia added slowly, to slight alkaline reaction, a drop of methyl orange having been added to the solution. Then add sufficient ammonium arsenate to precipitate the magnesia, and slowly add ammonia with constant stirring to the *hot* solution until the magnesium ammonium arsenate comes down, or if so much calcium oxalate is present that this cannot be observed, add about 10 cc. strong ammonia water. Let cool and add 10 to 15 cc. more strong ammonia. Add the ammonium arsenate to the hot solution within a few minutes after the solution has been made slightly alkaline in the precipitation of calcium oxalate, as magnesium oxalate soon begins to come down, which is, of course, one of the sources of error in the standard gravimetric procedure. After the arsenate has been added, it is immaterial how long the determination stands before filtering. Let stand over night,[1] filter and wash thoroughly with dilute ammonia water. The precipitate is then transferred to a 300 to 500 cc. Erlenmeyer flask. If a paper filter has been used, the quantitative transfer is most conveniently made by spreading the paper out on the inner surface of a 4-inch funnel, of which the stem has been bent to rest against the inner wall of the flask into which it has been inserted. The precipitate is rinsed off with hot water, then with dilute acid.[2] Add 10 cc. sulfuric acid (1 acid to 1 water), make up to about 75 to 80 cc. and titrate hot with permanganate solution. Let cool and add 25 cc. more of the acid. It is well not to have the bulk of the solution much over 125 cc. when about to titrate the magnesia; still, if much lime is present, the 75–80 cc. mentioned above may not be sufficient, in which case, a larger bulk and more acid can be used. These proportions of acid are necessary in order to give a satisfactory end point. Add 5 grams of potassium iodide[3] and immediately titrate to a straw color with sodium thiosulfate. Stopper the flask, and cover with black paper, or set in the dark for about 5 minutes. Eight minutes should elapse between the putting in of the iodide and the last part of the titration. Complete the titration drop by drop. Read the end point and place in the dark for one minute. If there is a return of color, discharge it. Usually there will be none if the last drops of thiosulfate have been added slowly. The writer strongly concurs in what Frankforter and Lillian Cohen[4] say about the use of starch, namely, that it is very much better to do without it. The writer tried four samples of starch, and was unable to obtain any satisfactory end point at all. Methylene blue is also useless as an indicator in the strong acid solution. There is no indefiniteness in the end point when simply the fading out of the brown color of iodine is depended on.

The amount of acid prescribed will be found sufficient when amounts up to 40 to 50 cc. tenth normal thiosulfate solution are required. If more magnesia is present, more acid must be added, which can even be done during the titration if done carefully. It is much better, however, to use a stronger solution of

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[1] *Bull.* **422**, U. S. G. S., page 119.

[2] Hillebrand, *loc. cit.*, p. 128.

[3] From a qualitative experiment, it appears to be practicable to precipitate the calcium, add tartaric acid, make alkaline, and precipitate the magnesia with arsenate, the iron and alumina remaining in solution in the well-known combination with alkaline tartrate. Some other hydroxy organic solvents for iron oxide were tried, *e. g.*, sucrose and mannite, but did not work so well. No quantitative experiments were made in this direction. This plan would be convenient where iron and alumina are not wanted, or are determined on separate portions of the material.

[4] The precipitation of calcium in acid solution yields larger crystals, as many authors have mentioned, and free from material contamination by occluded magnesia.

[1] One determination gave good results after being shaken twenty minutes after cooling, and immediately filtered.

[2] If too strong acid is used, the filter paper is acted on, giving presumably a cellulose hydrolysis product, which produces a color with iodine. If 50 cc. strong sulfuric acid (sp. gr. 1.84) are mixed with 500 cc. water, and the mixture applied at water bath temperature, all the precipitate will be promptly dissolved and the filter paper not attacked.

[3] If much magnesia is present, it is well to add the potassium iodide slowly, as otherwise a precipitate sometimes falls out which does not readily redissolve. Its composition was not studied.

[4] *Loc. cit.*

thiosulfate, say fifth normal. One cubic centimeter tenth normal thiosulfate solution equals theoretically only 0.002016 magnesia (MgO), so that a fifth normal solution would not be unduly strong. Apply a correction for iodine set free by the light, etc., by titrating as described above 10 cc. and 20 cc. of a solution of ammonium arsenate (of which the exact concentration need not be known—about 20 grams to liter is convenient). If 10 cc. required *x* cc. thiosulfate and 20 cc. required *y* cc., then the correction is $(2x - y)$ cc.

It is very important, as the experiments cited show, to standardize the volumetric solutions by weighing out and titrating some suitable compound for the permanganate, pure Iceland spar,[1] and for the arsenate, specially prepared magnesium oxide, or some samples of magnesium ribbon. Very considerable errors will be made by assuming the theoretical values for the solutions.

The following results were obtained:

	CaO taken Grams	Prmgt. Cc.	CaO found Grams	MgO taken Grams	Thio-sulfate Cc.	MgO found Grams	Error in MgO Mg.
1......	0.0517	18.70	0.0527	0.0391	18.32	0.0380	—1.1
2......	0.0517	18.40	0.0518	0.0781	37.31	0.0774	—0.7
3......	0.0517	18.38	0.0518	0.1172	56.63	0.1174	+0.2
4......	0.1292	45.97	0.1295	0.0391	18.49	0.0383	—0.8
5......	0.1292	45.94	0.1294	0.0781	37.38	0.0775	—0.6
6......	0.1292	45.86	0.1291	0.1172	56.17	0.1165	—0.7
7......	0.1292	45.90	0.1292	0.0977	47.36	0.0982	+0.5
8......	0.1292	45.92	0.1293	0.0977	46.48	0.0964	—1.3
9......	0.1292	45.64	0.1285	0.0977	46.42	0.0962	—1.5
10......	0.1292	45.72	0.1287	0.0977	48.00	0.0995	+1.8
11......	0.1292	45.67	0.1286	0.0977	47.93	0.0994	+1.7
12......	0.0517	18.42	0.0519	0.1953	95.36	0.1977	+2.4
	1.2404	440.52	1.2405	1.1526	555.85	1.1525	—6.7 +6.6

The results of the titration of calcium call for no special remark. With regard to the magnesium, it may be stated at once that the writer was unable to obtain the very exact results reported by Meade. Meade, however, worked under ideal conditions as to the composition of his solutions, while the results here set forth were obtained under the conditions existing in actual analysis. The writer's results are, however, comparable with those of Frankforter and Lillian Cohen. In cases of this kind we do better to consider the absolute rather than the relative error. The results of the latter are reported in parts per million of Mg, having been obtained from water analyses in which 500 cc. water were used. Thus the results must have been multiplied by two. In the writer's results, as previously mentioned, the standard for the volumetric solutions is taken from the mean of all titrations, while the volumetric results of Frankforter and Lillian Cohen are in the mean 3.3 per cent higher than their gravimetric results. If we make the results of Frankforter and Lillian Cohen comparable with those of the writer by dividing by two, converting Mg into MgO and adding 3.3 per cent to each gravimetric result, we find that the average error amounts to 1.7 mg. MgO in 84.1 mg. MgO, and that the maximum error amounts to 6.5 mg. MgO in 131 mg. MgO. In the writer's results the average error amounts to 1.1 mg. MgO in 96.0 mg. MgO, and the maximum error to 2.4 mg. MgO in 195.3 mg. MgO. It will be noticed that the writer's results would be improved by standardizing at two different concentrations. The irregularities seem to be due to a lack of absolute uniformity in the composition of the magnesium ammonium arsenate.

There seems to be no limit in reason to the amount of magnesium which may be titrated, if the concentration of the acid is kept sufficient, but the strength of the thiosulfate solution should be so adjusted —and the principle is, of course, valid in all volumetric work—that not more than 30 to 50 cc. are used in a titration. If it is not so adjusted, the addition of the considerable volume of thiosulfate solution used in the titration so reduces the acid concentration that a good end point cannot be obtained.

The permanganate was standardized with Sörensen's sodium oxalate as supplied by the Bureau of Standards and was found to be 0.0996 normal, which would amount to 0.002794 CaO per cc. For the 440.52 cc. of permanganate used in all the titrations, we should have 1.2309 grams CaO, instead of 1.2404, which would correspond to a loss by solubility of 0.79 mg. per determination. The conditions of each experiment were kept uniform. The thiosulfate solution was standardized by twice sublimed iodine and by permanganate, both according to the directions in Treadwell and Hall.[1] It was found to be 0.1011 normal, corresponding to 0.002038 MgO per cc. or a total of 1.1328 grams MgO instead of 1.1526. This would correspond to an average loss of 1.65 mg. MgO per determination. Whether this loss is caused by solubility or by the magnesium ammonium arsenate as precipitated not corresponding to its formula on the average, the writer does not know. These figures are given to emphasize the necessity of standardizing the volumetric solutions with the same substances and under the same conditions as are used in practice.

This method of determining calcium and magnesium is obviously not adapted to use in making *complete* rock analysis, nor is any volumetric method.[2]

Outside of technical uses, there are many cases in soil and rock work where only partial analyses are desired. For example, in a very interesting article by E. S. Bastin,[3] it is shown how chemical composition serves as a criterion for identifying metamorphosed sediments. Substantially the only elements considered are iron and alumina, and the ratios MgO/CaO and K_2O/Na_2O. It is believed that the present method would be useful in this sort of work, especially where it is desired to make a large number of determinations. It is also to be noted that sodium and potassium may be determined in the filtrate from the precipitation of calcium and magnesium, the arsenic being volatilized by means of hydrobromic acid as shown by Browning and Drushel.[4]

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

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[1] Hillebrand, *loc. cit.*

[1] Page 602ff, Vol. II. The standardization by permanganate agrees well with that by iodine, and is much more convenient, even if the permanganate itself has to be standardized with sodium oxalate.

[2] Hillebrand, *loc. cit.*, p. 121.

[3] *Journal of Geology*, **17**, 445 (1909).

[4] *Am. J. Sci.*, **23**, 293 (1907).

COMPARISON OF THE KJELDAHL-GUNNING-ARNOLD METHOD WITH THE OFFICIAL KJELDAHL AND OFFICIAL GUNNING METHODS OF DETERMINING NITROGEN

By T. C. Trescot[1]

Received September 3, 1913

It has been brought to the attention of the Nitrogen Laboratory of the Bureau of Chemistry that the modified method for determining nitrogen, known as the Kjeldahl-Gunning-Arnold method,[2] can be carried out in a shorter time than the Gunning method or the Kjeldahl method and with as accurate results as either of them. This method is identical with the official Kjeldahl method[3] except that 10 grams of crystallized potassium sulfate are added as in the Gunning method, and potassium permanganate is omitted. Investigations were carried out on a variety of substances in order to compare more fully this modification with the standard Gunning and Kjeldahl methods.

The following table gives the maximum, minimum, and average percentages of nitrogen found in various substances by means of the different methods, employing the periods of digestion which the experience of this laboratory indicates are necessary to secure complete oxidation. The reagents have been checked by blanks by all methods. Column 2 gives the number of determinations which were made on a typical sample of each of the substances indicated in column 1.

It will be noted that the results by the Kjeldahl-Gunning-Arnold method carried out with a one and one-half-hour period of digestion are higher than those by the Gunning method for three or four hours, excepting in the cases of cheese and flour, in which they are practically the same. Compared with the results of the Kjeldahl method with three or four hours digestion they are practically the same, excepting in the cases of leather, leather waste, linseed meal, and gelatin, in which they are slightly higher. In the case of cyanamide the one and one-half-hour digestion by the Kjeldahl-Gunning-Arnold method gave results (not given in the table) which indicated incomplete oxidation and it was found necessary to heat this substance for two and one-half hours. With this longer period of oxidation the results of the modified method were the same as those of the Kjeldahl and Gunning methods.

Determination of Nitrogen by Gunning, Kjeldahl, and Kjeldahl-Gunning-Arnold Methods

	Gunning method				Kjeldahl method				Kjeldahl-Gunning-Arnold method							
Substance	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.
		4 hours.				4 hours.				1½ hours.				4 hours.		
Hair waste	10	9.09	8.93	9.01	6	9.09	8.98	9.04	9	9.09	8.98	9.03	10	9.09	8.87	8.98
Dried blood	10	8.93	8.70	8.80	10	8.93	8.81	8.88	10	8.98	8.81	8.90	10	8.93	8.81	8.89
Bone meal	9	3.26	3.14	3.17	10	3.26	3.14	3.20	9	3.26	3.14	3.19	8	3.26	3.14	3.21
Leather	9	6.18	6.01	6.07	10	6.23	6.06	6.12	9	6.26	6.12	6.18	9	6.23	6.06	6.16
Leather waste	10	7.69	7.64	7.67	8	7.80	7.69	7.74	9	7.80	7.75	7.79	9	7.80	7.75	7.77
Cottonseed meal	9	6.79	6.68	6.74	9	6.96	6.79	6.88	9	6.96	6.85	6.88	10	6.96	6.85	6.91
Linseed meal	10	4.97	4.86	4.94	8	5.08	5.00	5.03	10	5.14	5.01	5.08	10	5.14	5.02	5.07
Gelatin	8	15.90	15.78	15.87	8	16.11	15.72	15.98	8	16.17	16.06	16.08	8	16.17	16.06	16.10
										2½ hours.						
Cyanamide	9	13.64	13.47	13.56	7	13.59	13.53	13.57	3	13.59	13.59	13.59	7	13.64	13.59	13.61
										2 hours.				3 hours.		
Beef extract(a)	3	9.14	9.10	...	3	9.22	9.11	...	3	9.27	9.18	...	3	9.27	9.18	...
Desiccated meat(b)	3	12.74	12.74	12.74	2	12.86	12.86	12.86	3	12.91	12.86	12.89	3	12.91	12.86	12.89
		3 hours.				3 hours.				1½ hours.						
Flour	8	1.80	1.74	1.76	9	1.80	1.74	1.76	9	1.77	1.74	1.76	9	1.80	1.74	1.77
Bread	2	1.99	1.96	1.98					2	2.08	2.05	2.07				
Gluten bread	2	10.44	10.36	10.40					2	10.58	10.58	10.58				
Macaroni	2	2.25	2.25	2.25					2	2.27	2.25	2.26				
Ground rye hay	2	2.47	2.47	2.47					2	2.58	2.53	2.55				
Shorts	2	2.50	2.47	2.49					2	2.53	2.50	2.52				
Bran	3	2.78	2.75	2.77					3	2.81	2.75	2.79				
	2	2.84	2.84	2.84					2	2.92	2.89	2.91				
Molasses feed	2	1.88	1.85	1.87					2	1.94	1.94	1.94				
	3	1.71	1.60	1.66					3	1.77	1.74	1.75				
Milk	2	0.528	0.528	0.528					2	0.550	0.547	0.549				
Condensed milk	2	1.30	1.30	1.30					3	1.33	1.29	1.31				
	3	1.19	1.17	1.18					3	1.25	1.22	1.23				
	3	1.19	1.17	1.18					3	1.24	1.19	1.22				
Evaporated milk	3	1.10	1.08	1.09					3	1.10	1.09	1.10				
	3	1.18	1.17	1.18					3	1.17	1.14	1.15				
	3	1.06	1.05	1.06					2	1.08	1.07	1.08				
	3	1.07	1.07	1.07					3	1.08	1.08	1.08				
			4 hours.													
Cheese	3	3.90	3.87	3.89					3	3.93	3.83	3.87				
	3	4.57	4.52	4.54					3	4.60	4.56	4.58				
	3	3.50	3.47	3.49					3	3.49	3.47	3.48				

(a) The maximum and minimum of 3 analyses for 4½ hours by the Kjeldahl-Gunning-Arnold method were 9.27 and 9.18, respectively.

(b) Two analyses for 4½ hours by the Kjeldahl-Gunning-Arnold method gave 12.91 and 12.86, average 12.89.

The general conclusion from these results is that the Kjeldahl-Gunning-Arnold method with one and one-half hours' oxidation, except in the case of cyanamide, which requires two and one-half hours, gives more concordant and reliable estimations of nitrogen

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[1] Chief, Nitrogen Laboratory, Bureau of Chemistry.

[2] U. S. Dept. Agr., Bureau of Chemistry, *Circ.* **108**, p. 15 (1912).

[3] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **107**, *Rev.*, p. 5.

than do the official Gunning or official Kjeldahl methods, both of which require from three to four hours for oxidation, depending upon the material.

Bureau of Chemistry
U. S. Department of Agriculture
Washington

ORTHO-TOLIDINE AS A REAGENT FOR THE COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF FREE CHLORINE

By J. W. Ellms and S. J. Hauser

Received August 25, 1913

With the increasing use of very small quantities of chlorine, either free or in the form of hypochlorites for the disinfection of water for drinking purposes, a colorimetric method for the detection and estimation of small amounts of free chlorine is desirable.

STARCH-IODIDE METHOD

The volumetric method in which iodine is liberated from potassium iodide by the chlorine, and the iodine titrated with sodium thiosulfate, using starch as an indicator, offers some difficulties when very small quantities of chlorine are to be determined. Both the sodium thiosulfate and the potassium iodide solutions deteriorate on standing. Frequent standardization of the sodium thiosulfate is always necessary if accurate estimations are to be made. Free iodine is liberated from solutions of potassium iodide on standing, and errors from this source must be constantly guarded against in estimating small quantities of free chlorine. Starch as an indicator in this method is open to an objection on the score of not being sensitive, unless freshly prepared solutions are used. The indefiniteness of the color end point, due to the liberation of free iodine from the potassium iodide, and the consequent deepening of the color are defects which make the detection of small amounts of free chlorine uncertain. Under the most favorable conditions the starch-iodide method is capable of detecting quantities of free chlorine not lower than 0.03 part per million. This method, therefore, for the foregoing reasons lacks reliability for use in determining the residual free chlorine which may be left in the treated water.

ACETIC ACID SOLUTION OF ORTHO-TOLIDINE

The ortho-tolidine test for free chlorine, as suggested by Earl B. Phelps, in which an acetic acid solution of this reagent is used, furnishes a delicate qualitative test, but is open to certain objections for quantitative purposes on account of variations in color produced by waters of different composition.[1] According to this method a one-tenth per cent solution of *o*-tolidine in 10 per cent acetic acid is employed. With two drops of this reagent in 50 cc. of the water containing about 0.05 part per million of free chlorine a yellow color is supposed to be developed. Dittoe and Van Buskirk found that instead of a yellow color developing with very small quantities of chlorine, a green color was produced which changed from green to yellow and finally to deep red as the concentration of the free chlorine was increased. In one instance when testing for chlorine in a sample of the water supplied to the city of Columbus, Ohio, a light blue color developed on adding *o*-tolidine. No explanation for these color changes is attempted by the above writers. It is apparent, however, that *o*-tolidine could not be very well employed in a colorimetric estimation, unless these color changes were eliminated.

A limited amount of study of the various factors affecting these color changes has been undertaken by the authors, and a reliable mode of procedure for a colorimetric determination worked out. A possible explanation of the reactions involved is offered, which seems to account for some of the color changes, although the authors have not had the opportunity of making a sufficiently thorough investigation to enable them to explain completely all of these complex reactions.

In using the acetic acid solution of *o*-tolidine with small amounts of chlorine, it was found that different shades of color were produced, ranging from a yellowish green to a blue. Although in this test the dyes are produced in an acid solution, nevertheless the variations in the colors formed appeared to be intimately associated with the original degree of alkalinity of the water. Waters that are naturally alkaline from the carbonates of calcium and magnesium, which they contain, or those rendered artificially so by any of the fixed alkalies, act similarly. The higher the original alkalinity of the water containing free chlorine, the bluer is the shade of color produced. The more nearly neutral is the water being examined, the yellower is the tint. In natural waters of moderate hardness, which have not been materially modified by some method of purification, the usual tint obtained is a yellowish green.

By increasing the concentration of the acetic acid a more yellowish green color is produced; but only by adding very large quantities of acid is a yellow color formed. On the other hand the addition of a very small quantity of a highly dissociated acid, such as hydrochloric or sulfuric, produces a deep yellow color with small amounts of free chlorine. This yellow color is not affected by the original degree of alkalinity of the water being tested, nor is the tint modified by any change in the concentration of the acid.

By increasing the amount of free chlorine, the acetic acid solution of *o*-tolidine produces first a solution with a yellowish green color, changing to an orange and then to a deep red. Still larger quantities of chlorine produce a dark red precipitate. Small quantities of bromine and iodine produce, with an acetic acid solution of *o*-tolidine, green-colored solutions. With larger amounts bromine acts as does chlorine, but iodine tends to form a precipitate more readily, and it is of a bluish color.

With increasing concentrations of solutions of potassium bichromate or potassium permanganate, but with no halogens present the acetic acid solution of *o*-tolidine produces first green-colored solutions, then yellow solutions and finally deposits brown-colored precipitates. These precipitates are soluble in hydrochloric acid and give yellow-colored solutions. On the addition of nitric acid to an acetic acid solution

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[1] "Report on the Public Water Supply of Cleveland with reference to the Treatment with Calcium Hypochlorite," by W. H. Dittoe and L. H. Van Buskirk, Ohio State Board of Health, *Bull.* **3**, No. 1 (January, 1913).

of *o*-tolidine a yellow-colored solution is formed.

The acetic acid solution of *o*-tolidine darkens on standing, and especially so when exposed to the light. Old solutions give slightly different shades of color with small amounts of free chlorine, than do those which are freshly prepared. The green colors produced with small amounts of free chlorine fade within a few minutes, and are probably not reliable for longer than five minutes for colorimetric estimation against standards prepared with known amounts of chlorine. This reagent is sufficiently delicate to detect quantities of free chlorine as low as 0.01 part per million. The objections to making use of the acetic acid solution of *o*-tolidine for the quantitative determination of small amounts of free chlorine may be summed up as follows:

1st. Waters of varying degrees of alkalinity produce different shades of color with similar amounts of free chlorine.

2nd. Fading of the colors occurs within a few minutes.

3rd. Deterioration of the reagent with age, especially in the light.

HYDROCHLORIC ACID SOLUTION OF ORTHO-TOLIDINE

Since the addition of small amounts of highly dissociated acids, such as hydrochloric and sulfuric, was found to give a yellow color with small amounts of free chlorine, when using the *o*-tolidine reagent, and since this color was neither affected by the degree of alkalinity of the water being tested, nor by changes in the concentration of the acid, it led to the preparation of a hydrochloric acid solution of *o*-tolidine in place of the acetic acid solution. The strength of this hydrochloric acid solution was one-tenth per cent *o*-tolidine in a 10 per cent solution of hydrochloric acid. This reagent does not deteriorate on standing. It produces with small quantities of free chlorine a yellow color.

The yellow color is produced uniformly with small amounts of free chlorine, regardless of the soluble constituents of the water being tested. The alkalinity of the water in no way affects the shade or tint produced. The presence of sulfates, chlorides and nitrates of the alkalies and alkaline earth bases do not interfere with the test. The yellow color develops in about three minutes and is permanent for at least one-half hour. There is a good gradation of color for increasing amounts of free chlorine. The test is delicate enough to detect 0.005 part per million of free chlorine.

With large amounts of free chlorine, the hydrochloric acid solution of *o*-tolidine changes from yellow to orange then to red and finally throws down a dark red precipitate. Bromine and iodine both produce yellow-colored solutions with this reagent. Large quantities of bromine behave as does chlorine, but iodine solutions do not appear to form precipitates. Solutions of potassium permanganate and potassium bichromate produce a yellow color with this reagent, which deepens with increased concentration of the above compounds, but do not form precipitates. Nitric acid gives a yellow-colored solution with this reagent, which could be due either to the oxidizing action of the nitric acid, or of the chlorine formed by the oxidation of the hydrochloric acid of the *o*-tolidine solution.

METHOD OF ANALYSIS

The method of making the colorimetric test consists in adding 1 cc. of the one-tenth per cent *o*-tolidine solution in 10 per cent hydrochloric acid to 100 cc. of the water to be tested for free chlorine. When the free chlorine exceeds 3 parts per million it is necessary to use more of the reagent. The water and the reagent are well mixed and are allowed to stand for five minutes. They are then compared with standards of known strength prepared at the same time or with permanent standards as described below. From a solution of chlorine, standardized by means of a *N*/100 thiosulfate solution, a series of standards are prepared by dilution with redistilled water. The strength of the chlorine solution should be determined at the time the standards are to be prepared. The latter must be freshly made and immediately compared with the samples being tested. Water for dilution of standards should be as free from organic matter as redistillation with alkaline potassium permanganate will make it. Ordinary distilled water contains enough organic matter to quickly reduce the chlorine and thus cause it to disappear.

To avoid the difficulties inherent in preparing standards as above described, permanent standards may be made from solutions of copper sulfate and potassium bichromate in sulfuric acid solution. For standards between 0.01 part per million and 10 parts per million the proportionate volumes of the two solutions are given below.

Parts per million	Copper sulfate Cc.	Potassium bichromate Cc.
0.01	...	0.8
0.02	...	2.1
0.03	...	3.2
0.04	...	4.3
0.05	0.4	5.5
0.06	0.8	6.6
0.07	1.2	7.5
0.08	1.5	8.7
0.09	1.7	9.0
0.10	1.8	10.0

NOTE—Potassium bichromate solution: 0.025 gram + 0.1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

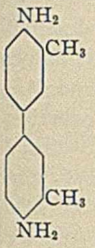
Copper sulfate solution: 1.5 grams $CuSO_4.5H_2O$ + 1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

Standards higher than 0.10 part per million require a stronger potassium bichromate solution; *i. e.*, 0.25 gram + 1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

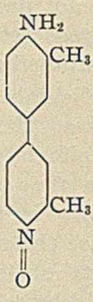
Parts per million	Copper sulfate solution Cc.	Potassium bichromate solution Cc.
0.10	1.8	1.0
0.20	1.9	2.0
0.30	1.9	3.0
0.40	2.0	3.8
0.50	2.0	4.5
0.60	2.0	5.1
0.70	2.0	5.8
0.80	2.0	6.3
0.90	2.0	6.7
1.00	2.0	7.2
2.00	2.0	12.0
3.00	2.0	21.0
4.00	2.0	30.0
5.00	2.0	39.0
6.00	2.0	46.0
7.00	2.0	56.0
8.00	2.0	63.0
9.00	2.0	70.0
10.00	2.0	75.0

SUGGESTIONS AS TO THE CAUSES FOR COLOR CHANGES

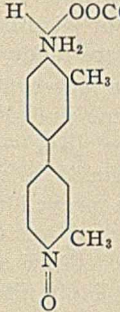
Ortho-tolidine is an organic compound of the formula $C_{14}H_{16}N_2$.[1] It is a homolog of benzidine and is a powder melting at 129° C. It may be prepared from *o*-nitrotoluene by reduction with zinc dust and sodium hydroxide. The resulting hydrazo-toluene is converted into the *o*-tolidine by boiling with hydrochloric acid. It may be purified in a manner similar to that of benzidine. Its structural formula may be written as at (1):



(1)



(2)



(3)

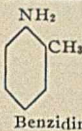
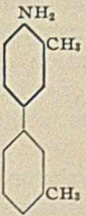
It is a *p*-2-diamido-*m*-2-dimethyldiphenyl compound, and probably produces dyes of the same general type as those derived from benzidine. Oxidation of *o*-tolidine probably produces a nitroso compound of formula (2): this compound is probably blue in color. Salts of *o*-tolidine upon oxidation produce a yellow dye, a possible formula for the acetic acid salt being (3).

The green color produced by the action of the chlorine on the acetic acid solution of *o*-tolidine is probably a mixture of the blue compound (2) and the yellow compound (3). In the hydrochloric acid solution of *o*-tolidine, HCl is merely substituted for $HOOCCH_3$. The slight dissociation of acetic acid and the hydrolysis of the acetate perhaps account for the slow formation of the yellow dye in the acetic acid solution, while the large dissociation of hydrochloric acid might be the reason for the rapid development of the yellow color in the hydrochloric acid solution.

The red color and red precipitate produced by large amounts of chlorine may be a substitution product of the nitroso compound resulting from the complete oxidation of all the *o*-tolidine present.

Aniline treated with a solution of bleaching powder produces certain color reactions, but it requires a considerable amount of chlorine for their development. Similarly ortho-toluidine forms colored solutions with chlorine, which are likewise slowly developed, although somewhat more rapidly than in the case of aniline. As has been previously noted benzidine readily produces colored solutions with chlorine, similar to those formed with *o*-tolidine. Its sensitiveness to chlorine is much greater than is that of aniline or *o*-toluidine but somewhat less than that of *o*-tolidine.

The colors produced by a solution of bleaching powder in gradually increasing quantities with neutral and with acid alcoholic solutions of aniline, *o*-toluidine, benzidine and *o*-tolidine are shown in the following table:

	Color of Precipitate in		
	Neutral alcoholic solution	Alcohol and acetic acid.	Alcohol and HCl.
Aniline  	Yellow-green-brown	Brown-purple-red	Yellow-purple-red
o-Toluidine  	Yellow-orange-brown	Purple-blue-red	Purple-red
Benzidine  	Yellow-orange-red	Green-orange-red	Yellow-orange-red
o-Tolidine  	Yellow-orange-red	Green-orange-red	Yellow-orange-red

A blue color reaction produced by the action of hypochlorites on methyl-aniline and ethyl-aniline has been recently reported by Leech.[1] He suggests that the blue dye, possibly a member of the "indo" series of dyes, results from the oxidation of the methyl or ethyl group. It seems to the authors that in the case of *o*-toluidine and *o*-tolidine that the dyes are produced as a result of the oxidation of the amido group, and not the methyl group, since in aniline and benzidine, having no methyl groups, similar dyes are formed by the action of hypochlorites.

Cincinnati Filtration Plant
Cincinnati, Ohio

THE QUANTITATIVE ESTIMATION OF GLIADIN IN FLOUR AND GLUTEN

By Geo. A. Olson

Received July 26, 1913

Since Einhof[2] separated alcohol-soluble proteins from wheat, rye and barley, much interesting research work has been done on prolamines. It was not, however, until Osborne and Voorhees[3] presented a study on the proteins of the wheat kernel that a clear understanding as to the nature of vegetable proteins was established. Of particular interest was the research on gliadin, the prolamine of wheat. It has been further believed that the proportion of gliadin to glutenin determines the quality of the gluten which in turn

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[1] Beilstein, 3rd edition, Vol. 4, page 980.

[1] "A Color Reaction of Hypochlorites with Methyl-Aniline and Ethyl-Aniline," by Paul N. Leech, *Jour. Am. Chem. Soc.*, **35**, No. 8 (August, 1913).

[2] See "The Proteins of the Wheat Kernel and Vegetable Proteins," by Thomas B. Osborne. Also *Trans. of the Canadian Institute*, **7**, 1903, by George G. Nasmith.

[3] *Amer. Chem. J.*, **15**, 392 (1893).

determines the quality of a flour for bread-making purposes.[1]

Following Millon's[2] work on the quantity of gluten contained in different kinds of wheat, another series of investigations bearing on the relationship of the gluten to the baking qualities of flour was commenced. Heinrichs[3] failed to establish any relationship between the gluten and baking quality, but Fleurent[4] was led to believe that the alcohol-soluble portion of the gluten, rather than gluten, determines the baking qualities of flour. The method adopted by Fleurent for the extraction of gliadin cannot be said to be satisfactory since the diluted alcohol contains potassium hydroxide and potassium hydroxide like sodium hydroxide is a solvent for glutenin as well as for gliadin.

Based upon Osborne's and Voorhees' work, Teller[5] worked out a method which he used for the estimation of gliadin in wheat at different periods of growth. He, and subsequently Chamberlain[6] and others,[7] observed that a part of the alcohol-soluble nitrogen was extracted by salt solution. The writer in his studies on the nitrogen components of wheat flour has confirmed this work. The fact that the quantitative methods which we follow for the estimation of proteins in wheat flour are far from satisfactory, led the writer to carry out a series of experiments, some of the results of which are recorded below.

The strength of alcohol most suitable for the extraction of gliadin from flour, or gluten, has never been determined. It is known that above certain strengths of alcohol little or no gliadin can be extracted, while below this limit all the gliadin can be extracted, provided enough solvent is used. Teller[1] studied the solubility of proteids in different strengths of alcohol and found that while the quantity of nitrogen extracted increased with the dilution of alcohol until a maximum amount of alcohol-soluble nitrogen products had been extracted, solutions containing from 40 per cent to 60 per cent alcohol gave identical results. From 65 per cent to 95 per cent by volume, the per cent of nitrogen products decreased rapidly. Osborne and Voorhees in their work used an alcohol of 0.90 sp. gr. Later Shutt[8] and Hummel[9] observed between the range of 60 per cent to 75 per cent alcohol, by weight, that the nitrogen content of flour soluble in alcohol decreased with the increased strength of alcohol. Between 60 per cent and 86.4 per cent alcohol, by weight, Shutt observed the same order of solubility: with 86.4 per cent alcohol only 0.12 per cent nitrogen; compared with 60 per cent alcohol 0.94 per cent nitrogen was noted. Hoagland,[10] working with two samples of flour, observed that more nitrogen was extracted with water than with alcohol of strengths ranging from 10 to 20 per cent by weight. Increasing the strength to 75 per cent by weight, Hoagland found that alcohol of 40 to 45 per cent by weight extracted as much or more nitrogen products than strengths ranging between 60 to 75 per cent by weight. He believes a 50 per cent alcohol by weight to be the logical strength to use. It should be remembered that Osborne and Voorhees separated the gliadin or its nitrogen from the alcohol-soluble nitrogen. The fact that larger quantities of nitrogen-carrying bodies are extracted with weaker alcohols does not prove that larger quantities of gliadin are extracted, yet nitrogen determinations are made and it is assumed that such is the case.

The observations of Kjeldahl,[1] Mathewson,[2] and Osborne and Harris[3] showed the specific rotation of gliadin, $[\alpha]_D$ —92 to be uniformly constant. Snyder[4] introduced a method for the estimation of gliadin which proved unsatisfactory in the hands of others. Thatcher[5] was unable to use the method on soft wheat flours. Shaw and Gaumitz[6] state in their paper that "the gliadin nitrogen should be corrected for the amide nitrogen present, but for most practical purposes this may be neglected," especially "with old and unsound flours a correction must be made for the soluble amide bodies." Chamberlain also is of the opinion that amide compounds soluble in alcohol are considered as gliadin in the proposed methods.

Greaves,[7] in his thesis work, with the aid of the polariscope, found that 70 per cent alcohol extracted more nitrogen in smaller quantities of flour than where the same quantity of alcohol acted upon larger quantities of flour. Chamberlain recommended that at least 100 cc. of alcohol per 2 grams of flour should be used. In working with alcohol ranging from 60 per cent to 80 per cent by weight, Greaves obtained the largest amount of nitrogen, with a few exceptions, with 70 per cent alcohol. The highest specific rotation $[\alpha]$ —89.80 was observed with 74 per cent alcohol, and he is of the opinion that this is more nearly true gliadin than gliadin extractions made with other strengths of alcohol.

In studies with hot alcohol compared with cold, Chamberlain[8] obtained more gliadin nitrogen in cold alcohol than in case of hot alcohol. Leach[9] recommends 100 cc. of 75 per cent hot alcohol per gram of material. Hoagland found that at a temperature of 75° C., and below the latter temperature, there is practically no temperature effect on the amount of nitrogen extracted. Greaves, employing tightly stoppered pressure flasks, obtained higher results with hot alcohol compared with cold.

In the earlier investigations on gliadin the experimental work was directed towards the preparation of pure gliadin, so that it was possible to properly identify and classify it. In the latter researches, when quantitative methods were desired, the sum total nitrogen

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[1] *Agr. Gazette N. S. Wales*, Sept., 1896. *Jour. Amer. Chem. Soc.*, **1900**, 263. *Ibid.*, **1905**, 1068. *Compt. rend.*, **1896**, 123, 155.

[2] *Jour. f. prakt. Chem.*, Bd. **61**, 344 (1854).

[3] *Berichte d. Landw. Versuchs. Rostock*, **1894**.

[4] *Compt. rend.*, **1896**, 327.

[5] *Ark. Bull.* No. **53**.

[6] U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. **81**.

[7] *Ibid.*, *Bull.* No. **90**.

[8] Central Exp. Farm, Ottawa, Can., **1907**.

[9] U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. **105**.

[10] THIS JOURNAL, **3**, No. 11, 838.

[1] *Centralbl. Agr. Chem.*, **25**, 197 (1896).

[2] *Jour. Amer. Chem. Soc.*, **28**, 1482 (1906).

[3] *Ibid.*, **24**, 844 (1903).

[4] *Ibid.*, **26**, 263 (1904).

[5] *Ibid.*, **29**, 910 (1907).

[6] *Calif Bull.*, No. **212**.

[7] *J. Biol. Chem.*, **9**, 3–4, 271.

[8] *Jour. Amer. Chem. Soc.*, **28**, No. 11.

[9] *Food Inspection and Analyses*, p. 232.

extracted by alcohol has been considered pure gliadin. In literature, there is nothing to show that all of the nitrogen compounds present in the alcohol-soluble is the nitrogen of pure gliadin. There is, on the other hand, some indication that a part at least of the nitrogen products is a part of less complex substances than gliadin, *e. g.*, amides. There is some evidence that substances closely allied to gliadin are present and which O'Brien[1] believes "closely merge into one another."

The general methods adopted for the separation of gliadin from its solvent have been either to dilute the alcohol and add salt solution or increase the strength of alcohol by adding absolute alcohol. Osborne states that distilling off the alcohol *in vacuo* causes the settling out of gliadin. This latter method has been made use of by the writer when handling large quantities of material.

But where the quantity of material is small and the exact purity of the material is of secondary importance, the writer has evaporated off the alcohol in the open, thereby causing precipitation or settling out of protein. Owing to the peculiar properties of gliadin and the similar properties of the coagulum it is reasonable to believe that they are one and the same substance. The gliadin, however, is purer than the precipitate due to the fact that it is redissolved and precipitated a number of times. The nitrogen bodies dissolved by the alcohol and not precipitated are non-gliadin bodies which from a quantitative point of view are generally included as gliadin nitrogen.

This means of separating the alcohol-soluble nitrogen materials into two groups offers a satisfactory working basis for the estimation of gliadin in flour or gluten. In some respects such a method is similar to the one in vogue for the estimation of casein in milk.

In order to learn whether or no it was possible to make use of the above method for the estimation of gliadin it was necessary to include with it the estimations for the salt-soluble protein substances found in flour.

In the preliminary experiments a series of four flours were selected. These were first extracted with one per cent salt solution (NaCl), followed by treating the insoluble residue with sufficient 95 per cent alcohol to make an alcohol 70 per cent by volume. A direct 70 per cent alcohol separation was also made. Besides this, 50 cc. aliquot of the direct alcohol-soluble separation was evaporated to within 5 cc., 50 cc. of water added, boiled, and then cooled to room temperature. A heavy coagulum or settling out resulted upon the evaporation of the alcohol and increased in amount upon cooling after the boiling.

An aliquot of the 1 per cent salt-soluble was evaporated to dryness and then extracted with 70 per cent alcohol, in order to remove the gliadin which, according to Teller and confirmed by Chamberlain, is appreciably soluble in 1 per cent salt solution. The residue remaining after the alcohol extraction should be composed largely, if not all, of edestin and leucosin. The alcohol extraction in the dried salt solution should carry with it the coagulable and non-coagulable nitrogen which was removed by the salt solution.

Nitrogen determinations were made by the straight Kjeldahl method in the flour, the direct extraction of the flour with 70 per cent alcohol, the coagulum in this alcohol-soluble, the alcohol-soluble resulting after the extraction of the flour with 1 per cent salt solution, the salt-soluble extraction and the salt-soluble insoluble in 70 per cent alcohol. The results obtained for the above determinations are recorded in Table I.

TABLE I.—ALCOHOL-SOLUBLE PROTEINS BY DIRECT, INDIRECT AND COAGULATION METHODS

No.	Per cent total nitrogen	Per cent alcohol-soluble nitrogen direct	Per cent alcohol-soluble nitrogen coagulated	Per cent salt-soluble nitrogen	Per cent alcohol-soluble nitrogen in salt soluble	Per cent alcohol-soluble in nitrogen in the insoluble salt residue	Per cent total alcohol-soluble nitrogen indirect
1	1.47	0.82	0.61	0.40	0.25	0.35	0.60
2	2.07	1.11	0.73	0.45	0.29	0.52	0.81
3	2.18	1.22	0.87	0.47	0.32	0.61	0.93
4	2.73	1.64	1.12	0.61	0.33	0.84	1.17

The data given in Table I give results by the direct process of extracting flour for nitrogen-carrying bodies as well as the reverse process. The results obtained are not comparable with each other in the two methods. More than this, the data show that salt extracts a part of the alcohol-soluble nitrogen-carrying bodies and 70 per cent alcohol by volume applied directly to a flour removes larger amounts of protein than can be accounted for by the indirect method. The excess amount of alcohol-soluble by the direct method possibly has been altered upon evaporating the salt-soluble and hence is no longer soluble in this strength of alcohol. The data further show that a large part of the alcohol-soluble nitrogen-carrying bodies are coagulated when the alcohol is removed and boiled with water. These results further indicate that a part of the alcohol-soluble nitrogen-carrying bodies is estimated as leucosin and edestin when 1 per cent salt solution is used. Similar results were obtained by Chamberlain who extracted the flour with alcohol followed by extracting the alcohol residue with a 5 per cent solution of potassium sulfate. The amount of nitrogen-carrying bodies extracted from the alcohol residue as obtained by him was only one-fifth as much as that obtained by the direct extraction of the flour with 5 per cent potassium sulfate.

Perhaps the most interesting results obtained were the remarkably close agreement between the nitrogen in the alcohol-soluble coagulum and that of the alcohol-soluble nitrogen where the flour had first been extracted with 1 per cent salt solution together with that extracted in the direct salt-soluble. These data add further evidence that alcohol extracts other nitrogenous substances from flour than gliadin and that "gliadin is appreciably soluble in 1 per cent salt solution." In this series of experiments approximately 72 per cent of the total alcohol-soluble nitrogen is gliadin nitrogen

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[1] *Annals of Bot.*, **1895**, p. 182.

based on either the coagulum nitrogen or the alcohol-soluble nitrogen by the indirect method.

Owing to the close agreement in the nitrogen content in the coagulum compared with the nitrogen content in the alcohol-soluble by the indirect method it appears reasonable to the writer that either one of the two methods mentioned here would be satisfactory for the estimation of gliadin nitrogen. The method for the determination of the coagulable nitrogen is the shortest and the better one to follow of the two and as a result the writer has devoted his time to a study of this method.

As has been stated, the strength of alcohol best suited for gliadin estimation has never been fixed. Greaves believes that a 74 per cent alcohol is the proper strength to use in polariscopic estimations, while variable strengths have been suggested in gravimetric estimations. For this reason it is necessary to determine a strength that would be suitable for the work involved.

Two samples of flours were digested with cold 45, 50, 55, 60, 65, 70, 75, 80, and 85 per cent alcohol by volume and the nitrogen determined in an aliquot of the alcohol-soluble as well as in the coagulum resulting from another aliquot of the alcohol-soluble. Nitrogen determinations were also made in the phosphotungstic precipitates resulting from the coagulum filtrates. The results for nitrogen in the alcohol-soluble, the coagulum filtrate and the sum of the last two determinations are recorded in Table II of this paper.

TABLE II—AMOUNT OF COAGULABLE NITROGEN OBTAINED IN DIFFERENT STRENGTHS OF ALCOHOL

No.	Material	Per cent N in 45 per cent	Per cent N in 50 per cent	Per cent N in 55 per cent	Per cent N in 60 per cent	Per cent N in 65 per cent	Per cent N in 70 per cent	Per cent N in 75 per cent	Per cent N in 80 per cent	Per cent N in 85 per cent
A.	Direct.....	1.23	1.29	1.30	1.30	1.25	1.21	0.99	0.78	0.33
	Coagulum..	0.87	0.82	0.84	0.84	0.77	0.75	0.61	0.59	0.15
	Precipitated filtrate...	0.39	0.45	0.42	0.42	0.41	0.39	0.32	0.23	0.14
	Total.......	1.26	1.27	1.26	1.26	1.18	1.14	0.93	0.82	0.29
B.	Direct......	1.36	1.63	1.63	1.62	1.57	1.45	1.05	0.86	0.16
	Coagulum..	1.14	1.18	1.21	1.21	1.17	1.08	0.72	0.50	0.02
	Precipitated filtrate...	0.24	0.37	0.34	0.35	0.35	0.31	0.36	0.26	0.13
	Total.......	1.38	1.55	1.55	1.56	1.52	1.39	1.08	0.78	0.15

There are several things of interest to be noted in the data given in Table II. The per cent of nitrogen obtained in the coagulum after removing the alcohol runs quite uniformly regardless of strengths of alcohol ranging between 50 per cent to 65 per cent inclusive alcohol by volume. From 70 per cent there is a marked decrease in the per cent of nitrogen until at 85 per cent only about 25 per cent of the total nitrogen in the alcohol-soluble is obtained. The per cent of nitrogen in the phosphotungstic acid precipitated filtrate bears a similar relation. The sum of the per cents of nitrogen in the coagulum and phosphotungstic acid precipitate agree fairly well with the per cents of nitrogen obtained by the direct alcohol extraction.

In regard to the per cents of nitrogen-solubles in different per cents of alcohol it will be noted that the results agree with those observed, first by Teller, and later by other investigators. From these results it appears that a 50 per cent alcohol by volume is satisfactory to use for the estimation of the per cent of nitrogen in the coagulum. The slight variations noted in the totals compared with the results by the direct method are undoubtedly due to analytical error.

The following method was finally adopted for the study of coagulum fraction of the alcohol-soluble. Four grams of flour were digested with 200 cc. of 50 per cent alcohol by volume, shaking the entire contents at intervals of five minutes apart during the first two hours, then allowing to stand twenty-four hours followed by filtering clear. Aliquots of 50 cc. each were taken from the thoroughly mixed filtrate, evaporated slowly to within 5 cc. volume, 50 cc. of water added to each and further evaporated at a temperature near to boiling until contents of beakers approximately amounted to 10 cc., repeating 50 cc. of water were added and again evaporated down to within 35 cc. The beakers were then removed, 25 cc. water added, allowed to cool to room temperature (21°) and finally filtered. In case of turbid filtrates, the filtrates were repeatedly filtered until clear. The coagulum is difficult to remove in most instances, owing to the sticky nature of this substance, and in such cases the mass was gathered by the use of steel spatula and policeman and transferred to filter paper, occasionally using cold, distilled water to facilitate the transferring and washing of the coagulum. Nitrogen determinations were made according to the Kjeldahl method. The proper corrections for paper and reagents were taken into consideration in all determinations for nitrogen.

The filtrates resulting from the separation of the coagulum were treated with sufficient phosphotungstic acid and nitrogen determined in precipitate and filter paper.

In a series of experiments comprising sixty different flours obtained from different sources, representing different climatic zones in the United States, some of which known as spring or winter wheat patents, others straight, or bakers, some of better baking qualities than others, were subjected to the above mentioned method for the determination of gliadin. The average maximum and minimum results for per cents of total nitrogen in flour, alcohol-soluble nitrogen, coagulable nitrogen in alcohol-soluble and nitrogen in phosphotungstic acid precipitate are recorded in Table III. In addition the per cent of coagulable nitrogen expressed in per cent of total nitrogen in the flour and alcohol-soluble are included.

TABLE III—PER CENT NITROGEN IN ALCOHOL FRACTIONS

	Per cent total nitrogen in flour	Per cent total alcohol-soluble nitrogen	Per cent coagulable nitrogen	Per cent phosphotungstic acid nitrogen	Per cent error	Per cent coagulable: Of total N	Per cent coagulable: Alcohol-soluble nitrogen
Average (60)....	1.97	1.105	0.755	0.295	0.033	38.32	68.32
Maximum......	2.72	1.560	1.210	0.440	0.19	50.0	86.40
Minimum......	1.31	0.610	0.440	0.120	0.09	31.0	50.50

According to the results summarized in Table III, it will be noted that the per cent of coagulable nitrogen of total nitrogen in the flour is 38.52, while the per cent of coagulable of total alcohol-soluble is 68.32. It is further noted that all of the alcohol-soluble nitrogen is not coagulable nitrogen and that which is not coagulable is precipitated by phosphotungstic acid. If the coagulable nitrogen contains all of the gliadin nitrogen of flour, it will be noted that this nitrogen does not bear any relation to the total alcohol-soluble, nor total nitrogen of the flour.

In connection with this work it was thought desirable to carry out a few comparative tests as to the purity of the coagulum from a nitrogen point of view with the mass obtained in the alcohol-soluble. Four flours from as many different states were selected for this work. The per cent of total solids, per cent of nitrogen in the solids, the per cent coagulum, per cent of nitrogen in coagulum, per cent ash in coagulum, and per cent of sugar in filtrate resulting from the separation of the coagulum are recorded in Table IV.

TABLE IV—PURITY OF ALCOHOL-SOLUBLE COMPARED WITH PURITY OF COAGULUM

	Per cent total solids	Per cent nitrogen in solids	Per cent coagulum	Per cent nitrogen in coagulum	Per cent ash in coagulum	Per cent sugar in filtrate
Kansas	10.11	8.61	4.31	13.69	0.11	0.121
So. Dakota	12.02	9.90	5.98	14.88	0.12	0.058
Washington	11.10	8.47	6.12	12.09	0.23	0.266
New York	10.50	5.14	5.18	10.42	0.39	0.244

The degree of purity of the alcohol-soluble based upon the nitrogen content and total solids is approximately less than one-half the purity of pure gliadin (17.6 per cent N) and for the coagulum the nitrogen content (av. 12.77) agrees with the nitrogen content of gluten (12.77 per cent N).[1] The per cent of sugar found and the per cent of ash are small and seemingly do not influence the purity of the proteins to any great extent. Just how much fat the coagulum carries was not determined, but from determinations made in non-ether extracted preparations of gliadin sometimes as high as 13.5 per cent of ether extract was found and presumably the larger amount of fat in the coagulating method includes fat in the coagulum which fat, if included in gliadin, would reduce the nitrogen per cent in gliadin to figures practically as low as those obtained by the writer for the coagulum.

In research bearing on the properties of gluten and its effect upon the baking qualities of flour, we have been exceedingly fortunate in working out a method of preparing gluten in dry form which when moistened with water takes on all of the characteristics of the gluten from which it was prepared. It occurred to the writer that it might be well to try the above method for the estimation of gliadin on prepared glutens obtained from flours in which the method had been tried directly. Accordingly, one-half gram lots of 10XX bolted gluten from six different flours were digested with two hundred centimeters of 50 per cent alcohol by volume and the method as described above was followed from this point. The per cent of nitrogen in dried gluten, the per cent nitrogen in the alcohol-soluble, the per cent nitrogen in coagulable of the alcohol-soluble, the per cent nitrogen in the phosphotungstic acid precipitated filtrate, the error in the determinations, and the amount of gluten in 100 grams of flour from which data the grams of nitrogen in the gluten, the alcohol-soluble and coagulable, have been calculated and are recorded in Table V. The per cent of coagulable nitrogen as found in the alcohol-soluble extract of the flour is introduced in the last column for comparison.

When the possible variations in the results for the determinations of dry gluten, the solubility of gliadin in the process of washing the gluten out of the flour, as well as the possible error involved in making nitrogen determinations, are considered it will be noted (Table V) that the per cent coagulable nitrogen found in alcohol-soluble of the gluten compares remarkably closely with the coagulable nitrogen obtained by the direct extraction of the flour with alcohol. In two instances, *viz.*, B. L. and M. 15, the error is somewhat large, but on closer study it will be further noted that the results obtained in the gluten run lower in all instances except one than was the case in the determination in the flour. A possible explanation for the lower results other than those mentioned above may be either that the total alcohol-soluble material contained in the gluten was not entirely extracted or the alcohol-soluble obtained in flour contained other proteins which coagulate with the coagulum and do not combine with the glutenin to form gluten.

TABLE V—PER CENT COAGULABLE NITROGEN IN GLUTEN AND CALCULATED IN PER CENT OF FLOUR

No.	Per cent N in gluten	Per cent N alcohol-soluble	Per cent N in coagulable	Per cent N in phosphotungstic precipitate	Error	Per cent gluten in flour	Per cent gluten N in per cent of flour	Per cent alcohol-soluble in per cent of flour	Per cent coagulable N in per cent of flour	Per cent coagulable found in flour
O. C.	13.66	6.64	6.32	0.46	+0.12	14.20	1.95	0.94	0.90	0.96
R. W. B.	13.96	8.56	5.76	2.68	+0.12	9.56	1.33	0.82	0.55	0.56
B. L.	14.38	6.64	4.96	1.60	—0.08	9.35	1.34	0.56	0.46	0.58
P.	12.96	6.88	4.88	2.04	+0.04	17.20	2.23	1.18	0.84	0.92
L. C.	14.24	7.52	6.56	0.96	0.00	11.60	1.65	0.87	0.76	0.69
M. 15	14.28	6.48	4.96	1.50	—0.02	12.70	1.81	0.82	0.63	0.74

At any rate, gluten prepared in the manner described is excellently suited for the preparations of the component proteins of gluten in pure form. The ether-soluble materials can be removed first, then the alcohol-soluble, etc.

It is a recognized fact that gliadin is slightly soluble in water, somewhat in 1 per cent salt solution and practically insoluble in 10 per cent salt solution. Accordingly, one would expect to find a part of the gliadin in solution in the filtrates resulting from the

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[1] THIS JOURNAL, 4, No. 3 (1912).

separation of the coagulum of the alcohol-soluble. In the writer's experience it has been found that the coagulum is difficultly soluble in cold water. Further, upon evaporating the filtrates very small quantities of coagulum result which when transformed into the coagulable state remain practically insoluble. The amount of coagulable material which passes into the filtrates must be exceedingly small and in no case has the writer obtained sufficiently large quantities to warrant a determination to be made. From a quantitative point of view, it is safe to assume that practically all of the gliadin nitrogen has settled out or coagulated and the nitrogen bodies present in the filtrates are of less complex form.

Owing to the difficulties met with in transferring the sticky coagulum formed in the method described above and since the nitrogen contained in the coagulum, together with that found in the filtrate, equal the nitrogen found in the alcohol solution, the writer has deemed it a better method of procedure to estimate the nitrogen in the filtrate resulting from the separation of the coagulum and deduct this result from the nitrogen found in the alcohol-soluble extraction to get the gliadin nitrogen contained in the flour. The method for the estimation of gliadin nitrogen would then read as follows:

Digest four grams of flour with 200 cc. of 50 per cent alcohol by volume. Shake the contents at five-minute intervals for the first two hours, then let stand over night and finally filter clear. Determine the per cent of nitrogen in 25 cc. aliquots of the alcohol-soluble. Evaporate slowly 50 cc. aliquots of the alcohol-soluble to within 5 cc. volume, add 50 cc. distilled water, bring near to boil, and continue process until volume has been approximately reduced to 10 cc. Repeating, add 50 cc. of water and boil down to within 35 cc. volume. Allow contents of beakers to cool to room temperature, then filter. If necessary, repeat filter until filtrate becomes practically clear. Estimate the per cent of nitrogen contained in the filtrate and deduct this result from the per cent of alcohol-soluble nitrogen to get the per cent of gliadin nitrogen in the flour.

CONCLUSIONS

I. Alcohol solutions extract two groups of nitrogen-carrying bodies in wheat flour and gluten. Upon evaporating off the alcohol followed by the addition of water, one of the groups, *viz.*, gliadin, separates out, the other remaining in solution.

II. Salt solution of 1 per cent strength extracts a part of the gliadin contained in wheat flour.

III. The gliadin nitrogen obtained by the indirect method is much lower than that obtained by the direct method, but agrees remarkably closely with the results obtained for nitrogen in the coagulum in the alcohol-soluble.

IV. Of the two methods for the estimation of gliadin, the coagulation method is the shorter and is more suitable to use for this reason than the indirect method.

V. Alcohols ranging between 50 per cent to 65 per cent, inclusive, by volume, extract equivalent amounts of coagulum nitrogen. Above 65 per cent alcohol by volume there is a rapid falling off in the amount of coagulum nitrogen obtainable. Alcohol of 50 per cent by volume has been adopted by the writer for the determination of gliadin nitrogen.

VI. About 68 per cent of the total alcohol-soluble nitrogen is coagulable.

VII. Alcohol-soluble, incoagulable nitrogen is precipitated by phosphotungstic acid. This, together with the coagulable nitrogen, equals the total alcohol-soluble nitrogen.

VIII. In the same flours as much coagulable nitrogen is obtained in specially prepared gluten as in case of the flour.

IX. The easiest and shortest method for the estimation of the gliadin in flour is to estimate the nitrogen in the uncoagulable portion of the alcohol-soluble and deduct this result from the total alcohol-soluble nitrogen.

WASHINGTON EXPERIMENT STATION
PULLMAN

QUALITY OF THE MASSACHUSETTS MILK SUPPLY AS SHOWN BY THE INSPECTION OF THE STATE BOARD OF HEALTH

By HERMAN C. LYTHGOE

Received August 14, 1913

During the past year an investigation of the milk supply was undertaken with special reference to certain enzyme and other reactions which could possibly differentiate raw milk from pasteurized milk and new milk from old milk. The nature of these reactions and the source of the substances causing them are not yet clearly settled, but a study of the literature shows the following reactions which may be of an enzyme nature:

Raw milk contains a diastase capable of hydrolyzing 0.01 to 0.02 per cent of starch, a catalase which will liberate oxygen from hydrogen dioxide, a peroxidase which will cause hydrogen dioxide to react with certain organic substances, thereby producing colors, and reductases capable of decolorizing methylene blue solutions. Pasteurization has more or less influence upon the above reactions depending upon the temperature of pasteurization and the length of time subjected to this temperature, and the reactions are also modified by the age of the milk.

The reductases are produced by bacteria according to Konning,[1] Seligman,[2] and Grimmer.[3] On the contrary Seligman[2] states that some reductase may possibly exist in milk as an enzyme. Romer and Sames[4] question the enzyme nature of reductase and state that it is produced by the destruction of the cells of the mammary glands during milking, as the first milkings have but slight reducing properties and the last milkings are highly reducing.

Sames[5] is opposed to the enzyme nature of reductase and thinks that the Seligman assumption that the reduction is due to bacteria is too far reaching. Salus[6]

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[1] *Milchwirtschl. Zentr.*, **4**, 156.

[2] *Z. Hyg.*, **58**, 1.

[3] *Milchwirtschl. Zentr.*, **6**, 243.

[4] *Z. Nahr. Genussm.*, **20**, 1.

[5] *Milchwirtschl. Zentr.*, **6**, 462.

[6] *Arch. Hyg.*, **75**, 371.

is of the opinion that reductase is a product of cell transformation. Openheimer[1] states that reductase has nothing to do with bacteria and is difficult to distinguish from bacterial reductases.

The peroxidase according to Jensen[2] comes from the animal and is not formed by growing bacteria in milk. This is confirmed by Konning,[3] Kooper,[4] and Fred.[5] Bordas and Touplain[6] claim that this reaction is due to the casein or to calcium caseinate. They heated milk to 80°, 100°, and 120°, and after centrifuging obtained a cream giving a positive reaction, a skimmed milk giving a negative reaction and a precipitate giving a positive reaction when macerated with water, the heated milk before centrifuging giving a negative reaction. Sarthou[7] and Meyer[8] were unable to obtain these results, the latter stating that the results of Bordas and Touplain were not reliable and the reaction obtained was due to foreign dirt. Nicolas[9] disagrees with Bordas and Touplain but thinks that the casein plays an important part in the reaction. Hesse and Kooper[10] state that the peroxidase reaction is due to alkalinity; when milk is heated its alkalinity is decreased and it will give no reaction with the reagents. The heating according to Kooper[11] causes a precipitation of the calcium salts. Grimmer[12] is of the opinion that the peroxidase reaction is due neither to inorganic catalyzers nor to alkaline reaction but is a function of the milk albumin or is due to a substance allied to it which appears to be a protein or is absorbed by the albumin.

Milk catalase according to Fred[13] and Kooper[14] is of bacterial origin. Kooper states that catalase passes into the cream, that its growth increases with the acidity up to 40 or 50° of acid and then decreases. This is confirmed by Faitelowitz[15] who states that the decrease is due to the lactic acid formed and if the acid is neutralized, the catalase will still be active.

On account of their probable bacterial origin, the reductase and catalase reactions are of value in investigating the hygienic quality of milk. The reductase test is carried out in two ways: with a methylene blue and formaldehyde solution and with a methylene blue solution without formaldehyde known as F. M. reductase and M. reductase, respectively. The formaldehyde causes an acceleration in the time of reduction, fresh milk reducing the F. M. solution in a few minutes and the M. solution in several hours. According to Barthel[1] fresh milk containing 10,000 bacteria per cc. decolorized the M. solution in 11 hours, and the same milk four days old containing 47,500,000 bacteria per cc. decolorized in 14 minutes. He also states[2] that when the reduction takes place in less than one hour the milk has more than 10,000,000 bacteria per cc. and when the reduction requires from 1 to 3 hours the number of bacteria is from 10 to 4 million per cc. Barthel is of the opinion that milk decolorizing methylene blue in less than one hour is bacterially too impure for food and that good commercial milk should require at least three hours for decolorization.

Angelici[3] states that there is no absolute parallelism between the methylene blue reduction and number of bacteria, but that this test is well adapted to sanitary control. Fred[4] states that most but not all milk bacteria reduce methylene blue, and that milk reducing methylene blue in from one hour to 15 minutes contains from 15 to 50 million bacteria per cc. and milk requiring seven hours or more contains less than 1 million bacteria per cc.

Giffhorn[5] has made a study of these reactions and his results are given in the following table. The peroxidase reaction was preformed with active guaiac solution:

TABLE I—ENZYME REACTIONS OF MILK ACCORDING TO GIFFHORN

Character of milk	Guaiac reaction	M. reductase	F. M. reductase	Diastase	Catalase
Fresh and normal	Positive		5–12 minutes	Digests 0.01 to 0.02 per cent starch	5–70 mm.
Too old for use	Positive		1–5 minutes	Normal	High
Too old for use		Less than 1 hour	1–5 minutes	Low	Low
From diseased udders		Less than 1 hour	Slow	Digests 0.024 per cent starch	High
Heated above 72° was high in bacteria before heating and has stood a considerable time.....	Negative	Less than 1 hour	Less than 1 hour	None	High
Heated from 65°–72°	Positive			None	

Another property of milk of hygienic significance is its ability to coagulate with alcohol. If 95 per cent alcohol is added to milk in increasing quantities it will eventually cause coagulation. As coagulation is caused by the development of acid in the milk it is possible by using the correct strength and amount of alcohol to differentiate between milk above and below a certain acidity. The usual procedure is to add to the milk an equal volume of 68 per cent alcohol by volume. Milk which gives a precipitate under these conditions is sour enough to curdle when boiled.

According to Henkel[6] fresh milk does not coagulate with an equal or a double volume of 68 per cent alcohol or with an equal volume of 70 per cent alcohol. Suzinger[7] as a result of two years' work states that an equal

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[1] *Arb. kgl. Inst. experim. Therap. zu. Frankfurt a/M.*, **1908**, 75.

[2] *Rev. gen. lait.*, **6**, 85.

[3] *Milchwirtschl. Zentr.*, **4**, 196.

[4] *Z. Nahr. Genussm.*, **20**, 564.

[5] *Centr. Bakt. Parasitenk.*, *II Abt.*, **35**, 391.

[6] *Compt. rend.*, **148**, 1057. *Ann. Fals.*, **2**, 193. *8th Intern. Congr. Appl. Chem.*, **18**, 69.

[7] *Compt. rend. soc. biol.*, **68**, 434.

[8] *Arb. Kais. Gesundh.*, **34**, 115.

[9] *Bull. soc. chim.*, **9**, 266.

[10] *Z. Nahr. Genussm.*, **21**, 385.

[11] *Ibid.*, **23**, 1.

[12] *Milchwirtschl. Zentr.*, **2**, 295.

[13] *Centr. Bakt. Parasitenk.*, *II Abt.*, **35**, 391.

[14] *Z. Nahr. Genussm.*, **20**, 564.

[15] *Ibid.*, **21**, 294.

[1] *Z. Nahr. Genussm.*, **15**, 385.

[2] *Ibid.*, **21**, 513.

[3] *Clin. Vat.*, **34**, 388.

[4] *Centr. Bakt. Parasitenk.*, *II Abt.*, **35**, 491.

[5] Diss., Bern, 1909.

[6] *Milchwirtschl. Zentr.*, **3**, 387.

[7] *Ibid.*, **5**, 292.

volume of 68–70 per cent alcohol coagulates colostrum, milk from cows far along in lactation, milk from diseased udders as well as milk otherwise abnormal, and possibly milk from cows calving prematurely, but fresh normal milk does not usually coagulate with 68–70 per cent alcohol.

Barthel[1] says the reaction indicates souring with great certainty, and Rammstedt[2] states that it is a good preliminary test for freshness of market milk. Bolle[3] says it is not always trustworthy, as some milk will coagulate with alcohol and will not upon boiling. Fendler and Borkel[4] prefer to use a double volume of 50 per cent alcohol. Morres[5] has improved the test by adding alizarin to the alcohol. The alizarin is an indicator and the colors produced vary from lilac-red in fresh milk through the browns to a yellow in sour milk. This overcomes the objection of Bolle, by giving an additional indication of the amount of acid present.

The following table is given by Morres:

TABLE II—RELATION BETWEEN ACIDITY AND ALCOHOL PRECIPITATION IN MILK

Acidity Degrees Soxhlet-Henkel	Color of alizarin	Nature of precipitate with 68 per cent alcohol	Nature of the milk
7.0	Lilac-red	No precipitate	Normal and fresh
8.0	Pink	Very fine precipitate	Beginning to sour
9.0	Brownish red	Fine precipitate	Sourness increasing
10.0	Reddish brown	Precipitate	Critical state
11.0	Brown	Heavy precipitate	Coagulates on boiling
12.0	Yellowish brown	Very heavy precipitate	Coagulates on boiling
14.0	Brownish yellow	Very heavy precipitate	Coagulates on boiling
16.0 and above	Yellow	Very heavy precipitate	Coagulates on boiling

In the investigation made in this department the reductase, peroxidase, and alcohol precipitation reactions were employed; the details of the methods are as follows:

Reductase Reaction.—Schardinger's Test[6] *(F. M.):* Twenty cc. of milk are mixed in a test tube with 1 cc. of a solution containing 5 cc. of a saturated alcoholic solution of methylene blue and 5 cc. of 40 per cent formaldehyde in 190 cc. of water. The contents of the tube are covered with a layer of liquid petroleum to prevent access of air, and the tube is then placed in a water bath at a temperature of 45° to 50° C. Raw milk will decolorize this reagent in less than 20 minutes; pasteurized milk will take a longer time.

Schardinger Test (M): This is carried out in the same manner as the F. M. reaction except that the reagent consists of 5 cc. alcoholic methylene blue solution and 195 cc. of water.

Peroxidase Reaction.—(a) Rothenfusser's Test:[7] Dissolve 1 gram of *p*-phenylenediamine hydrochloride in 15 cc. of water. Dissolve 2 grams of crystallized guaiacol in 135 cc. of 96 per cent alcohol. Mix these solutions and keep in an amber-colored bottle. To 10 cc. of milk add 0.5 cc. of the above reagent and 3 drops of 3 per cent hydrogen dioxide. A blue-violet coloration is developed in raw milk and if the milk has been heated to a sufficiently high temperature no color is produced. *(b) The Benzidine Test:*[1] Dissolve 4 grams of benzidine in 100 cc. of 96 per cent alcohol. To 10 cc. of milk add 1 cc. of this reagent, 3 drops of 30 per cent acetic acid and 2 cc. of 3 per cent hydrogen dioxide; a blue coloration is produced with raw milk and none with milk heated to a sufficiently high temperature.

Alcohol Precipitation Test: Dissolve 0.3 gram of alizarin in one liter of 68 per cent alcohol (by volume). To a measured quantity of milk in a test tube add an equal volume of the reagent and shake.

The following experiments were undertaken to determine the influence of time and temperature of pasteurization upon these tests.[2] Five one-pint portions of known purity raw milk were gradually heated (rise of temperature about 2° C. per minute) in a water bath to temperatures of 60, 65, 70, 75 and 80° C. The samples were held at these temperatures for thirty minutes and portions removed every ten minutes. Portions were also removed when the temperature reached 40° and 50°. All these portions were subjected to the Schardinger, Rothenfusser and benzidine reactions and upon a few, bacterial counts were made. The results, including the examination of a sample of commercially pasteurized milk which had been heated to a temperature of 63° C. and held there for 35 minutes, are shown in the following tables:

TABLE III—SCHARDINGER TEST (F. M.). THE FIGURES SHOW THE MINUTES REQUIRED TO DECOLORIZE THE SOLUTION

Temp. of milk	Time held 0	10 min.	20 min.	30 min.	35 min.
20°	5				
40°	5				
50°	6				
60°	7	8	9	10	
63°					—a
65°	9	12½	16	21	
70°	12	20	85	—	
75°	40	—	—	—	
80°	—	—	—	—	

a — = no decolorization in several hours.

TABLE IV—BACTERIA PER CC.

Temp. of milk	Time held 0	10 min.	20 min.	30 min.
20°	18,000			
40°	180			
50°	120			
60°				60
65°				
70°	40			30
75°				
80°	Spores only			Sterile

Three identical samples of milk, pasteurized by being heated to 63° and held there for 35 minutes, were obtained from a milk contractor. The samples were kept in the refrigerator and a new bottle opened

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[1] *Z. Nahr. Genussm.*, **21**, 513.

[2] *Z. öffent. Chem.*, **17**, 441.

[3] *Z. landw. Versuch.*, **13**, 292.

[4] *Z. Nahr. Genussm.*, **21**, 477.

[5] *Ibid.*, **22**, 459.

[6] *Ibid.*, **5**, 1113.

[7] *Milchwirtschl. Zentr.*, **6**, 468.

[1] *Z. Nahr. Genussm.*, **16**, 172.

[2] This experimental work was performed with the collaboration of Mr. Lewis I. Nurenberg, Asst. Analyst of the Mass. State Board of Health.

Table V—Rothenfusser Reaction

Temp. of milk	Time held 0	10 min.	20 min.	30 min.
20°	+			
40°	+a			
50°	+			
60°	+	+	+	+
65°	+	+	+	+
70°	+	faint	faint	faint
75°	—a	—	—	—
80°	—	—	—	—

a + = color produced. — = no color produced.

Table VI—Benzidine Reaction

Temp. of milk	Time held 0	10 min.	20 min.	30 min.
20°	+a			
40°	+			
50°				
60°	+	+	+	+
65°	+	+	+	+
70°	faint	faint	very faint	very faint
75°	—a	—	—	—
80°	—	—	—	—

a + = color produced. — = no color produced.

each day and tested. The results are given below:

	F. M.	Benzidine test	Rothenfusser test	68 per cent alcohol
1st day.....	—	faint	+	no ppt.
2nd day.....	—	+	+	no ppt.
3d day......	10 min.	+	+	no ppt.

From the above experiments we may conclude that it is impossible to detect commercially pasteurized milk by means of the peroxidase reaction, but it can be detected within two days by the Schardinger reaction. The impracticability of the benzidine and Rothenfusser tests as applied to market milk is shown by the fact that but 7 out of a total of 2470 samples of Massachusetts market milk gave a reaction for teated milk. Of these same samples, 348 were pasmurized according to the Schardinger test which is more in accord with the conditions of the Massachusetts milk supply.

Although there is a relation between the M. reductase and the alcohol precipitation test, there does not appear to be an exact parallelism. This may be due to the fact that pasteurization increases the time of the M. as well as the F. M. reduction, and subsequent souring may not develop sufficient reductase to reduce methylene blue within one hour. The following table has been prepared from the results of examination of 77 samples of milk, all of which reduced methylene blue and 48 of which gave precipitates with 68 per cent alcohol:

Table VII—Relation between Alcohol Precipitation and M. Reductase

Time of reduction of methylene blue	Color of precipitate with 68 per cent alcohol and alizarin
30 minutes and above	No precipitate
25 minutes	Reddish brown precipitate
20 minutes	Brownish red precipitate
15 minutes	Brown precipitate
10 minutes	Brownish yellow precipitate
5 minutes and less	Yellow precipitate

This shows that the alcohol precipitation method is less sensitive in detecting old milk than the M. reductase reaction, but it is easier to perform, and if a precipitate is given, the sample no doubt is or has been high in bacteria.

The following tables give the statistics of the examinations of milk during the year ending February 28, 1913:

Table VIII—Summary of Milk Statistics

Month 1912	Number above standard(a)	Number below standard	Total samples collected	Skimmed samples marked	Skimmed samples not marked	Watered sample	Pasteurized samples	Pasteurized samples below standard	Per cent of skimmed samples not marked	Per cent of watered samples	Per cent of pasteurized samples	Per cent of pasteurized samples below standard	Per cent of total samples below standard	Samples giving ppt. with 68 per cent alcohol	Pasteurized samples giving ppt. with 68 per cent alcohol	Samples reducing methylene blue in 30 min. to 1 hour	Samples reducing methylene blue in less than 30 minutes	Per cent total samples giving ppt. with alcohol	Per cent pasteurized samples giving ppt. with alcohol	Per cent samples reducing M. in 30 min. to 1 hour	Per cent samples reducing M. in less than 30 min.
March........	270	43	313	3	1	3	82	7	0.3	1.0	26.2	8.5	13.7	18	4	..	..	5.8	4.9	..	..
April.........	281	96	377	.	5	6	61	16	1.3	1.6	16.2	26.2	25.5	34	3	..	..	9.0	4.9	..	..
May..........	304	109	413	1	5	19	24	5	1.2	4.6	5.8	20.8	26.4	25	1	..	..	6.1	4.2	..	..
June..........	341	169	510	1	5	29	36	8	1.0	5.7	7.1	22.2	33.2	16	.	..	..	3.1	...	..	..
July..........	275	195	470	2	1	25	7	2	0.2	5.3	1.5	28.6	41.5	23	1	..	..	4.4	14.5	..	..
August........	295	154	449	1	17	4	45	3	3.8	0.9	10.0	6.7	34.3	39	5	12	39	8.7	11.1	2.7	8.7
September....	311	139	450	3	..	13	61	10	...	2.9	13.5	16.4	30.9	28	1	15	39	5.6	1.4	3.3	8.6
October.......	397	127	524	6	7	9	73	8	1.3	1.7	13.9	11.0	24.2	29	7	5	26	5.5	10.4	0.9	5.0
November....	247	87	334	1	8	17	50	12	2.4	5.1	15.0	24.0	26.1	12	1	1	7	3.6	2.0	0.3	3.6
December.....	365	34	399	2	5	3	85	6	1.5	0.9	21.3	7.1	8.5	2	.	.	2	0.5	....	...	0.5
1913																					
January......	276	120	396	1	5	42	50	7	1.3	10.6	12.6	14.0	30.6	20	.	1	9	5.3	...	0.3	2.3
February.....	250	70	320	.	8	25	39	5	2.5	7.8	12.2	12.8	21.9	10	2	3	2	3.0	5.1	0.1	0.1
Totals........	3612	1343	4955	21	67	195	613	89	1.4	3.9	12.4	14.5	27.2	256	25	37	124	5.2	4.1	1.3	4.3

(a)Legal milk standard in Massachusetts: 12.15 per cent solids; 3.35 per cent fat

A study of the summary of Tables VIII and IX shows that of 4955 samples examined, 262 or 5.3 per cent were adulterated, 67 of which were skimmed and 195 contained added water. Ten hundred and eighty-one or 21.6 per cent of the total samples were below the legal standard and could not be declared adulterated. Of the total samples 613 or 12.4 per cent were found to be pasteurized according to the Schardinger F. M. reaction of which 89 or 14.5 per cent were below the legal standard.

The commercial pasteurized milk is as a rule prepared on a large scale and represents mixed milk

TABLE IX—QUALITY OF AVERAGE MILK

Month 1912	Average of all samples			Average of samples not declared skimmed or watered				Average of raw samples not declared skimmed or watered				Average of pasteurized sample not declared skimmed or watered			
	Solids Per cent	Fat Per cent	Solids - not - fat Per cent	Number	Solids. Per cent	Fat Per cent	Solids - not - fat Per cent	Number	Solids. Per cent	Fat Per cent	Solids - not - fat Per cent	Number	Solids Per cent	Fat Per cent	Solids - not - fat Per cent
March	12.61	3.76	8.85	306	12.66	3.80	8.86	224	12.68	3.82	8.86	82	12.57	3.72	8.85
April	12.68	3.86	8.82	366	12.74	3.90	8.84	306	12.82	3.95	8.87	60	12.43	3.74	8.69
May	12.46	3.86	8.60	388	12.67	3.94	8.73	364	12.68	3.94	8.74	24	12.47	3.78	8.69
June	12.33	3.73	8.60	475	12.42	3.78	8.64	445	12.42	3.78	8.64	30	12.47	3.73	8.74
July	12.21	3.72	8.49	442	12.33	3.77	8.56	435	12.33	3.77	8.56	7	12.29	3.66	8.63
August	12.34	3.76	8.58	427	12.71	3.91	8.80	382	12.68	3.89	8.79	45	12.88	4.09	8.79
September	12.46	3.77	8.69	434	12.54	3.83	8.71	375	12.58	3.82	8.76	59	12.38	3.81	8.57
October	12.69	3.84	8.85	502	12.77	3.91	8.86	429	12.76	3.89	8.87	73	12.82	3.95	8.87
November	12.65	3.87	8.78	308	12.81	3.96	8.85	258	12.83	3.97	8.86	50	12.69	3.84	8.85
December	12.94	3.94	9.00	389	12.99	3.99	9.00	304	13.05	4.01	9.04	85	12.75	3.90	8.85
1913															
January	12.45	3.82	8.63	348	12.75	3.94	8.81	299	12.78	3.97	8.81	49	12.59	3.77	8.82
February	12.57	3.80	8.77	287	12.76	3.89	8.87	250	12.77	3.91	8.86	37	12.67	3.80	8.87
Totals and Averages	12.56	3.82	8.74	4672	12.67	3.88	8.79	4071	12.68	3.88	8.80	601	12.62	3.84	8.78

rather than milk from individual cows and therefore should always be above the standard unless for some unknown reason an unusual amount of low-grade milk which is produced on many of the farms is run into the mixer. The analyses of the samples of milk from one of the milk corporations shows that with the exception of those few samples which for removal of cream have resulted in prosecution, the per cent of solids and of fat followed the seasonable variation of milk for that year as shown by our average analysis of all the good samples. In many localities, however, small dealers buy milk from these contractors to mix with their own supply which is insufficient to supply their customers and which may be naturally below the standard. Another way to account for below standard pasteurized milk is that many small dealers buy pasteurized milk and add water to it, and others buy pasteurized skimmed milk to mix with a high-grade whole milk, thereby producing below standard milk which would give a reaction for heated milk and in which the adulteration could not be detected if skilfully performed.

The pasteurized samples showed less variation in solids and less adulteration than the total milk. The variation in solids of the total, raw, and pasteurized samples is shown in Table X from which it may be seen that the percentage of samples with total solids between 12.15 and 13 per cent is greatest in pasteurized milk and least in raw milk.

There is a popular opinion prevailing that the large dealers are manipulating their output by adding skimmed milk, this opinion originating, no doubt, from the fact that this form of adulteration could be carried out successfully if judiciously performed. The figures in Table IX would indicate that this opinion is wrong. The average milk free from adulteration had a total solid content of 12.67 per cent and fat content of 3.88 per cent. This was reduced to 12.56 per cent solids and 3.28 per cent fat (the average of the total milk samples) by the addition of 0.39 per cent of water and the removal of 0.41 per cent of the cream (calculated from the composition of the average adulterated sample, 10.5 per cent solids, 2.6 per cent fat representing the addition of 10 per cent water and the removal of 23 per cent of the fat). The average of the pasteurized milk is 12.62 per cent total solids and 3.84 per cent fat which is lower than the average raw milk by 0.06 in solids and 0.04 in fat. This does not indicate watering but may be accomplished by the addition of 0.5 per cent of skimmed milk. It does not seem feasible that a large corporation would do this to such a slight extent as the resulting profit of about 0.1 per cent would no doubt be offset by the cost of manipulation. That the fat is lower in the average pasteurized milk than in the average raw milk is probably due to the fact that large dealers separate their cream as a rule from milk of an unusually high fat content, thereby leaving for the trade, milk of slightly lower fat content than the average.

TABLE X—VARIATION IN MILK SOLIDS

	Above 15 per cent	Between 14 and 15 per cent	Between 13 and 14 per cent	Between 12.15 and 13 per cent	Between 11 and 12.15 per cent	Between 10 and 11 per cent	Between 9 and 10 per cent	Between 8 and 9 per cent	Below 8 per cent
Total samples:									
Number	66	257	1081	2366	1125	125	47	14	10
Per cent	1.3	5.0	21.2	46.5	22.1	2.5	0.9	0.3	0.2
Raw samples:									
Number	59	235	963	2000	1048	110	42	12	9
Per cent	1.3	5.3	21.5	44.6	23.4	2.5	0.9	0.3	0.2
Pasteurized samples:									
Number	7	22	118	366	77	15	5	2	1
Per cent	1.1	3.6	19.3	59.7	12.5	2.5	0.8	0.3	0.2

The sale of pasteurized milk is increasing, and notwithstanding that some authorities declare pasteurized milk inferior to raw milk in many respects, it seems that pasteurization is the only solution of the problem of furnishing the public in large cities with a wholesome supply of milk. These cities are so remote from the source of production that the milk is often 72 hours old before it is delivered to the consumer. In the localities where pasteurized milk is sold, about 18 per cent of the samples collected were found to be pasteurized and in the area of greater Boston 621 samples were collected in Boston, Brookline, Cambridge, Chelsea, Everett, Malden, Milton, Newton, Revere, and Somerville of which 211 or 34 per cent were pasteurized. This is, no doubt, below the true figure on account of the fact that the samples are taken uniformly from the different dealers and not in proportion to the size of their routes; the dealers selling the most milk are without doubt those who sell the pasteurized milk, while the man with the small route generally sells raw milk.

The number of adulterated samples are about the same as found in past years. The laboratory records would indicate that there is more watering done by the producer and more skimming is practiced by the small retailer. The adulteration of milk is not as a rule carried on by the same men. We make but few complaints in court alleging a second offense, for after one prosecution the convicted person either ceases the adulteration, or else goes out of the business. The actual market conditions are better in this respect than our figures show because we collect such a large number of samples from suspected persons. No doubt less than 2 per cent of our milk supply is subject to adulteration.

The alcohol precipitation test showed that 5.2 per cent of the total samples and 4.1 per cent of the pasteurized samples were sufficiently old when they reached the laboratory to curdle on boiling. The results of the M. reductase test showed that 5.6 per cent of the samples collected during seven months were too old to use as food when they reached the laboratory. If these samples could have been tested at the time of taking, the figures would have been lower during the summer months but not much difference could have been expected during cold weather. The pasteurized samples were better in this respect than the raw samples. These figures are higher than would be consistent with a thoroughly hygienic milk supply for if 94 per cent of the samples reached the laboratory in good condition the other 6 per cent collected at the same time would have done so if fresh. An example of very old milk was shown in the samples furnished to a contractor, which were nearly sour when they reached the laboratory, about two hours after being delivered by the producer. It is fortunate that these conditions are unusual or it would be impossible for the consumers in congested districts to obtain any sweet milk.

SUMMARY

1. It is possible to detect commercial pasteurized milk by the Schardinger reaction but not by the peroxidase reaction.
2. The amount of pasteurized milk on the market is greatest in the large districts.
3. The average quality of the milk is considerably above the legal standard.
4. The average quality of the pasteurized milk is very slightly below that of the raw milk but this does not appear to be due to adulteration.
5. Pasteurized milk shows less fluctuation in composition than raw milk, and the percentage of samples below standard is less of the former.
6. Fresh milk will not coagulate with an equal volume of 68 per cent alcohol.
7. Ninety-four per cent of the samples delivered at the laboratory gave reactions for fresh milk; the balance was too old for use as fresh milk.

I wish to acknowledge my indebtedness to my assistant Mr. Lewis I. Nurenberg for collaboration in the experimental and routine work, and to Mr. Henry N. Jones for making the bacterial counts.

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THE DETECTION OF GELATIN IN SOUR CREAM

By Armin Seidenberg

Received August 4, 1913

The usual method for the detection of gelatin in food products such as milk or cream and that adopted provisionally by the United States Department of Agriculture[1] consists in the removal of the proteids with acid mercuric nitrate and the precipitation of the gelatin in the filtrate with picric acid. It, however, has been frequently noticed that a sweet cream which gave no precipitate with picric acid would, after souring, show quite a perceptible turbidity on its addition, often heavy enough to lead to the assumption that gelatin was present. It seems most probable that this is due to protein decomposition products not precipitated by the acid mercuric nitrate. G. E. Patrick, in an address on "The Detection of Thickeners in Ice Cream,[2] made before the 24th Annual Convention of Official Agricultural Chemists, speaks of what is probably the same or a very similar decomposition product, often found in ice cream after it has soured. He is not certain as to the exact nature of this substance, but believes it to be due to the action of bacteria. He finds that this "pseudo-gelatin," as he calls it, forms a precipitate with picric acid similar to that formed by gelatin under the same conditions and mentions that there is no method known for distinguishing the one from the other. His suggestion, that formaldehyde be added in the laboratory to prevent the bacterial action which produces this decomposition product, is of course not applicable to creams received sour.

The picric acid precipitate from the sour cream is flocculent, resembling $Al(OH)_3$ in form and settles quite rapidly, while that due to gelatin is small and granular, much like $BaSO_4$ in form, settles very slowly and on shaking the test tube thoroughly will coalesce in large lumps leaving the solution almost clear. While these differences are quite well defined, the large number of sour cream samples received in this laboratory made a method leaving less room for doubt, in the detection of even small amounts of gelatin, very desirable. After some experimenting I found that there was a sharply defined difference between the solubilities of the two precipitates in hot, neutral water. While both precipitates are soluble on heating in slightly acid solutions, only the gelatin picrate is soluble in hot, neutral water alone. The picric acid precipitate from the sour cream is seemingly entirely insoluble in hot water, after all the picric or other acid has been removed.

To 10 cc. of the cream are added an equal volume

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[1] U. S. Dept. Agr., *Bull.* **107** (rev.), p. 121.

[2] U. S. Dept. Agr., *Bull.* **116**, p. 24.

of acid mercuric nitrate, the mixture shaken, 20 cc. of water added, again shaken and filtered after 5 minutes. To the filtrate an equal volume of picric acid is added when if gelatin or the soluble decomposition products from the sour cream are present, a precipitate is formed. This is the method mentioned in *Bulletin* **107** of the U. S. Dept. of Agriculture.

In order, definitely, to determine the nature of this precipitate, proceed as follows: Cork test tube which should be a large one, and shake very thoroughly. In this way the gelatin picrate will coalesce and filtration be much more rapid. If possible allow to stand for some time after shaking; most of the liquid can then be siphoned off. The precipitate after being brought on to the filter is washed with water containing two to three drops of ammonium hydroxide to 100 cc. until the washings are slightly alkaline to litmus, and then with neutral water until the washings are neutral to litmus. This will remove all excess of picric acid. The precipitate is then transferred to a small beaker and 10 to 20 cc. distilled water added and heated to boiling. If the precipitate is very small in amount it need not be taken from the filter paper, but both can be boiled together.

Filter hot into a test tube. The filtrate will contain the gelatin picrate but not the precipitate derived from the proteids in the sour cream. Cool this filtrate and add an equal volume of picric acid, when, if gelatin was present in the original cream, a decided precipitate will be formed. When large amounts of gelatin are present the solution may become turbid on merely cooling.

In order to determine the delicacy of this method, 25 cc. of a 1 per cent solution of gelatin containing 0.25 gram of gelatin were added to 50 grams of sour cream. The sour cream thus contained only 0.5 per cent of gelatin, which had little thickening effect on it. By using 20 to 25 cc. of this cream instead of 10 cc. as above the presence of the gelatin could be determined with certainty. The above method has been in use in this laboratory for some time and has been found to work satisfactorily, provided the conditions described are obtained. Even smaller quantities of gelatin than this can, of course, be detected by using a larger amount of the original sample.

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A STUDY OF THE COMPOSITION OF CIDER VINEGARS MADE BY THE GENERATOR PROCESS

By L. M. Tolman and E. H. Goodnow

Received August 18, 1913

When an investigation of the composition of cider vinegar was undertaken by the Bureau of Chemistry about four years ago, a study of the literature on the subject showed that the existing data were composed almost exclusively of analyses of vinegars made by the old barrel process. The authenticity of the two or three samples of generator vinegars reported was not beyond question because of the extreme difficulty of obtaining true samples of such vinegar. There was practically no analytical basis on which the purity of a given cider vinegar could be determined, and only the most obvious adulterations or substitutions could be detected with certainty. Apparently authentic cider vinegars were reported as containing amounts of solids varying from 1.18 to 8.00 per cent of ash from 0.19 to 0.57 per cent with the other constituents in the same general proportions. A review of the extensive data on fermented ciders, however, showed no such wide variations in composition, and plainly indicated that this marked difference in the composition of cider vinegars was due not to a similar difference in the composition of the raw material, but rather to the method of manufacture. As a new and scientifically controlled process of manufacture had become widely established, and was the source of practically all of the "commercial" cider vinegar on the market, it seemed probable that the product prepared by this process might differ perceptibly from the "barrel" vinegars, and this study was projected with this idea in view.

The essential differences between the barrel method and the generator method of making cider vinegar will be apparent from a brief description of these processes. The conversion of apple juice into vinegar in the barrel was, until recent times, the generally accepted method in this country. Although no longer used for the preparation of cider vinegar in large amounts on a commercial scale, it is still very largely employed on the farm as the source of the family supply. The general procedure is as follows: The juice expressed from the apples is allowed to ferment in a barrel, usually of 40 to 50 gallons capacity, until practically all of the sugar has been changed into alcohol, and the resulting hard cider stored in some dark place, frequently a cellar, where the formation of acetic acid takes place gradually. Under the most favorable conditions the conversion into vinegar is slow. The long period of storage required gives opportunity for infection by harmful organisms, with the development of mal-fermentations, which frequently change the character and composition of the product to a marked degree. The conditions of storage, temperature, cleanliness of the barrel and surroundings are factors entering largely into the quality of the finished vinegar. The simplicity of the method as regards mechanical features is more than offset by the disadvantages of an uncontrolled acetification.

The rapid or generator process is carried on in this country in a very uniform practice which may be outlined as follows: Large quantities of apples are pressed and the juice collected in tanks, holding from 200 to 1,000 barrels where it is allowed to ferment until the sugar is almost completely removed. It is obvious that this alcoholic fermentation on a large scale in contrast to the fermentation on a small scale in the barrel, tends to produce a uniform product. The hard cider thus obtained is run over the generators, which consist of upright cylindrical tanks filled with beech shavings, corn-cobs, rattan, or some similar porous material saturated with strong vinegar. The alcohol is converted almost immediately into acetic acid. The entire process is under exact control, and can be completed in a very short time compared with the old method. There is practically no opportunity for mal-fermentations to develop and their occurrence would be readily detected. Fully 90 per cent of the cider vinegar made on a commercial scale in the United States is manufactured by this generator process.

It was impossible to establish a fair standard for judging the purity of generator vinegars on the basis of the existing analytical data on barrel vinegars. Before such a standard could be established some data with reference to the composition of generator vinegars must be available and the changes taking place during this method of acetification clearly understood.

Table I—Analyses of Ciders and Vinegars from Tanks 1 and 2

Cider and Vinegar	Date 1912	Alcohol by volume Per cent	Solids. Grams per 100 cc.	Total Fehling reducing bodies. Grams per 100 cc.	Total sugars as invert Grams per 100 cc.	Non-sugars. Grams per 100 cc.	Ash. Grams per 100 cc.	Alkalinity of soluble ash. Cc. N/10 acid per 100 grams	Total acids as acetic Grams per 100 cc.	Fixed acids as malic Grams per 100 cc.	Ash in non-sugars Per cent	Pentosans. Grams per 100 cc.	Glycerol. Grams per 100 cc.
Tank 1:													
CIDER:													
First day's run	Jan. 18	7.9	3.05	....	0.57	2.48	0.34	39.0	0.48	0.15	13.7	0.153	0.31
Eighth day's run	Jan. 25	7.8	3.09	....	0.58	2.51	0.35	39.8	0.50	0.18	13.9	0.156	0.29
Eleventh day's run	Jan. 29	7.8	3.09	....	0.58	2.51	0.35	39.2	0.48	0.17	13.9	0.158	0.31
Fourteenth day's run	Feb. 1	7.8	3.07	....	0.57	2.50	0.34	38.6	0.46	0.19	13.6	0.165	0.30
Vinegar from previous run used to start this tank, generated	Jan. 17	0.38	2.45	0.69	0.43	2.02	0.34	35.6	5.75	0.04	16.8	0.176	0.27
VINEGAR:													
First day's drip	Jan. 18	0.40	2.48	0.58	0.41	2.07	0.34	36.4	5.73	0.04	16.4	0.179	0.28
Third day's drip	Jan. 20	0.41	2.56	0.59	0.41	2.09	0.34	36.8	5.72	0.05	16.2	0.176	0.27
Sixth day's drip	Jan. 23	0.45	2.54	0.63	0.45	2.09	0.33	37.6	5.71	0.05	15.8	0.180	0.29
Eighth day's drip	Jan. 25	0.40	2.59	0.68	0.48	2.11	0.34	36.8	5.91	0.05	16.1	0.181	0.28
Tenth day's drip	Jan. 27	0.46	2.70	0.70	0.50	2.20	0.33	37.4	5.85	0.06	15.5	0.180	0.27
Thirteenth day's drip	Jan. 30	0.46	2.76	0.70	0.52	2.24	0.33	36.6	5.76	0.06	14.7	0.195	0.29
Sixteenth day's drip	Feb. 2	0.42	2.79	0.74	0.55	2.25	0.34	37.2	5.76	0.07	15.1	...	0.28
Tank 2:													
CIDER:													
First day's run	Feb. 3	7.75	2.78	....	0.37	2.41	0.35	38.4	0.50	0.19	14.5	0.120	0.30
Ninth day's run	Feb. 11	7.7	2.76	....	0.36	2.40	0.35	36.8	0.48	0.20	14.6	0.111	0.31
Fourteenth day's run	Feb. 16	7.6	2.73	....	0.35	2.38	0.35	36.6	0.48	0.20	14.4	0.114	0.31
Seventeenth day's run	Feb. 19	7.6	2.72	....	0.33	2.39	0.38	39.6	0.52	0.22	13.8	0.118	0.29
VINEGAR:													
Second day's drip	Feb. 4	0.43	2.81	0.77	0.56	2.25	0.35	37.2	5.74	0.08	15.5	0.183	0.28
Eighth day's drip	Feb. 10	0.43	2.79	0.73	0.53	2.26	0.36	38.4	5.80	0.07	15.9	0.175	0.28
Thirteenth day's drip	Feb. 15	0.40	2.80	0.72	0.53	2.27	0.36	38.8	5.98	0.06	15.9	0.178	0.29
Seventeenth day's drip	Feb. 19	0.37	2.78	0.72	0.52	2.26	0.35	38.4	6.02	0.07	15.5	0.172	0.29
Vinegar made from following tank	Feb. 27	0.35	2.69	0.69	0.49	2.20	0.33	38.4	6.02	0.07	15.0	0.161	0.27

Accordingly, arrangements were made with a favorably situated cider vinegar factory where the so-called "single-run" generator system was used. In this system the cider is mixed with a slightly larger quantity of strong vinegar to reduce the alcoholic content of the feed to such an extent that a single passage through the generator would completely convert the alcohol in the mixture into acetic acid. This factory was so arranged that all of the 60 generators in operation were fed from a central supply tank system and all of the finished vinegar was collected in one central receiving tank. Thus by determining the composition of the cider and vinegar which were mixed to supply the generators, and finally of the vinegars produced, the changes taking place during the conversion of cider into vinegar could be closely followed.

In a small laboratory established at the factory, certain determinations, such as solids, ash, sugar, acidity, alcohol and color, were made. Each day samples were taken of the cider, of the vinegar used to mix back for the feed and of the finished vinegar coming from the generators, thus practically establishing a chemical control of the manufacture. The amounts of cider and vinegar used for the feed were carefully measured so that its composition could be accurately calculated. By carrying this experiment over a period of about two months and running some 40,000 gallons of cider over the generators, some interesting and conclusive figures were obtained.

At the beginning of this experimental run the shavings in the generators were saturated with vinegar made from the cider used in the previous run just completed. Before vinegar representative of the new tank of cider could be obtained, it was, therefore, necessary that this vinegar should be completely displaced. As 3 or 4 barrels of vinegar were held absorbed in the packing material of each of the generators, several days would be required before such displacement would normally occur. Another factor which would retard the securing of a vinegar characteristic of this tank of cider lay in the method of feeding the generators. The cider stock was not fed "straight," but instead first mixed with a slightly larger volume of vinegar. For the first day's feed, January 18, vinegar from the drip of January 17 was used for this "mixing back," and each day the vinegar for this purpose was taken from the drip of the preceding day. With this system, it can readily be seen that considerable time must elapse before the vinegar dripping from the generators would be characteristic of the cider stock being fed, especially if there was much difference in the composition of the cider stock and of the vinegar from the previous tank.

In the preceding table a sufficient number of analyses of the ciders and vinegars taken at intervals during the running of Tanks 1 and 2 has been given to show the changes in composition observed. Each tank contained about 20,000 gallons of cider which was practically of constant composition from the first pumpings to the last, so that for the purpose of comparison a slight variation need not be considered.

Although the vinegar produced on the first day of the experimental run, January 18th, did not differ perceptibly from that of the previous day, decided changes were noted as the operations continued. The total acidity showed a good average yield of acid and remained nearly constant for the entire period, varying only 0.3 gram during the run of the two tanks. Less than 0.5 per cent alcohol remained unconverted in the finished vinegar coming from the generators.

The fixed acids are noticeably affected by the acetification process. The cider of Tank 1 contained about 0.15 gram fixed acids and the vinegars mixed back for the feed 0.04 gram, so that the feed had a fixed acid content of about 0.10 gram. The vinegar coming from the generators contained 0.04 gram fixed acids, and, although the amount increased to 0.08 gram as the run progressed, due to a similar proportional increase in the fixed acid content of the cider, there was a loss of approximately 60 per cent in the generators. This elimination of fixed acids during the acetification process is shown graphically by the curves in Fig. 1. There appears to be a very uniform and constant loss during acetification. In this respect the generator method produces effects similar to the barrel process, in which the fixed acids gradually disappear during the conversion of the cider into vinegar. As the sweet cider probably contained from 0.3 to 0.4 gram of fixed acids, it is apparent that the loss of fixed acids in both the alcoholic and acetic fermentations is very large.

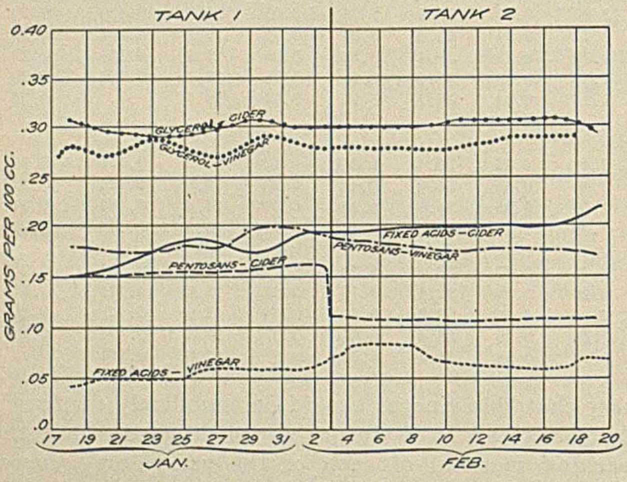

Fig. 1—Variations of Fixed Acids, Pentosans, and Glycerol during Conversion of Cider into Vinegar

The most notable change was in the content of solids. The first day's drip showed 2.48 grams while the feed had 2.72 grams, calculated from the proportions of carefully measured cider and vinegar used, and the cider itself 3.05 grams. Thus the vinegar coming from the generator contained 0.24 gram less solids than the feed running onto the generator, and 0.57 gram less than the cider stock. This apparent reduction of solids in the generator during the acetification process is readily accounted for when the mechanical features of the process are taken into consideration. In each of the 60 generators at least 200 gallons of vinegar were held in the shavings, making approximately 12,000 gallons of vinegar in the series of generators at the start. To each generator every day were fed 40 gallons of mix, containing approximately 18 gallons of cider. The vinegar of this mix had practically the same composition as the vinegar in the generators, the vinegar from the previous day's drip being used for making up the feed. Thus each day a 40-gallon feed containing only 18 gallons of the cider was run into at least 200 gallons of vinegar in the generator, and 40 gallons of this mixture dripped out. Consequently only a slight change in the composition of the vinegar dripping from the generator could be expected from day to day, because of the comparatively small volume of the cider fed. When it is borne in mind that there were but 20,000 gallons of cider in Tank 1

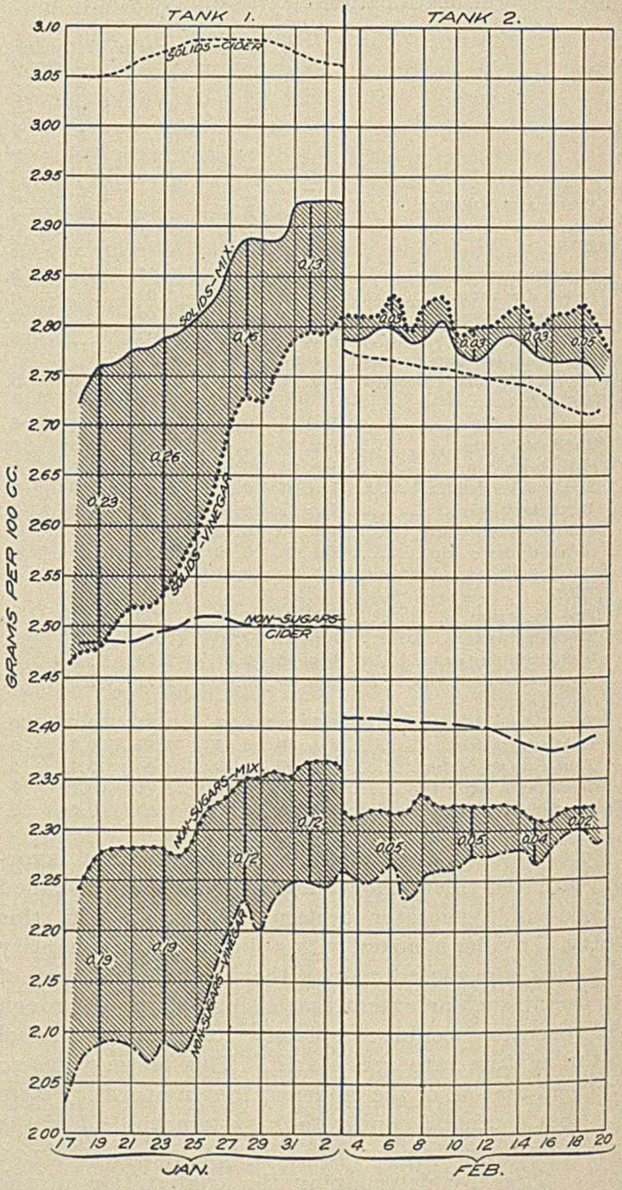

Fig. 2—Curves for Solids and Non-Sugars

and at least 12,000 gallons of vinegar to be displaced in the generators before a vinegar truly characteristic of this cider could be obtained, besides the retarding effect of mixing back each day with a more than equal amount of vinegar from the drip, it is evident that the changes observed must be gradual. That such was the case is shown by the analyses given in Table I and the curves in Fig. 2.

It will be noted that the solids in the vinegar showed an almost uniform daily increase, gradually approaching the solids content of the cider. At the end of 17 days' run on this tank, when the last of the cider had been fed on, the vinegar of the drip contained 2.79 grams solids, an increase of 0.31 gram during the run of this tank, or an average increase of nearly 0.02 gram per day.

The following tank of cider was much lower than the first in solids, having a content of 2.78 grams. The vinegar dripping from the generators contained 2.81 grams solids and the mix for the first day of the run, February 3, 2.78 grams. Thus at the beginning of the run of this tank the solids content of the mix being fed to the generators was practically identical with both that of the vinegar soaked in the shavings, and the cider stock being used, in sharp contrast with the wide differences noted at the start of the run of Tank 1. Were there any appreciable loss of solids in the generator during the acetification process, it would be plainly apparent under these conditions.

From the analyses given in Table I and the curves in Fig. 2, it will be noted that the solids content of the vinegar was almost constant during the run of this tank, and very slightly in excess of the solids in the mix, showing conclusively that there is no appreciable loss of solids in the generation of vinegar by this method. The variations observed in the running of Tank 1 were due mainly to the lag caused by the mixing back with vinegar of a different composition and by the large amount of vinegar of a different composition in the generators when the experiment began. The results indicate that if Tank 1 had been much larger, containing perhaps 40,000 gallons, and the experiment could have been continued for two weeks longer, a vinegar of practically the same composition as the cider would have come from the generator. This is shown clearly by the curves for the solids in Fig. 2. In the case of Tank 1, where the solids of the cider and of the vinegar soaked in the generator, varied widely, there is a decided rise in the curves for both vinegar and mix, these two curves approaching each other. In the case of Tank 2, in which the solids of the cider and the vinegar retained in the generators were practically the same, the curves show no appreciable change during acetification.

The variations in the non-sugar solids during acetification were similar to those already noted in case of the total solids. The cider of Tank 1 had a non-sugar content of 2.48 grams, while the vinegar from the previous day's drip and the vinegar which was absorbed in the filling material of the generator contained only 2.02 grams of non-sugars, and the mixture of cider and vinegar run onto the generators contained 2.22 grams. Thus at the beginning of the experimental run the vinegar coming from the generator and retained in the generator contained about 0.2 gram non-sugars less than the mix fed to the generators and 0.46 gram less than the non-sugar solids in the cider. As the run progressed the non-sugars in the finished vinegar increased gradually, as will be seen from the curves in Fig. 2, approaching the amount present in the feed; but this increase is not quite as rapid as the increase in the total solids.

In the case of Tank 2, the non-sugar content of the cider was 2.41 grams, and that of the vinegar coming from the generator 2.25 grams, so that the mixture of the two going onto the generator contained 2.33 grams. During the run the non-sugar solids in the drip increased very slightly, the vinegar containing 2.26 grams at the end of the run or only about 0.05 gram less than the mix being fed on, but it is probable that this slight loss is more apparent than real. The non-sugars are the resultant of the difference between the total solids and the total sugars, calculated as invert sugar, and any error in the determination of either of these constituents would affect the result for the non-sugars. The total sugars are determined after inversion by their reducing power on Fehling solution. There is present in cider vinegars a substance formed during the acetification which reduces alkaline copper solutions, and thus interferes with the estimation of the sugars by the usual reduction method. Attention was called to the presence of this substance by Mr. Balcom, associate referee on vinegar, in his report to the Association of Official Agricultural Chemists. It was, of course, necessary to modify the method for determining the sugars to eliminate the reducing effect of this substance, which was easily accomplished as it is volatile and readily distilled off by repeated evaporations of the vinegar to a small volume on a steam bath. The following procedure was adopted for the determination of the sugars: 50 cc. of the vinegar were evaporated on the steam bath to 10 cc., and two additions of 10 cc. water with subsequent evaporations to 10 cc. made. This solution was then made up to volume and the reducing sugars determined in the usual manner. From the difference between the Fehling reduction of the vinegar direct and after evaporation, the volatile reducing bodies can be approximated quantitatively in terms of their reducing power. A direct determination can also be made on the distillate from vinegar. For this purpose 100 cc. of the vinegar were distilled down to 10 or 15 cc., 100 cc. of water added and a second distillation made, the two distillates being kept separate. The Fehling reduction was made on the distillates and on the residue made back to volume, following the same procedure as in the determination of invert sugar. The results calculated to grams invert sugar from the Fehling reduction for a few samples of the vinegars from these runs are given in Table II.

It is quite apparent that the presence in vinegars of a substance with a reducing power equivalent to 0.15–0.20 gram invert sugar would cause an appreciable error in the determination of the sugars, and conversely,

Table II—Fehling Reducing Bodies

(Calculated as invert sugar)

Vinegar of	Direct after inversion Grams per 100 cc.	After evaporating 3 times. Grams per 100 cc.	On residue from distillation. Grams per 100 cc.	Distillate			Total reducing bodies in residue and distillate Grams per 100 cc.
				First 100 cc. Grams per 100 cc.	Second 100 cc. Grams per 100 cc.	Total Grams per 100 cc.	
Jan. 22......	0.62	0.45	0.44	0.13	0.01	0.14	0.58
Jan. 23......	0.65	0.45	0.46	0.15	0.01	0.16	0.62
Jan. 24......	0.66	0.48	0.48	0.14	0.01	0.15	0.63
Jan. 28......	0.68	0.50	0.52	0.13	0.02	0.15	0.67
Feb. 6......	0.77	0.56	0.55	0.16	0.01	0.17	0.72
Feb. 8......	0.77	0.56	0.56	0.16	0.02	0.18	0.74
Feb. 11.....	0.73	0.53	0.55	0.14	0.01	0.15	0.70
Feb. 13.....	0.73	0.53	0.53	0.14	0.02	0.17	0.70
Feb. 17.....	0.73	0.52	0.53	0.16	0.02	0.18	0.71

the non-sugars, by the Fehling reduction method. Our subsequent work on cider vinegars has shown that these bodies are frequently present in still larger amount. Although their exact composition has not been determined, they appear to be of an aldehyde nature, not acetaldehyde as might be inferred from its close relation to ethyl alcohol and acetic acid, but some more complex derivative.

The examination of daily samples of the vinegars made in these experimental runs showed an average of 0.18 gram of these volatile reducing bodies calculated as invert sugar in the finished vinegar, while in the ciders there are none. The formation of these bodies in the generation of vinegar has undoubtedly given rise to the idea that there is an increase in sugars during the process of converting cider into vinegar. In all probability this error in the determination of the sugars is the explanation of the abnormally low non-sugar solids occasionally reported in analyses of vinegars made a number of years ago. After carefully correcting for the amount of volatile reducing bodies present, there actually appears to be a slight increase in the amount of sugar present in the vinegar, as determined by reduction, over that present in the cider.

During the experimental run the total sugars in the vinegar made from Tank 2 decreased from 0.56 to 0.52 gram, while the mixture fed onto the generators contained 0.47 gram, showing a slight increase of sugars which can be accounted for only on the ground of the actual development of reducing bodies. This increase is probably due to the increase in pentosans, which was particularly noticeable in the run of Tank 2, the cider of which contained 0.12 gram of pentosans, while the vinegar coming from the generators contained 0.18 gram, an increase of nearly 50 per cent (see Fig. 2). The small amount of invert sugar present in the fermented cider is not appreciably affected during the acetification, nor are the ash, the ash constituents, or the alcohol precipitable bodies noticeably influenced by the passage through the generator. There is an appreciable loss of color, which, however, largely returns to the vinegar on storage. This loss of color was not observed in the experimental runs with other kinds of generators in other factories; apparently it is associated with the small-sized type of generator used in this plant. The glycerol content of the cider and of the finished vinegar remained practically constant throughout the whole experimental run, as will be seen by noting the curves of Fig. 1. The difference between the glycerol in the cider and in the finished vinegar is very slight, and as this variation is undoubtedly due partly to the factor of the vinegar introduced from the previous run the actual loss in acetification is negligible.

The actual yield of acid was almost constant throughout the run, although considerably below the theoretical yield. Theoretically, 1 part by weight of alcohol or 1.26 parts by volume of alcohol should yield 1.304 parts by weight of acetic acid. As the cider of Tank 1 contained approximately 7.85 per cent by volume of alcohol and 0.23 gram per 100 cc. of acetic acid, the theoretical yield would be calculated as follows:

Calculation of Acid Yield

Tank 1

	Grams of acetic acid
Theoretical yield:	
7.85 per cent alcohol by volume in cider..............	8.12
Acetic acid in cider..................................	0.23
Total....................................	8.35
Yield in practice:	
Average of vinegar for run..........................	5.75

Actual yield is 68.9 per cent of theoretical yield

Tank 2

	Grams of acetic acid
Theoretical yield:	
7.60 per cent alcohol by volume in cider..............	7.87
Acetic acid in cider..................................	0.31
Total....................................	8.18
Yield in practice:	
Average of vinegar for run..........................	5.78

Actual yield is 70.6 per cent of theoretical yield

These calculations and all comparisons between the ciders and vinegars have been made without allowing for any loss in volume by evaporation in passing through the generator. Under normal conditions of working, the loss from this source is not material.

The percentage of ash in the non-sugar solids of the cider in Tank 1 was 13.7 and of the vinegar at the start 16.8. Only fractional variations in this ratio were observed during the run of this tank, and the drip at the end contained 15.1 per cent of ash in the non-sugars. The cider in Tank 2 contained 14.5 per cent of ash in the non-sugars, and the vinegar during the run varied from 15.5 to 15.9 per cent. The slightly higher percentage of ash in the non-sugars of the vinegar was undoubtedly due to the slight apparent loss of non-sugars during acetification already discussed in connection with the increase in pentosans and total Fehling reducing bodies. There appears to be a very constant relation between the amounts of non-sugar

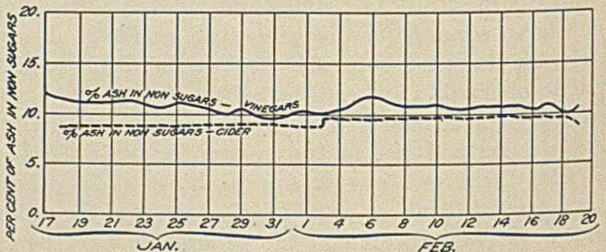

Fig. 3—Percentage of Ash in Non-Sugars

solids and ash which is of decided value in detecting the addition of ash material in the case of adulterated or imitation vinegars. The curves showing the variations in this ratio for these runs have been plotted in Fig. 3.

CONCLUSIONS

The results of this investigation show conclusively that vinegar manufactured by the generator process is uniform in its composition; as uniform as the cider—from which it is prepared—in which respect it differs materially from the vinegars manufactured by the old barrel process. With the exception of the conversion of the alcohol into acetic acid there is but little change in the composition of the cider as it is being converted into vinegar. The most marked difference, other than the oxidation of the alcohol into acid, is the elimination, or, perhaps, destruction of the fixed acids. Here there appears to be an almost constant loss during acetification. On the other hand, there is a considerable formation of pentosans in the generator. No appreciable loss in solids or non-sugars takes place, and the other constituents are practically unaffected. The amount of glycerol in the cider remains almost unchanged by its passage through the generator, and, as it is a product of the alcoholic fermentation, it is an important factor for the detection of adulteration in commercial vinegars. The percentage of ash in the non-sugar solids is remarkably constant, varying only within slight limits, and is of decided value as a standard for judging the purity of cider vinegars.

The results indicate plainly that, given the composition of a hard cider to be used in the manufacture of vinegar by the generator process, it is possible to approximate very closely the composition of the vinegar which can be made from it.

Bureau of Chemistry
U. S. Dept. of Agriculture
Washington

ON THE DECREASE OF AVAILABLE PHOSPHORIC ACID IN MIXED FERTILIZERS CONTAINING ACID PHOSPHATE AND CALCIUM CYANAMID

By R. N. Brackett

Received July 25, 1913

About two years ago one of the fertilizer companies in this state found that one of their brands ran deficient in available phosphoric acid, although it was thought that ample provision had been made in overage for that ingredient. A representative of the company stated that calcium cyanamid had been used as one of the ingredients of his mixture. As this material usually contains an excess of free lime it appeared possible that the cause of the deficiency in available phosphoric acid in his goods might be traceable to the fact that the soluble or the reverted phosphoric acid had been to some extent converted into insoluble.

Preliminary experiments[1] on mixtures containing cyanamid showed that there was a slight decrease of available, due to the increase of the insoluble over that calculated for the mixture.

In the early spring of 1912 a mixer in a near-by town made up a mixture to analyze: 10 per cent available phosphoric acid, 4 of ammonia and 4 of potash, using calcium cyanamid as one ingredient of his mixture. His formula was as follows:

	Pounds
Acid phosphate, 16 per cent	1250
Calcium cyanamid	200
Dried blood	250
Muriate of potash	175
1/2 and 1/2 mixture (composed of 1/2 16 per cent acid phosphate and 1/2 C. S. meal, damaged)	125
	2000

Upon having this mixture analyzed in a commercial laboratory it was found to be deficient in available phosphoric acid. We received a sample through a purchaser, and also found it deficient in available phosphoric acid, analyzing about 8–4–4, instead of 10–4–4. At our request this mixer consented to send us samples of the materials above mentioned.

Before these materials were received, we made up a mixture[1] of an acid phosphate and cyanamid, using the proportions given above. The acid phosphate used gave as an average of six analyses:

	Per cent
Total phosphoric acid	18.37
Water-soluble phosphoric acid	13.58
Insoluble phosphoric acid	1.74

On a 0.3 gram sample, the cyanamid analyzed 14.97 per cent of nitrogen.

The mixture consisted of 250 grams of the acid phosphate and 40 grams of cyanamid, a ratio of one part of the cyanamid to 6.25 parts by weight of the acid phosphate; the initial temperature of the materials was 21° C. and upon mixing the temperature increased to 32° C.

Results (Zerbst and Hutson)

	Phosphoric acid—Per cent			
	Total	Water-soluble	Insoluble	Available
Original acid phosphate	18.37	13.58	1.74	16.63
Analysis of the mixture, calculated, if no change on mixing	15.84	11.71	1.50	14.34
Average of five analyses, 5 days after mixing	15.82	3.96	1.58	14.24
Average of three analyses, 12 days after mixing	...	3.54	1.69	14.13
Average of four analyses, 19 days after mixing	...	3.45	1.78	14.04
Average of six analyses, 26 days after mixing	...	...	2.28	13.54
Average of two analyses, 33 days after mixing	...	...	2.75	13.07
Average of three analyses, 40 days after mixing	...	...	3.21	12.61
Average of three analyses, 47 days after mixing	...	...	3.57	12.25

Work discontinued at end of 47 days.

These results would appear to indicate that the conversion of the water-soluble or of the dicalcium phosphate to tricalcium is not simply a function of the temperature and of the alkalinity of the cyanamid, as is held by some, but that the element of time is perhaps of equal importance with the temperature. Hence it might well happen that a mixture freshly made up would show the required and desired amount of available, and yet be found deficient when analyzed some weeks later. The results of this experiment

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[1] Made by L. D. Boone. Results not available.

[1] This work was done by G. H. Zerbst and H. M. Hutson.

indicate that it would be very interesting to continue the analyses until the water-soluble had ceased to decrease and the insoluble to increase, and it is our hope to be able to take up this problem in the near future, working on a much larger scale.

On receipt of the above mentioned samples, a mixture was made of 3300 grams of the acid phosphate and 528 grams of the cyanamid, being a ratio of one part by weight of the cyanamid to 6.25 parts by weight of the acid phosphate; the materials were mixed in a glass jar; the initial temperature of the materials was 22° C.; upon mixing, the temperature rapidly increased to 52° C. As a mean of three analyses, the acid phosphate was found to have the following composition:

	Per cent
Total phosphoric acid	18.81
Insoluble phosphoric acid	0.34
Water-soluble phosphoric acid	16.98

RESULTS—(ZERBST AND HUTSON)

	Phosphoric acid—Per cent			
	Total	Water-Soluble	Insoluble	Available
Original acid phosphate	18.81	16.98	0.34	18.47
Analysis of mixture, calculated, if no change on mixing	16.21	14.64	0.29	15.92
Analysis of samples drawn within a few days after mixing, mean of 8 samples	16.17	1.91	1.35	14.82
Average of three samples drawn three weeks later	...	1.25	2.30	13.87

The work had to be discontinued at this point, as no more time was available for the men who had undertaken it. It is noteworthy that, while the water-soluble decreased only from 1.91 to 1.25 in three weeks, the insoluble increased from 1.35 to 2.30 per cent.

Last February, E. L. Hutchins, chemist to a near-by fertilizer plant, reported difficulty in making up a 10–4–4 mixture, using as one ingredient of his mixture calcium cyanamid. I regard this as the best instance of the danger of the decrease of the available phosphoric acid in mixtures in which cyanamid is used, which has come under my observation; and as an especially excellent illustration, as these experiments were conducted on a factory scale. With the permission of Mr. Hutchins, I give the following account of his experiments:

FORMULA USED

1250 pounds of 16 per cent acid phosphate
100 pounds of 10 per cent Kanona tankage
150 pounds of 11 per cent dried fish scrap
100 pounds of 16 per cent dried blood
150 pounds of 18 per cent cyanamid
52 pounds of 25 per cent sulphate of ammonia
140 pounds of 50 per cent muriate of potash
58 pounds of 18 per cent hard salts

2000

The acid phosphate actually analyzed:

	Per cent
Total phosphoric acid	17.24
Insoluble phosphoric acid	0.89
Available phosphoric acid	16.35

The above formula was made up as follows:

First day's run, January 20, 1913, amount made up 180 tons
Second day's run, January 21, 1913, amount made up 171 tons
Third day's run, January 22, 1913, amount made up 171 tons

Each of these runs was dumped into the same pile, sampled the same day and analyzed the next day. Samples were also taken the 24th and the 28th of January, and on the 5th of February, and these samples were analyzed with the following results:

			Phosphoric acid				
		Moisture	Total	Insoluble	Available	Ammonia	Potash
1.	Jan. 21, 1913	11.22	11.67	1.68	9.99	4.12	4.76
2.	Jan. 22, 1913	11.90	11.79	1.68	10.11	4.02	4.30
3.	Jan. 23, 1913	11.66	11.65	1.80	9.85	4.13	4.38
4.	Jan. 24, 1913	11.02	11.72	2.35	9.37	4.13	4.09
5.	Jan. 28, 1913	10.48	11.70	2.99	8.71	4.21	4.31
6.	Feb. 5, 1913	9.70	12.25	3.37	8.88	4.18	4.22

The sample analyzed January 28th was taken from the "face of the pile" and that of February 5th from the "base of the pile." Mr. Hutchins' attention was first attracted by the results of the analysis of January 24th, and he was led thereby to draw and analyze the other samples. It is evident from these results that in a mixed fertilizer containing acid phosphate and cyanamid in the ratio of one part of the latter to 8.33 of the former, there is an increase of the insoluble and a consequent decrease of the available phosphoric acid on standing, even a week or two; this change may cause the fertilizer to become deficient in available phosphoric acid.

Mr. Hutchins kindly furnished us with a considerable quantity of each of the materials used in his formula. Owing to some misunderstanding, the mixture was made up of one part of cyanamid to 9.8 parts of the acid phosphate. The rise of temperature was only six or eight degrees, but even with this ratio there was a gradual increase of the insoluble, as shown by the following results:

In the formula were used 6667.62 grams of acid phosphate and 680.11 grams of cyanamid, with the remainder of the ingredients in proportion.

RESULTS—(L. D. HUTSON AND J. F. KING)

		Phosphoric acid—Per cent		
	Total	Water-soluble	Insoluble	Available
Original acid phosphate	17.50	13.09	0.68	16.82
Calculated analysis of the mixture, made up March 1st, if no change on mixing	11.58	8.67	0.47	11.11
Analysis, sample drawn April 12, 1913	...	8.06	0.76	....
Analysis, sample drawn April 18, 1913	...	....	0.81	....
Analysis, sample drawn April 24, 1913	...	7.96	1.11	....
Analysis, sample drawn May 2, 1913	...	7.94	1.14	....
Analysis, sample drawn May 9, 1913	...	7.24	....	....

In addition to the facts above adduced, it may be interesting to state, as pointing in the same direction, that of the 70 samples of complete fertilizers found deficient in available phosphoric acid alone, during the past fertilizer season, seven were registered as having calcium cyanamid as one of their ingredients; eleven brands were not registered at all; and it is more than likely that cyanamid was an ingredient of many of the remaining 52 samples though the fact was not stated in the registration.

Acknowledgments are due Assistant Professor G. F. Lipscomb for his careful oversight of the work of the students; to the students themselves and to Mr. E. L. Hutchins for furnishing us with materials and for the use of his experiments and results.

CONCLUSIONS

I. From experiments conducted in this laboratory, it has been shown that when cyanamid is mixed with acid phosphate in the ratio of one part of the former to 6.25 or 8.33 or even 9.8 of the latter, there is, on standing, a gradual increase of the insoluble and consequent decrease of the available phosphoric acid in the mixture, and that this is true whether the mixture consists simply of the acid phosphate and cyanamid, or whether ammoniates and potash salts are also present.

II. The experience of at least three manufacturers working on a factory scale has shown that there is a decrease of the available phosphoric acid when calcium cyanamid and acid phosphate are used in mixed fertilizers in the ratio of one part of the former to 6.25 or 8.33 of the latter, thus confirming our own work done on a small scale.

III. The results of our fertilizer inspection analysis this past season point to the same fact; *i. e.*, that there is danger of falling off in the available phosphoric acid when calcium cyanamid and acid phosphate are used together as ingredients of a mixed fertilizer.

IV. The results of all these experiments indicate that the time element has an important influence in determining the increase of insoluble phosphoric acid, and must be considered in addition to the elements of temperature and the alkalinity of the cyanamid.

V. It appears from the facts given in this paper, that, though it may be said that the effect of mixing cyanamid with acid phosphate will not injure the fertilizer from the farmer's standpoint, the manufacturer must exercise some care as to the amount of the cyanamid used in a mixture, else his mixture may, upon inspection and analysis, be found deficient in available phosphoric acid.

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LABORATORY AND PLANT

THE DESIGN OF AN EXPERIMENTAL WOOD DISTILLATION PLANT

By H. K. Benson and Marc Darrin

Received August 18, 1913

The utilization of waste wood in the Pacific Northwest has recently attracted much attention. The interest lies partly in the necessity of clearing the logged off or "cut over" lands which now number over three million acres in the State of Washington alone. In a more popular sense, the interest, however, centers about the waste wood of the sawmills. In the latter it has been the practice to install wood burners or incinerators to dispose of the mill waste, and hundreds of cords of wood are thus destroyed daily. In the popular mind this waste is regarded as an economic crime, and several efforts have been made to establish a wood distillation industry in the Northwest, all of which have been commercial failures.

With a view to giving some assistance in solving this problem the University of Washington coöperated for some time with the Bureau of Plant Industry of the United States Department of Agriculture in land clearing studies and at the present time is in coöperation with the United States Forest Service in certain yield studies of distillation products from both Douglas fir stumps and the waste wood of sawmills operating in the western part of the State of Washington. After some years of experience with this problem, both from a theoretical standpoint and from practical participation in the industry, it appeared to the senior author of this paper that the failure of the commercial plants could, in each case, be traced to inferior and unusual methods of operation rather than to inferior products and lack of market as usually asserted. After personal visitation of the principal distillation plants in the United States by both of us, we selected the type of plant described in this article as most nearly applicable to economical operation in the distillation of mill waste. The plant thus designed has been erected coöperatively by the United States Forest Service and the University of Washington and is now in operation. In this article only the design of the plant will be described since the results obtained will be the subject of later publications by the Forest Service.

The general layout of the plant is indicated by the legend descriptive of Plate 1. The wood for distillation is measured (4), weighed (3), placed in retort buggies (7), and distilled in the retort (21). The products of distillation are conducted from the retort through a bottom vapor outlet (25), into the tar separator (26), thence into the condenser (29), and finally the gases are stored in the gas holder (14), where they are sampled and measured and finally pass to the furnace (18) for combustion. For the estimation of the liquid products, the distillate is pumped (39) from the pyroligneous acid tank (30) into a feed tank (38), from whence it flows by gravity into a copper still (36) heated by steam coils. The resulting distillate is separated (40) into light oil and crude wood vinegar (containing acetic acid, methyl alcohol, acetone, etc.) and stored in tanks for sampling.

The main interest centers, however, in the design of the retort. For experimental purposes a capacity of one-half cord was determined upon, which required dimensions approximately 18 feet 1 inch long. The shell of the retort is 4 feet 1 inch wide and 3 feet 2 inches high, made of one-fourth inch steel and is covered on the outside to a thickness of two inches with standard heat insulation material. At one end a furnace is provided, the heat from which is conducted through four iron flues of five inches diameter. These flues extend lengthwise within the retort as shown in Plates 2 and 3, terminating in return bends at the back end of the retort. From thence they extend to the front end of the retort where they enter a smoke chamber, which in turn opens into the stack. The course of the heated gases of combustion is shown by the arrows in Plate 2.

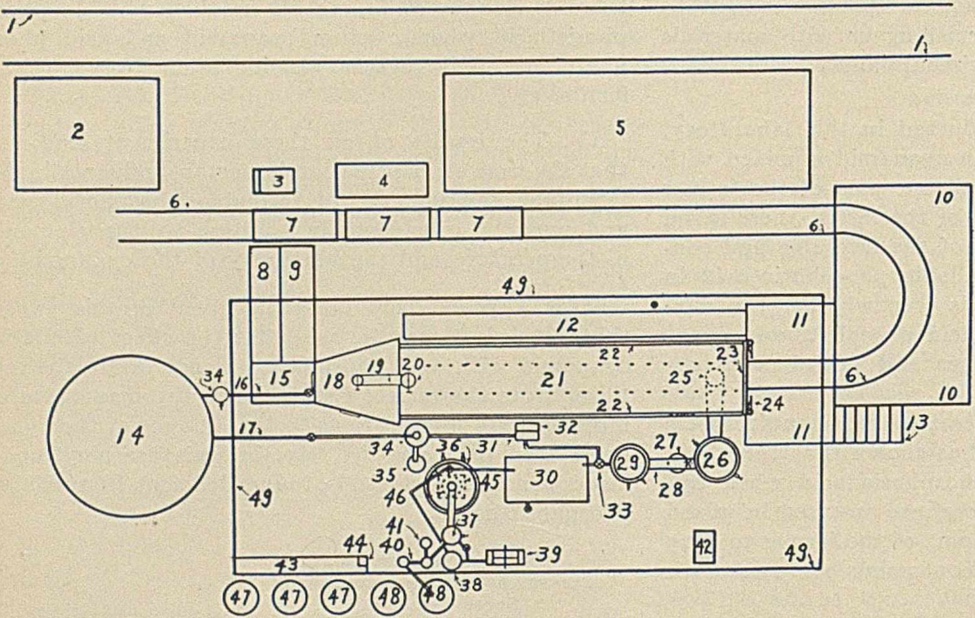

Plate 1

1. Railway switch.
2. Charcoal yard.
3. Platform scales.
4. Cord measure.
5. Wood yard.
6. Retort buggy track.
7. Retort buggies.
8. Charcoal chute.
9. Wood chute.
10. Retort buggy platform.
11. Retort door platform.
12. Retort running board.
13. Steps.
14. Gas storage tank.
15. Firing platform.
16. Gas pipe to furnace.
17. Gas pipe to tank.
18. Furnace.
19. Flue by-pass.
20. Stack.
21. Retort.
22. Heat insulation.
23. Retort door.
24. Door clamps.
25. Bottom vapor outlet.
26. Tar separator.
27. Separator tar tank.
28. Pipe to condenser.
29. Condenser.
30. Pyroligneous acid tank.
31. Gas booster.
32. Electric motor.
33. Gas vent to air.
34. Back-fire traps.
35. Gas tar tank.
36. Refining still.
37. Condenser.
38. Distillate feed tank.
39. Pump.
40. Oil separator.
41. Oil receiver.
42. Crude alcohol tank.
43. Work table.
44. Transformer and switch.
45. Sewage basin.
46. Still tar tank.
47. Tar tanks.
48. Crude wood vinegar tanks.
49. Building.

The wood for distillation is piled vertically in three retort buggies with sides made of steel screening. The buggies operate on steel rails which contain a removable section at the retort door, thus forming a continuous railway from the fore end of the retort to the wood yard and charcoal pile.

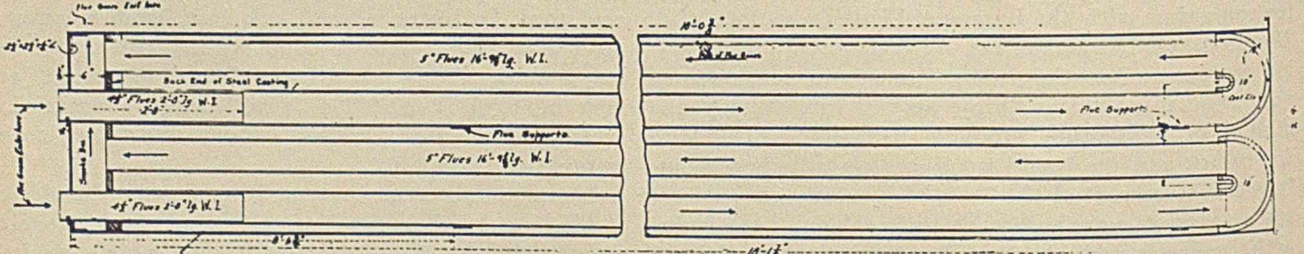

Plate 2

The retort door and door seat are made of cast steel and are carefully planed and milled so as to insure a tight fit. The door is shut tightly by means of four cast iron eccentric clamps which act on two steel bars extending across the outer surface of the door.

The outlet for the products of distillation is at the bottom of the retort, Plate 4, which is sloped so that the opening constitutes the lowest portion of the inner surface of the retort. The liquid and gaseous products are thus conducted from the retort through the outlet into the tar separator, which is air-cooled. The portions not condensing continue to the top of the separator into the water-cooled condenser, Plate 5. The distillates are collected in a storage tank and the combustible gases are stored in a gas holder.

The noticeable features in the design of the retort above described are: (1) the method of internal heating by means of flues located entirely within the main shell; and (2) the drawing off of vapors from the bottom of the retort.

The advantages of internal firing over the customary method of external heating are considered to consist largely in economy of fuel and control of temperature. By thorough insulation of the retort shell, radiation losses from the shell are minimized, the temperature of the stack gases is more nearly that of the retort interior, the uniform distribution of heat prevents local overheating, and the retort suffers less depreciation due to unequal strains from high temperatures than in the case of retorts exposed to the direct scaling and buckling action of heat.

A number of considerations determined the selection of a bottom vapor outlet. In the distillation of the coniferous woods it has been the writers' experience that coke deposits usually exist on charcoal drawn from the bottom of the retorts. It is generally assumed that such coke is the product of secondary distillation of tar. In other words, when tar is in the process of formation from wood, it forms a high boiling volatile mixture with the lighter- and lower-boiling products resulting from the decomposition of wood. A slight cooling of the vapor causes a change in the concentration of the vapor's constituents and tar is precipitated in minute particles which are carried along mechanically. This, however, causes an increase in the density of the vapor and it tends to fall back into the retort. When it does this it becomes reheated, but instead of acting as it did at the time of its formation, it is now fractionally distilled, giving off various light oils and finally being decomposed with coke as the residue.

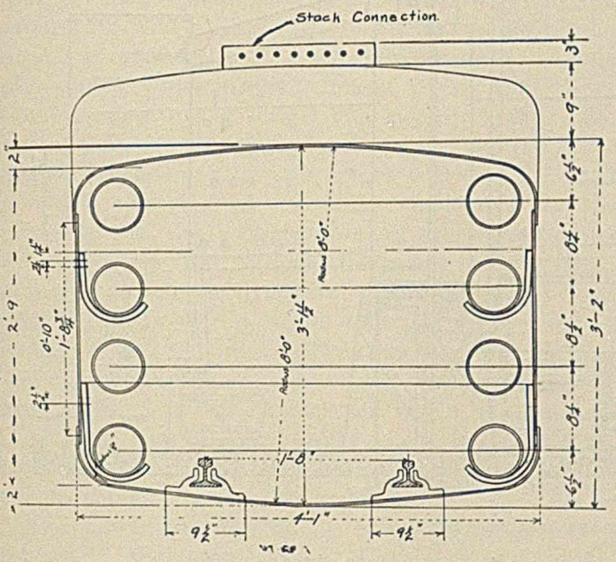

PLATE 3

The bottom outlet should eliminate this possibility through active convection currents and distribution of heat within the retort. Thus the vapors rise on either side of the retort in the flue area between the outer side of the buggy and retort. The vapors there pass along the top, approaching from both sides a region near the top center, pass through the wood (which is piled vertically) in the buggies, and thence along the bottom of the buggy and retort to the vapor outlet, which is under a slightly diminished pressure due to the suction produced by the condenser or the fan. Should the tar for the reasons above given become liquefied, it flows by gravity into the vapor outlet and is not subject to redistillation. This explanation has been verified by actual operation, coke being found on the charcoal only where oleo-resin or "pitch" had previously existed in the wood.

For the purpose of determining the size of flues the the following assumptions were made:

(1) The distillate has the same average properties as water.
(2) Maximum distillate per cord, 300 gallons.
(3) Radiation of insulation, 4.56 B. t. u. per sq. ft. per minute.
(4) Radiation of exposed door, 24.54 B. t. u. per sq. ft. per minute.
(5) Atmospheric temperature, 70° F.
(6) Maximum temperature inside retort, 700° F.
(7) Temperature of heating gases at entrance to flues, 1500° F.
(8) Average temperature of heating gases upon leaving flues, 700° F.
(9) Specific heat of retort steel and iron of buggies, 0.12.
(10) Specific heat of wood, 0.650.
(11) Maximum non-condensable gas per cord of wood, 10,000 cu. ft. weighing 0.08 pound per cu. ft.
(12) Specific heat of non-condensable gas, 0.237.
(13) Chemical reactions of an endothermic character balance those of an exothermic character.
(14) Average radiation of flues, 3.63 B. t. u. per hour per sq. foot per degree F.
(15) Average convection from flues, 1.06 B. t. u. per hour per sq. ft. per degree F.

With the further assumption that the time of distillation required 20 hours of firing, the total consumption of heat units was computed as shown on following page.

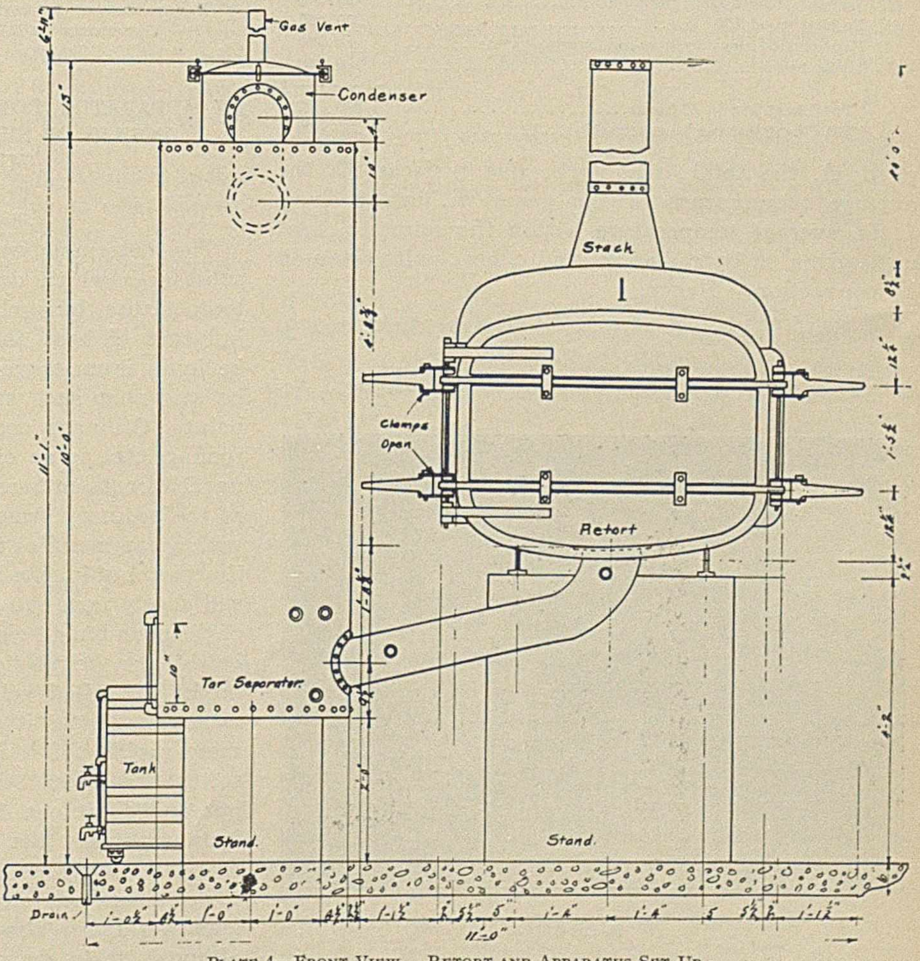

PLATE 4—FRONT VIEW. RETORT AND APPARATUS SET UP

To supply this heat, use was made of the following computation:

Q = A(T — t) (r + c) where Q denotes heat sup-

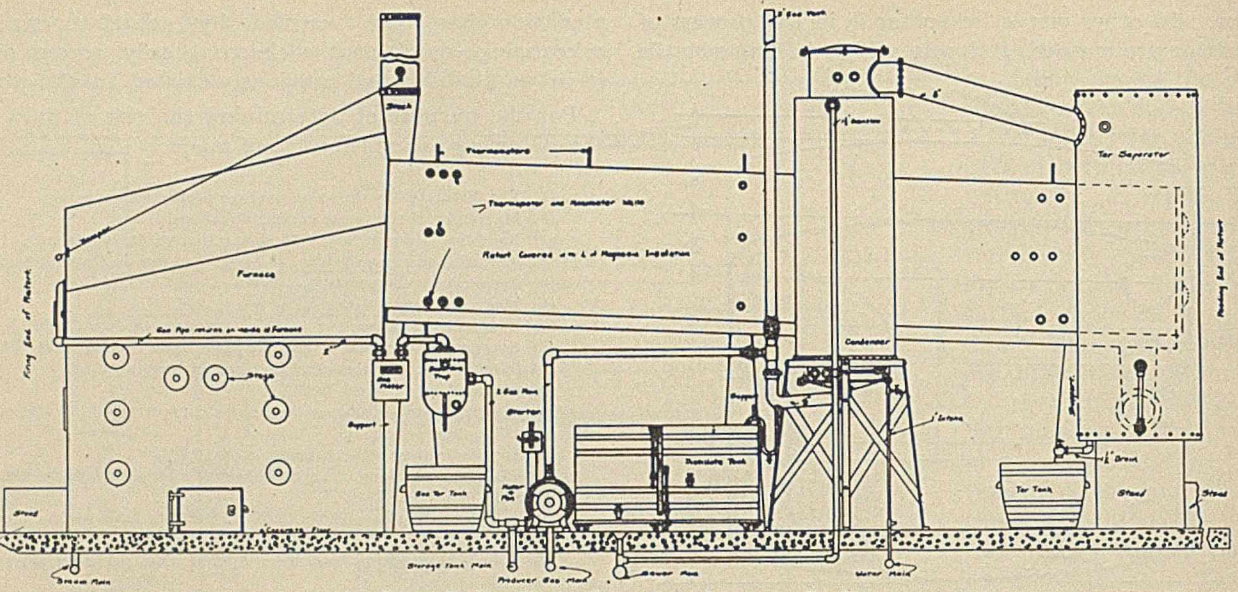

Plate 5—Side View. Retort and Apparatus Set Up

Total Consumption of Heat Units

	B. t. u.
(1) To heat and vaporize 150 gallons of distillate.........	1,430,000
(2) Radiation through insulation........................	1,512,000
(3) Radiation through exposed door.....................	412,000
(4) To heat buggies and retort 600° F...................	990,000
(5) To heat wood 300° F................................	300,000
(6) Heat carried away by non-condensable gases.........	56,700
(7) Minor losses.......................................	100,000
Total heat lost in 20 hours........................	4,800,700
Total heat lost per hour (roughly).................	250,000

plied; A, the total area of the flue surfaces; T, the average temperature of the gases within the flues; t, the average temperature within the retort; r, heat units given off by radiation; and c, heat units given off by convection. Hence,

$$Q = 0.416 \times 3.14 \times 16.6 \times 8\,(1500 + 700/2 - 700)\,(3.63 + 1.06),$$

or 325,000 B. t. u. will be supplied per hour. Accordingly by computation, the heat exchange is shown to be more than sufficient to produce distillation taking place under the conditions as above assumed, and this computation is verified by the results obtained in the operation of the retort, which requires from 18 to 20 hours per run of three-eighths to one-half cord of wood.

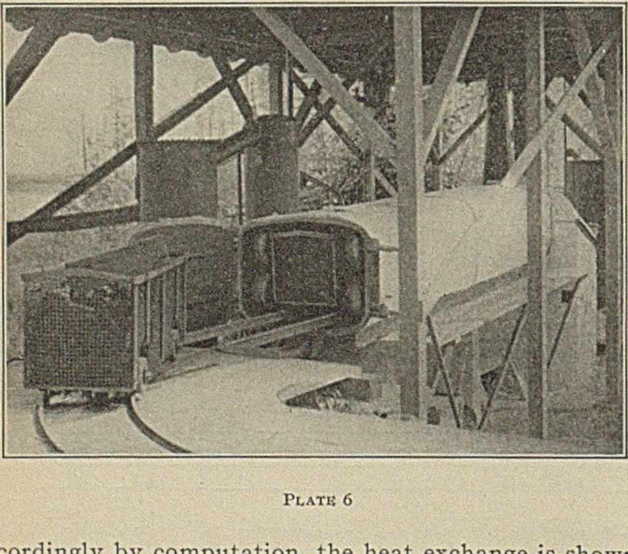

Plate 6

In Plate 6 is given a general view of the plant as it appeared shortly after its installation.

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AN APPARATUS FOR DETERMINING THE MELTING POINTS OF SUBSTANCES OF INDEFINITE MELTING POINT

By A. P. Bjerregaard

Received July 30, 1913

The determination of the true melting point of substances which do not melt sharply at a definite temperature but which gradually soften under the influence of heat and finally become soft enough to be liquid, is one of great difficulty. Indeed it can hardly be said that such substances have any true melting point. Ordinary coal tar pitch such as is used for roofing, etc., is an example of the class of substances under discussion here. As is well known this material at the ordinary atmospheric temperature when struck with a hammer flies to pieces like glass. Nevertheless, if a barrel of it stands for any length of time the pitch will slowly flow out of every crack and crevice or out of the open bung-hole just like a liquid. It may indeed be called a brittle liquid, and this class of substances might be called solid liquids. If coal tar pitch is warmed a little it gets softer and flows somewhat more rapidly; if it is further heated it becomes still softer and flows still more rapidly. Finally, when hot enough it can be made to flow nearly or quite instantaneously like water. When shall we say that coal tar pitch is melted?

Petroleum asphaltums prepared by oxidizing petroleum residuum also belong to this class of bodies, although their characteristics are somewhat different from those of coal tar pitch in that they are softer at ordinary temperatures and require higher temperatures to flow together when exposed for long periods of time to small degrees of heat. They also have a higher range of melting points as this term is understood in this article.

Experiment shows that an air-blown petroleum asphaltum which when heated rather rapidly becomes liquid at about 135° C., will flow down an inclined plane upon which it may be placed at 40° C. if kept at that temperature a long time, say 18 hours. Shall we say that this substance fuses at 40° C. or at 135° C.?

There appear to be two stages or two temperature points in this gradual softening, which may be of importance in the examination of these substances. *First*, there is that temperature point or approximate point, at which the firm solid or pseudo-solid material just begins to soften, so as to be slightly plastic, or so that if left a long time at that temperature it will flow and finally come to a level in its container. *Second*, there is a temperature at which the substance is so fluid that it can readily and quickly flow to a level in its containing vessel; in other words, it possesses the properties usually ascribed to liquids.

The apparatus now to be described is one for determining the temperature of this second kind of melting. It can scarcely be called a flow point apparatus, although the flow of the sample is measured.

It consists of a block of iron of suitable dimensions, with one face at an angle of 45° to the horizontal. This inclined face is provided with grooves, as further described below. The block is also provided with a small cistern to contain mercury in which is placed the thermometer for reading the temperature of the block. A useful size for this apparatus is about $4^1/_2$ inches wide, 4 inches high and about 5 inches long. This will contain 9 grooves of the size described below. A top view is shown in Fig. 1, and a side view in Fig. 2; here, *A* is the mercury cistern, *B* the inclined grooved face, *C* is a small stop arranged so that a sheet of glass, or transparent mica laid over the inclined face will be supported and prevented from sliding off, *D* is a series of step-like cuts made across the ribs between the grooves of the inclined face. The top cut *FH* is deeper than the second by one-eighth of an inch, the second cut *FG* is one-eighth of an inch deeper than the top of the ribs on the inclined surface. The length of the top cut is one-quarter of an inch from the angle *H* at the top, down to the step up *F* of the second cut; the length of the second cut is one-quarter of an inch from *F* to *G*.

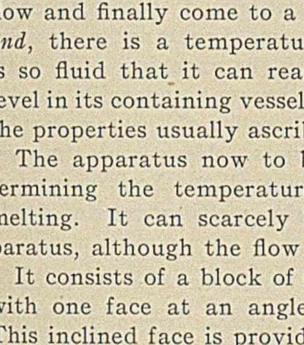


Fig. 1

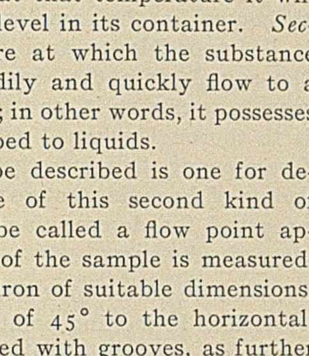


Fig. 2

The grooves are one-quarter inch wide, and their vertical sides are one-quarter inch deep to the beginning of the curved bottom. The latter is of semicircular cross-section with a radius of one-eighth inch. The ribs may be $^7/_{32}$ inch thick. The dotted line *I* represents the bottom of the grooves.

For use, mercury is poured into the cistern *A*, which does not need to be very wide (say $^1/_2$ to $^3/_4$ inch) and the thermometer is inserted. The samples of material to be tested are pressed into the topmost parts of the grooves between *F* and *H* so as to fill the space which is shaded in Fig. 2. About 0.17 gram of asphaltum is needed for this. A sheet of glass or mica is laid on *B* (to shut off cold air drafts), and heat is applied at *E* by means of a Bunsen burner. Each sample will gradually soften and sag down the groove; when it is liquid enough to reach from *F*, its original lower boundary, to *G*, a distance of one-quarter inch, the thermometer reading is taken as the melting point. Marks may be made at intervals down *B*, say at every one-half inch and the behavior of the flowing material as it passes each in succession may be studied as to temperature and time differences.

It is important that the amount of material used in comparative trials should be sensibly the same. Otherwise the melting points observed will differ somewhat according to the relative sizes of the samples. Thus in two trials, certain specimens of air-blown petroleum asphaltum were applied in differently sized pieces and each series tested at the same time with the following results:

MELTING POINTS OF DIFFERENTLY SIZED PIECES OF PETROLEUM ASPHALTUM

Sample	No. 1	No. 1	No. 2
Rate of heating for 10° C.	77 sec.	100 sec.	100 sec.
Small piece	184° C.	181° C.	183° C.
Medium piece	180° C.	175° C.	178° C.
Large piece	178° C.	171° C.	174° C.

It will be seen that sample No. 1 showed in one case a difference of 6° C. in melting point and in the other case of 10° C., depending on whether a large or a small piece was used. The large piece of No. 1 used at rate 77 sec. was not the same in size as that used in rate 100 sec.; the same remark applies to the medium and small pieces. The large pieces were about the size of peas, the small pieces about one-third this size.

In order to overcome this cause of discrepancy the space in the upper part of the groove should, as already said, be filled with the material to be tested, and then the top scraped off even with the surface of the partly cut off rib. By this means sensibly the same sized sample may always be subjected to test, thereby eliminating one of the uncertainties of the melting point of the substances under consideration.

The reason that a larger piece appears to fuse at a lower temperature than a smaller piece seems to be that the action of gravity is relatively greater at the same time that the action of capillarity is relatively less, with the larger piece. The first force tends to pull the mass down the incline, and so to render the apparent melting point lower. The second force tends to prevent the liquefied, or semi-liquefied sample from flowing down and, therefore, to render the apparent melting point higher. These circumstances necessarily operate in most other methods of determining the melting point of the classes of bodies under consideration. But in this apparatus the variations can be controlled by exactly filling the space as described, whereas in most other methods no such control is as easily obtainable.

As has already been stated material of indefinite melting point will flow at low temperatures if given time enough. Time is therefore an important factor in this determination and must be taken into account.

That the temperature at which substances of indefinite melting point actually fuse depends considerably on the rate of heating is illustrated by the following table:

MELTING POINTS OF AIR-BLOWN PETROLEUM ASPHALTUM FOR DIFFERENT RATES OF HEATING

Rate for 10° C.	43 sec.	65 sec.	68 sec.	75 sec.	113 sec.	126 sec.
Sample No. 1	119° C.	114° C.	114° C.	115° C.	...	112° C.
2	140	134	133	135	128° C.	128
3	157	154	150	149	147	147
4	161	160	156	156	151	150
5	...	170	169	166	157	...

It follows, if comparable results are desired, that the heating up must be conducted at a given rate.

For many purposes, however, where simply relative results are desired, there is no need of heating at a definite rate with this apparatus provided only that the rate of heating is comparatively uniform.

For such relative determinations the several samples to be compared are pressed into the grooves as described, and the several melting points observed are read and compared. Even very slight differences of melting point can be observed in this way.

A rate of about 100 seconds for a rise of 10° C. is the most convenient for use with an apparatus of the size already described. This rate is readily obtained with a good sized Bunsen burner burning so that the flame impinging on the bottom of the block forms a circular disk of about $3^1/_2$ inches in diameter—at least that is the size with the pressure of artificial gas in the city of Cleveland.

All methods heretofore proposed, so far as I am aware, for determining the melting points of substances of indefinite melting point are also subject to some rate of heating factor. This rate is controlled with great ease in the method here described, and may be entirely neglected with this apparatus under the conditions mentioned above.

The rate of heating is without influence on the temperature at which substances of sharp melting point fuse in this apparatus. For example a certain sample of commercial stearic acid, which fused quite sharply at $59^3/_4$° C. by the usual capillary tube method, fused by the iron block method at $59^3/_4$° C. when heated 10° C. in 125 seconds, and at 60° C. when heated 10° C. in 50 seconds. This last rate is about the fastest; it is feasible to use by this method. Substances of sharp melting point do not gradually sag down the incline as the heating progresses. They remain entirely unchanged until the temperature reaches the melting point, and then they suddenly fuse and flow down the inclined groove quite rapidly.

Hence, for determining the melting points of substances of sharp melting point for commercial purposes this apparatus will be found of great use.

Lastly, in at least some cases, the melting point of substances of indefinite melting point is influenced by the amount of working or kneading to which the sample has been subjected. This is exemplified by the following figures; the rate of heating was 10° C. in 77 seconds:

MELTING POINTS OF AIR-BLOWN PETROLEUM ASPHALTUM

	Not kneaded	Well kneaded
Small piece..............	170° C.	167° C.
Large piece..............	167° C.	160° C.

Here the kneading has lowered the melting point from 3° to 7° C. This is the most difficult condition to control in the samples submitted to test, because it is impossible to avoid some kneading in pressing the sample into the slot of the machine. The best way to overcome it, and to secure comparable results, is to thoroughly knead each pellet of the samples before pressing them into the slots. Here again the same factor of kneading enters into all methods heretofore proposed for determining the melting points of this class of substances.

As above stated all these conditions operate to cause variations in melting point in every form of apparatus heretofore proposed. But in none of them, so far as the author has tried them, is it possible to satisfactorily overcome the inaccuracies and variations caused by the peculiarities in behavior of these materials of indefinite melting point. But by means of the proper use of the apparatus herein described it has been possible to attain accuracy of results entirely unattainable before this apparatus was put into use.

During the two years in which this apparatus has been in use in this laboratory, the author has found it of great value for lubricating greases of every kind, for pitches, asphaltums, solid insulating compounds, and, in short, for every kind of substance whose melting point is lower than the boiling point of mercury and whose range of fusion is too wide for obtaining definite results by the capillary tube method. For such materials it appears to be as generally useful as the capillary tube is for those of sharp melting point.

The samples are quickly inserted into the slots, it takes but a short time to heat up to the melting point, the temperature is easily and accurately read, many samples can be tested at once, and the apparatus is easily cleaned.

The best way of cleaning this melting-point block is to immerse it while still warm into a can of liquid which is a solvent for the substance tested, for example naphtha, if petroleum pitch or lubricating grease is in the apparatus. After a short soaking the samples can usually readily be scraped or wiped out, and then the slots are easily washed with a small piece of cotton waste or other rag. After that it is rinsed with clean naphtha and allowed to dry, when it is ready for use.

LABORATORY OF THE CANFIELD OIL CO.
CLEVELAND, O.

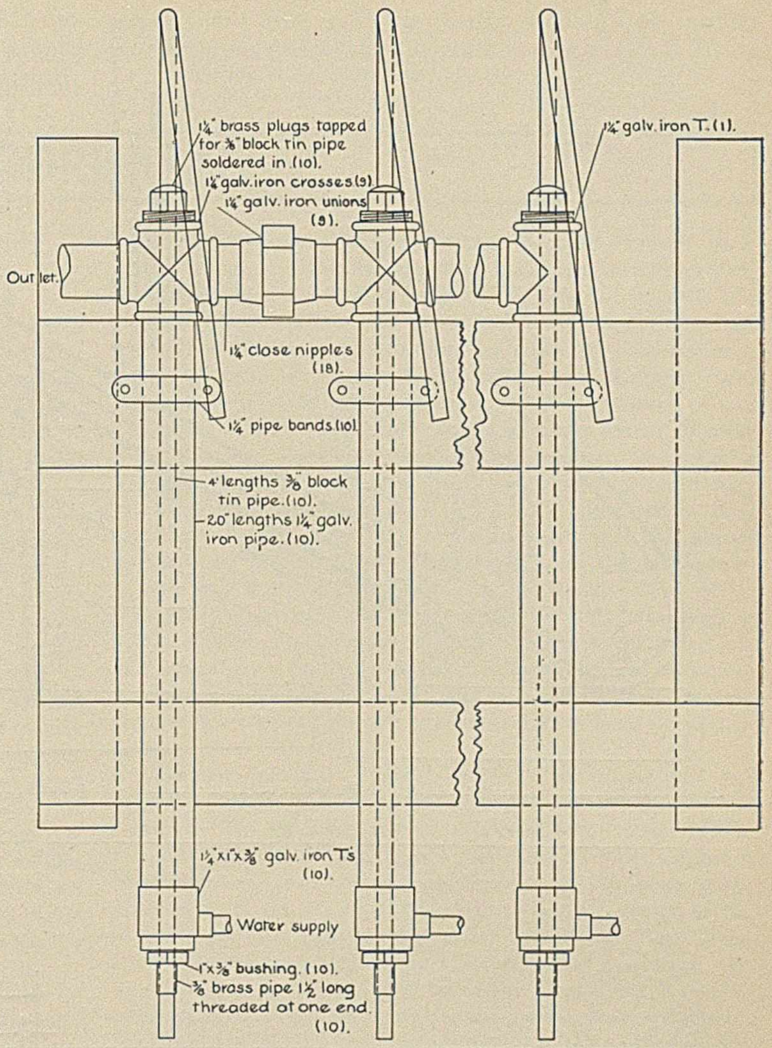
A MODIFIED BANK OF AMMONIA STILLS

By Fred Berry and L. H. Van Buskirk

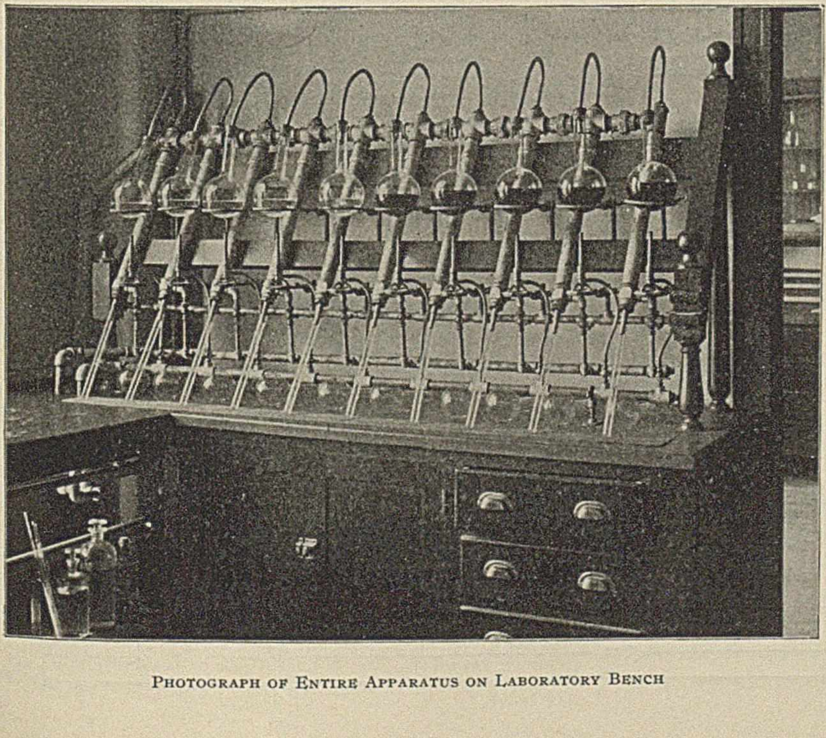
Received September 2, 1913

No doubt a majority of those in charge of laboratories where ammonia determinations are made, have been confronted, at one time or another, with the problem of designing or choosing some form of apparatus to be used for such determinations. Just such a problem had to be solved by the writers last year when plans were prepared for moving our laboratory into new quarters. The old bank of stills which had been in use here for many years had one large tank used as a condenser for the eight stills and the lower ends of the block-tin pipes were so located that one had to reach under a framework supporting the burners and flasks in order to replace or remove the nessler jars. This apparatus was in many respects far from satisfactory, but for one reason or another had not been replaced by a more convenient type.

When the necessity for such a change arose we were unable to secure much help in the way of drawings, specifications, etc., from other laboratories. We did, however, receive a photograph of an apparatus, of which this is a modification, but found some difficulty in estimating dimensions, etc., from a photograph alone. It occurred to the writers, therefore, that detailed specifications and drawings of this apparatus would be of great assistance to other workers who might care to duplicate it or construct a modification of it. While no claim is made for originality of principle, we do believe that some of the improvements added to former types are of distinct advantage and worthy of note.



Front View from Above the Level of the Table Top



Photograph of Entire Apparatus on Laboratory Bench

The distinguishing points of this apparatus, in common with others of similar style, when compared with the majority of other forms are:

1. Unit construction, *i. e.*, each still has an individual condenser.

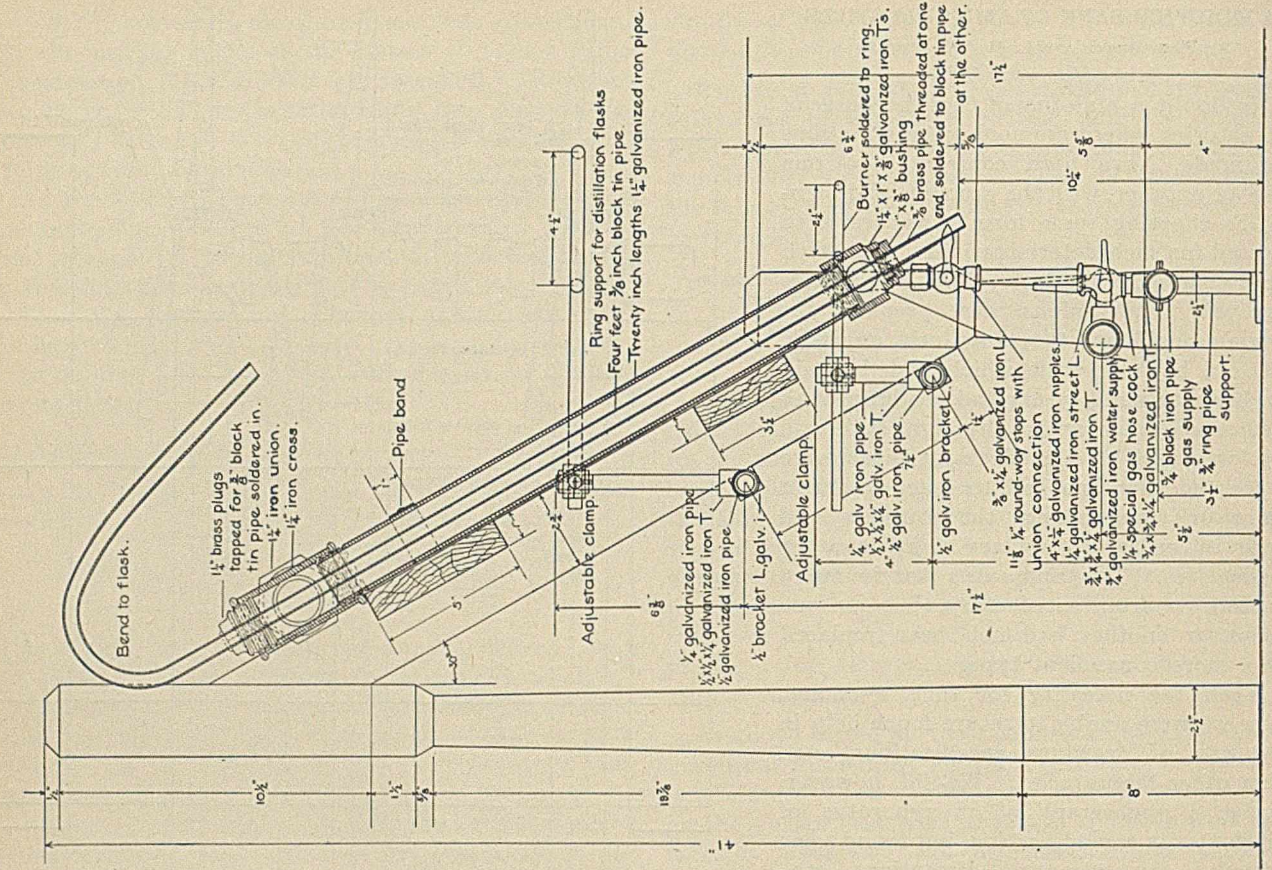
This means:

(*a*) Repairs can be made on one unit while others are in operation.

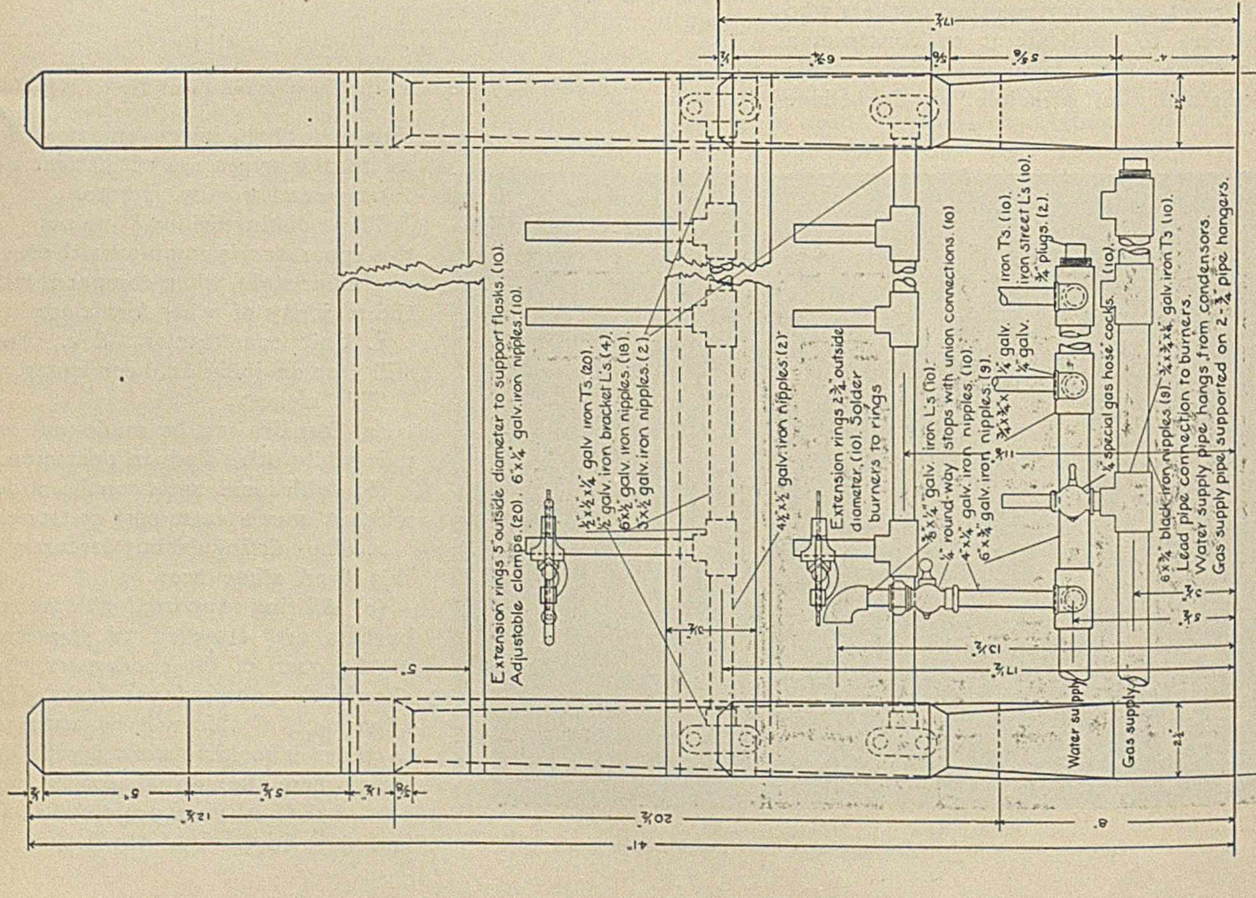
(*b*) Additional units can be added without much extra cost or trouble.

2. The distinguishing features of this type alone are:

(*a*) All ring supports for flasks and burners are attached to standards in the rear of the condensers, thus allowing free access to the flasks. The advantage of this will be apparent to those who have worked with the style where the uprights for the support of the flask rings projected above and were in front of the flasks.



CROSS SECTION OF AN ENTIRE UNIT



FRONT ELEVATION

(*b*) The block-tin pipes are soldered into brass nipples at the lower end and into brass plugs at the upper end of the condensers. This provides a perfectly tight joint and gives a certain amount of rigidity to the lower end of the tin pipes.

Ohio State Board of Health
Columbus, Ohio

ADDRESSES

OUR RADIUM RESOURCES[1]

By Charles L. Parsons[2]

The "wonders of radium," both fact and fable, have been treated so extensively in the scientific and public press that it is not my intention, nor is it at all necessary to repeat them here. Rather it is my wish to-day to present to a body of men interested in the development of American mining the present commercial situation as regards radium and its ores, and to point out, so far as I may, some of those future developments that already begin to be more or less distinctly visible.

A bulletin on the radium, uranium and vanadium situation, by R. B. Moore, physical chemist in charge of the Denver office of the Bureau of Mines, and K. L. Kithil, mineral technologist of the Bureau, will appear within a few weeks and will contain much detail of interest to the mining industry. Last April an advance statement, authorized by the Director, regarding this bulletin, brought out particularly the fact that practically all of the carnotite ore mined in the world in 1912 was shipped abroad and that this country was furnishing annually nearly three times as much radium from its Colorado carnotite deposits as all the rest of the world put together. It was further pointed out that this material has been bought by European buyers at a price entirely incommensurate with its radium value and that efforts should be made to keep at home both the radium itself and the profits of its manufacture; also that too much stress could not be laid upon the extensive waste of valuable radium ore thrown on the dumps of mines and prospects—much of it under such conditions that it could never be recovered.

The publication of this statement has already resulted in an increase of at least 33 per cent in the price of carnotite ore, and European buyers are awakening to the fact that they must pay to the American miner a price nearer the actual value of his ore. Also, a much lower grade of ore is now marketable, for whereas six months ago ore containing 2 per cent uranium oxide was the lowest grade accepted by European buyers, agents of these buyers are now asking for and actually purchasing ore containing no more than half this content of uranium. Furthermore, the operators are taking more care in separating their low-grade ore from the gangue and in protecting it from wind and weather. Moreover, old dumps are being sold and ore that a few months ago was thrown aside as valueless will be recovered from them.

In this paper I shall refer to other facts contained in this bulletin and shall mention some new developments having a direct bearing upon the American radium industry which have taken place since the manuscript was sent to the printer.

As is well known to all of you, the popular belief has been that the chief source of radium is the mineral pitchblende, especially that obtained from the mines now under the control of the Austrian government at Joachimsthal, Bohemia, and pitchblende is the richest and most eagerly sought uranium radium ore. Outside of the ore in Austria, the only pitchblende deposits of any size are those in Gilpin County, Colorado, from which some 30 tons more or less have been procured since the mineral became valuable as a source of radium. The Denver papers recently announced that these pitchblende-bearing mines have been acquired by Alfred I. duPont of Wilmington, Delaware, and it is greatly to be hoped that their exploitation under his direction will yield an increased supply of this valuable mineral. It is not, however, so generally recognized that the mineral carnotite, which outside of the United States occurs only in low-grade ores mixed with ilmenite in the Olray district of South Australia and as a calcium carnotite (communicated by W. F. Hillebrand) under the name of Tyuyamyunite in Ferghana, Russian Turkestan, is by far the more important source of radium. From the most authentic sources it can be definitely stated that the Australian and Russian deposits do not compare in extent or richness with our own. The American carnotite is accordingly the largest source of radium at the present time and at least four times as much radium was mined in America in the form of carnotite in 1912 as has been produced from Colorado pitchblende since it was first discovered in that State.

Outside of carnotite and pitchblende, the only other known source of radium is the mineral autunite. The autunite deposits of Portugal have probably furnished a few milligrams of radium to commerce, and from the Mt. Painter deposits in South Australia a few tons of autunite-bearing ores have been shipped to London.

American carnotite is found chiefly in Montrose and San Miguel counties, Colorado, and in Utah northwest of these counties. The Utah deposits are at Green River, Table Mountain, Richardson, Fruita, Moab, and some 16 miles southeast of Thompsons. The ores of these deposits are of a lower grade than those of the Paradox Valley, but they are nearer to the railroads and transportation costs are much less. The Green River deposits have apparently become regular producers. In Colorado, prospects have been opened at Coal Creek, 14 miles north of Meeker and at Skull Creek 65 miles west of Meeker; but the richest of all American carnotite localities and indeed the richest known radium-bearing region in the world is that of the Paradox Valley, Colorado, extending from Hydraulic on the north to the McIntyre district on the south.

Geologists are now in the field making a special study of these carnotite ores with special reference to their occurrence and origin, of which altogether too little is now known. In the Paradox region the deposits seem to lie invariably just above the fine-grained La Plata sandstone. This rock is usually exposed high on the sides of the canyons, some of which are excelled in extent and in natural beauty by only the Grand Canyon itself. In a few instances, as at Long Park and Club Ranch, the deposits are only a few feet under the surface, the higher formations having been eroded; but for the main part, the stratum in which the carnotite occurs, when not entirely eroded, is deep below the surface of the mesa. Accordingly prospecting is mainly carried on along the sides of the canyons, and where vanadium and uranium stains are seen upon the rock the prospector blasts his tunnel in the hope of developing a pocket of the ore. The fact that the ore occurs in pockets renders prospecting uncertain, and there appears to be no present hope of insuring a successful search for pockets that are not exposed or do not happen to be near the surface. Although it is probable that many other pockets of carnotite occur at the same geologic horizon, their discovery, except where the ore-bearing stratum has been exposed by erosion, appears at present to be an almost hopeless task. The eroded sides of the canyons have been prospected again and again but new claims are still being opened and are being sold by the prospector to the larger companies or operators who mine the ore. In such a sale the prospector

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[1] Paper presented before the American Mining Congress, Philadelphia, October 23, by permission of the Director of the U. S. Bureau of Mines.

[2] Chief of the Division of Mineral Technology, Bureau of Mines.

and the purchaser both take a decided risk, for at present no method is used to determine the extent of the ore in the pocket other than the "prospector's hole."

As few of the prospectors of the west are acquainted with carnotite and pitchblende, the following description of the ores has been issued from the Denver office of the Bureau of Mines and is sent to all who make inquiry:

"In reply to your letter for information concerning radium ores, the following facts may be of interest:

"Radium is found associated with uranium minerals only. Wherever uranium exists, radium is also found in the mineral; and where there is no uranium, radium has never been found. Uranium and therefore radium are found in this country in carnotite and its associated minerals, and in pitchblende. Carnotite is a lemon-yellow mineral usually found in pockets in sandstone deposits. The mineral may be in the form of light yellow specks disseminated through the sandstone, or as yellow incrustations in the cracks of the sandstone, or may be more or less massive, associated with blue, black, or brown vanadium ores.

"Pitchblende is a hard, blue-black ore that looks something like magnetite, but is heavier. It is found in pockets and veins in igneous rocks. This mineral is not nearly as widely distributed as carnotite. Occasionally it is found associated with an orange mineral called gummite.

"The best way to test these ores is to wrap, in the dark, a photographic plate in two thicknesses of black paper. On the paper lay a key and then, just above the key, suspend two or three ounces of the ore, and place the whole in a light-tight box. Pressure of the ore on the key and plate should be avoided. After three or four days, develop the plate in the ordinary way; and if the ore is appreciably radioactive, an image of the key will be found on the plate.

"The U. S. Bureau of Mines, 502 Foster Building, Denver, Colorado, will be glad to receive any samples of ores giving promise of containing radium and associated rare minerals, as indicated by the test above described. Though it cannot undertake to make chemical analyses or assays of such minerals for private parties, it will indicate the advisability of further examination."

The Colorado carnotite deposits were apparently first noted as far back as 1881, when Andrew J. Talbert mined some of the ore and sent it to Leadville where it was reported as carrying $5 in gold per ton. This must have been an unusual ore as the carnotite now found does not carry the precious metal. In 1896, Gordon Kimball and Thomas Logan sent specimens to the Smithsonian Institution, Washington, D. C., and were informed that the minerals contained uranium. Shortly thereafter they mined 10 tons of ore, shipped it to Denver, and sold it for $2,700 on account of its uranium content. Three years later, in 1899, Poulot and Voilleque collected and sent to France specimens which were examined by Friedel and Cumonge who recognized the existence of a new mineral and named it "Carnotite" in honor of M. Carnot then President of the French Republic. In 1900, Poulet and Voilleque leached carnotite ores at Cashin in the Paradox Valley to extract the uranium. They shortly after completed a small mill in the McIntyre district south of the Paradox and in this project had the coöperation of James McBride, a mining engineer of Burton, Michigan. Their mill ran until 1902 and during that time produced 15,000 pounds of uranium oxide. The mill was started again in 1903 by the Western Refining Company but ran only a year. Up to 1904, the mills appear to have been run wholly with the idea of obtaining the uranium and vanadium from the ore for no radium was extracted. Shortly afterwards the Dolores Refining Company built a new mill a short distance from the old one but after running for some years, this mill, too, shut down. In 1912, the American Rare Metals Company acquired the mill of the Dolores Refining Company and is now operating it, with the special purpose of obtaining radium from the ores. The first attempt to extract radium in this country appears to have been made by the Rare Metals Reduction Company, under the management of Stephen T. Lockwood of Buffalo, N. Y. In September, 1900, Mr. Lockwood brought back from Richardson, Utah, samples of carnotite ore and in 1902 he published (*Eng. Min. Jour.*, of September 27th) the first radiographic plate from products of American carnotite. In June, 1902, he received 500 pounds of specially picked high-grade ore from Richardson, Utah, and in May, 1903, as a result of experimental work on this ore, he incorporated what was probably the first American company to operate a plant to produce radium as one of its products. In October, 1903, the first experimental plant was constructed and in April, 1904, the first 17-ton car of ore reached Buffalo from Richardson, Utah. The company obtained a fair percentage of extraction but the ore proved to be too low-grade and the Richardson deposits were abandoned. No radium in concentrated form was put upon the market, although barium sulfate concentrates were produced.

The General Vanadium Company which, with the Radium Extraction Company, is a subsidiary of the International Vanadium Company of Liverpool, England, was formed in 1909 and began work in 1910, the same year that the Standard Chemical Company of Pittsburgh, Pa., entered the field. Since that time these two companies have been engaged in mining carnotite. The ores from the General Vanadium Company have been shipped almost entirely abroad, while the Standard Chemical Company has shipped several hundreds of tons of carnotite to its works at Canonsburg, Pa. While it was stated at the time of the advance announcement of the bulletin to be issued by the Bureau of Mines that one American Company had actively entered into the production of radium no actual sale of American-produced radium could be authenticated. Since that time, however, the Standard Chemical Company has entered the American markets.

Besides the American Rare Metals Company and the Standard Chemical Company, a third company—the Radium Company of America with mines near Green River, Utah—has undertaken the production of radium in its plant at Sellersville, Pa. There is, therefore, every reason to hope that more and more of our ores will be worked up at home.

Besides the companies already mentioned, a number of independent operators mine and ship carnotite from the Paradox region and for the main part send their ores to Hamburg. Among the more prominent of these may be mentioned:

T. V. Curran, Placerville, Colo.
W. L. Cummings, Placerville, Colo.
O. B. Wilsmarth, Montrose, Colo.
David Taylor, Salt Lake City, Utah.

The costs of mining and especially of transportation are an important factor in the marketing of carnotite. The Green River deposits have a distinct advantage over the Colorado deposits in this respect, as they are nearer the railroad, but, as their ores do not average so high in uranium, this advantage is more apparent than real. The present costs of mining, sorting and sacking in the Paradox apparently vary from about $28 to $40 per ton. To this must be added an $18 to $20 hauling charge to Placerville, and, in most instances, an additional charge for burros from the mines to points that can be reached by wagon. The freight rate from Placerville to Hamburg *via* Galveston is $14.50 per ton, so that the average cost at present to the miner of laying down his ore at the European markets approximates $70 per ton. The selling price varies with the uranium content but is by no means proportional thereto, since a premium is always paid for rich ores. Very recently, however, a decided improvement has taken place and for 2 per cent ore, the price is now around $2.50 per pound for the contained uranium oxide with an allowance of about 13 cents per pound for the vanadium oxide content, so that the 2 per cent ore will now bring in Hamburg about $95 per ton. One per cent ore is now salable but unless this ore is taken from the dump, so that the mining cost may be disregarded, it will scarcely bear present transportation charges from the Paradox, although it is more than probable that it will soon be shipped regularly from the Utah field.

A price of $95 at Hamburg for 2 per cent ore leaves a fair margin of profit to the miner, as mining profits go, but when it is considered that this price represents only a little over one-sixth of the value of the radium content of the ore and that from this fraction of the value the American miner has to meet the outlay represented by the investment, by mining costs, transportation and assay costs and by losses in transit, it seems scarcely just that nearly five-sixths of the value should go to foreign manufacturers of radium, especially when the fact is considered that radium can be produced much more readily from carnotite than from pitchblende. There are two ways of reducing this difference between the actual value of the ore and the price that the miner receives. One is to hold our American ores for a higher price, and the second is to manufacture radium at home.

Large wastes are still taking place in the mining of carnotite, owing to the inability of the low-grade ores to bear transportation charges. As has already been pointed out, however, a distinct improvement in this respect has taken place within the last few months. The miners are beginning to realize the value of their old dumps and are attempting to save the low-grade non-shipping ore in such ways as will render its marketing possible when prices advance. The Bureau of Mines has done everything it can to impress the necessity of this truest kind of conservation upon the mine operator.

In addition there is prospect that most of the low-grade ores can be successfully concentrated by mechanical methods, and experiments at the Denver office of the Bureau of Mines indicate that a concentration of four to one can be obtained. In this concentration, however, there are losses which could be prevented by chemical concentration, but at the present time it costs more to ship the necessary chemicals to the mines than it does to ship the ores to places where these chemicals can be cheaply obtained. It would appear, however, that mechanical concentration can save at least one-half of the material that is now going to waste.

Although, until recently, the manufacture of radium from carnotite has been carried on almost wholly in France and Germany, there appears to be no good reason why our American carnotite should not be treated at home. Carnotite is much more easily treated than pitchblende and the essential features of methods for its chemical treatment are well known, although much of the mechanical detail of operation has been kept secret. As the mechanical requirements, however, are those which any well-grounded chemical engineer should be able to solve, there seems to be no good reason why any of our carnotite ores should be shipped abroad, even at two or three times the present market price of the material. As before stated, the essential features of chemical methods of extracting radium from its ores are well known. As regards the principles involved, the methods have advanced little beyond the original method published by Debierne.

The methods for carnotite may be described best in the words of Soddy, in an extract from "The Chemistry of the Radio Elements" by Frederick Soddy, page 45, published in 1911 by Longmans, Green & Co.

"The most important operations in the working up of radium-containing materials are the solution of the materials, consisting usually of insoluble sulfates, and the separation of the halogen salts of the alkaline-earth group in a pure state, followed by their fractional crystallization. The first operation is usually effected by vigorous boiling with sodium carbonate solution, filtering and washing free from sulfate. This is the well-known reaction studied dynamically by Guldberg and Waage, whereby an equilibrium is attained between the two pairs of soluble and insoluble sulfates and carbonates. Naturally the greater the excess of sodium carbonate the larger the proportion of insoluble sulfate converted into insoluble carbonate. In this operation it is advisable not to wash at once with water but with sodium carbonate solution until most of the sulfates are removed, as thereby the reconversion of the carbonates back into insoluble sulfates is largely prevented. In dealing with crude materials, for example, the radium-containing residues from pitchblende, it is often advantageous to precede this operation by a similar one, using a sodium hydrate solution containing a little carbonate which dissolves part of the lead and silica present. The carbonates washed free from sulfates are treated with pure hydrochloric acid which dissolves the alkaline earths including radium. From the solution the latter may be precipitated as sulfates by sulfuric acid and reconverted back into carbonates as before. Or sometimes more conveniently they may be precipitated directly as chlorides by saturating the solution with hydrogen chloride: this is a very elegant method of great utility in the laboratory, for the most probable impurities, chlorides of lead, iron, calcium, etc., remain in solution and only the barium and radium chlorides are precipitated, practically in the pure state, ready for fractionation."

The price of radium appears for some time to have been holding steady at about $120 per milligram of radium metal. This does not mean that the material is bought in the elementary condition but that the radium chloride and radium bromide, which are on the market, are paid for on the basis of the metallic radium they contain. This method of payment is a distinct advance over the old method of paying the same price indiscriminately for the chloride or bromide. This price of $120 per milligram of the metal is equivalent to approximately $91,000 per gram of radium chloride ($RaCl_2$), or $70,000 per gram of anhydrous radium bromide ($RaBr_2$). Whether this price will rise, fall, or remain stationary can not be predicted. There is no question that there is to be an increased radium production and that meso-thorium is also coming upon the markets in increasing quantity but the uses of and demand for radium are apparently developing at an even greater rate. Furthermore, the supply of the material is limited and no large resources are in sight. Only one estimate has been published of the total quantity of radium in the Colorado carnotite deposits and that was 900 grams. This estimate is at least five times as large as has been made by any employee of the Bureau of Mines, reckoning all known deposits in the whole American field, even including material too low grade to be marketable. Besides the radium, the uranium and the vanadium present in carnotite are available assets, and recent developments indicate that all the uranium produced will soon be readily sold, while it is well known that there is a ready market for vanadium for vanadium steel.

The value to the public of these deposits is, however, not to be measured in dollars and cents. The value of the radium output of America will never compare with that of several of our common metals. The total value of the radium in the world's output of radium ores in 1912 was little more than $1,000,000. Accordingly the value must ever be reckoned in what it can accomplish for the public knowledge and the public weal. No certain prediction can be made of the ultimate value of radium or of its possible applications to science or medicine, but enough has been done to show that radium is worthy of the fullest investigation by our highest scientific and medical authorities. Developments in its application to medicine are coming fast. The foreign medical press contains many apparently authentic reports of cures by its use. Interesting developments are also under way in America, and those who have had the largest personal experience in its use are most enthusiastic over its future application. The public may soon look to important publications from leading American authorities who have had real experience in radium therapy. It is to be greatly regretted that owing to the high price of the material, only three or four American surgeons have, so far as the Bureau of Mines is informed, been able to use it in quantities sufficient for the drawing of decisive conclusions. In the progress of the future applications of radium to the curing of disease, nothing is more to be feared than its use in nostrums of every kind. The "wonders of radium" have been so extensively exploited in the public press that already the name is being employed as a psychological agent in advertisements of all kinds of materials, many of which contain no radium at all or, if this element is indeed present, in such small quantities that no therapeutic value can be expected. As bearing on the need of further experiment, attention is called to the fact that the concentrated action of large quantities of radium may effect cures that have been impossible with the smaller amounts heretofore available to the medical profession. It is doubtful if there is at the present time in the hands of the medical profession of America more than a single gram of this rare element, and the results of investigations soon to be published will show that the concentrated action of the gamma rays from several hundred milligrams arrest certain forms of cancer and other malignant growths when smaller quantities are without beneficial effect. It is highly important that the medical profession should also have some guarantee of the material they purchase even if it is purchased in small quantities, and I am glad to note that the U. S. Bureau of Standards is preparing to standardize radium preparations. As several frauds in the sale of radium have already been perpetrated upon American physicians, they should all require that the quality of the material purchased should be certified under conditions which prevent error.

In closing, I take pleasure in saying that I am authorized by the Director of the Bureau of Mines to announce that a coöperative agreement has been entered into with the newly organized National Radium Institute, whereby the Bureau obtains the opportunity of a scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, vanadium, and uranium therefrom, with a view to increased efficiency of production and the prevention of waste.

The National Radium Institute was recently incorporated with the following officers:

Howard A. Kelly of Baltimore, *President.*

Curtis F. Burnam of Baltimore, *Vice-Prest.*

Archibald Douglas of New York, *Secretary and Treasurer.*

James Douglas of New York and E. J. Maloney of Wilmington, *additional Directors.*

The Institute has no connection with the mining of pitchblende, details of which recently appeared in the Denver papers. It has, however, obtained the right to mine 27 claims in the Paradox Valley region among which are some of the best mines in this richest radium-bearing region of the world. Nearly 100 tons of high-grade carnotite have already been procured. Under the agreement with the Bureau of Mines the technical operations of the mines and mill are to be guided by the scientific staff of the Bureau. Work will begin in an experimental plant to be erected in Colorado, using entirely new methods developed at the Denver office of the Bureau of Mines. Concentration experiments also will be conducted in the Paradox, probably at the Long Park claims, and if successful will be applied to reducing the wastes that now take place. Within a year at most the mill operations should make results certain and the extraction of ore and production of radium will then be continued on a larger scale. The separation of uranium and vanadium will also be studied, a contract having already been signed for all of these by-products that may be produced. All processes, details of apparatus and plant, and general information gained will be published for the benefit of the people.

The Institute is supplied with sufficient funds to carry out its plans. The Institute has been formed for the special purpose of procuring enough radium to conduct extensive experiments in radium therapy with special reference to the curing of cancer. It also expects to carry on investigations regarding the physical characteristics and chemical effects of radium rays and it hopes, in time, to be able to assist or perhaps even duplicate the effects of these rays by physical means.

Actual experience, especially of the Institute's president, in the application of the 650 milligrams of radium and 100 milligrams of meso-thorium already in his possession, has led him and his associates to believe that with larger supplies many of the variables that cannot now be controlled may be fully correlated, and that radium may become the most effective agent for the treatment of cancer and certain other malignant diseases. Important results have already been obtained by using high concentration of the gamma rays of radium with the alpha rays entirely cut off and the beta rays largely eliminated. Hospital facilities in both Baltimore and New York are already supplied.

The activities of the Institute are sure to be of benefit to the prospector and miner by providing a greater demand for his already rare ore; to the plant operator by developing methods and by creating a larger market for his product; and to the people by assisting, and possibly by succeeding, in controlling the most malignant of diseases. The radium produced is intended for the Institute's own use and will consequently remain at home.

The Bureau of Mines is especially fortunate in this opportunity to coöperate in the technological features of the work of the National Radium Institute.

Bureau of Mines, Washington

THE RELATION OF BIG BUSINESS TO INDUSTRIAL PROSPERITY WITH SPECIAL REFERENCE TO MINING[1]

By Charles R. Van Hise[2]

In an address before the American Mining Congress on the above subject, the speaker, one of the leading political economists of the country, declared that the Sherman anti-trust act was responsible for the tremendous waste in mining through permitting unrestrained competition. He said that when the Sherman act was passed, "immediately the wheels, so far as coöperation was concerned, were turned back to the conditions of the middle ages." He urged that an interstate trade commission and state trade commissions be established, which shall have substantially the same power to regulate coöperation in industry, that the Interstate Commerce commissions have in regard to public utilities.

"It seems that the Interstate and State Commerce Commissions and the administrative bodies for the pure food laws point the way for the next constructive step in the development of the laws. It would perhaps be chimerical, with public opinion as at present, to propose the repeal of the Sherman law, but the situation may be met by amendments to this law. The Sherman act can be left to apply, as defined by the Supreme Court, to monopoly. Unreasonable restraint of trade may be defined as monopolistic restraint of trade, and it is rather generally agreed that monopoly should be prohibited. To make the matter perfectly clear another amendment should allow reasonable coöperation, but such coöperation should be under the watchful eyes of administrative commissions in order to protect the public.

"There can be no question that the competitive system, when unrestrained, is positively opposed to the policy of conservation. This is true alike for minerals and timber. The minerals of

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[1] Abstracted by the American Mining Congress, Philadelphia, October, 22, 1913.

[2] President of the University of Wisconsin.

the earth require the building of the earth for their making. Mineral deposits are doubtless in the process of manufacture at the present time; but even if so, this is at so low a rate as to be negligible. From the point of view of mankind, the stores of minerals in the earth are deposits of definite magnitude upon which we may draw but once and which by no possibility can be increased. In this connection it should be recognized that modern civilization would not be possible without the mineral resources of the earth—no iron ships, no tools except those of stone, no fuel but wood. Without the sub-surface products of the earth we would at once return to the material conditions of the stone age. It is therefore incontrovertible that from the point of view of the human race, economic systems or laws which result in unnecessarily rapid use of the mineral stores of the earth are indefensible; but such are the economic theories and laws now dominant in the United States.

"The wastefulness of the competitive system may be proved with regard to every product which is taken from the earth. Lead and zinc in Wisconsin and Missouri are mined on a small scale under an extreme competitive system. The losses of these metals in their mining and metallurgy are nothing short of appalling. In southeastern Missouri, according to the late Dr. Bulkley, not less than 15 per cent of the metal is left under ground; the losses in concentration approach 15 per cent; the losses in smelting and concentration frequently amount to 15 or 20 per cent; thus making a total loss of from 45–50 per cent. These great losses are due to the system of numerous small holdings combined with the competitive system. High royalties on the part of the small feeholder are demanded of the operator. The operators desire to get large returns at the earliest practical moment upon this small investment. In consequence ore is left in the ground that should be mined; unnecessary losses take place in concentration, also unnecessary losses occur in smelting.

"But the most disastrous losses in mining as far as the future of the human race is concerned are in connection with coal. Director Holmes of the United States Bureau of Mines, in a paper upon mineral wastes, presents the facts in regard to the ruinous wastes of the unrestrained competitive system in connection with coal. He says that in the early days of mining when there was much subdivision of ownership not more than 30–40 per cent of the anthracite coal in the veins mined were brought to the surface, leaving from 60–70 per cent in the ground. He states that even at the present time not more than 50 per cent of the anthracite reaches the surface. The situation is similar for bituminous coal, but until recently the losses for such coal was substantially half. This loss has been somewhat reduced, but it continues to be appalling. Holmes estimates that since the beginning of mining in the United States, 'two billion tons of anthracite and three billion tons of bituminous coal have been left underground in such condition as to make its future recovery doubtful or impossible.' The principles which from the point of view of conservation should apply to the mining of coal are well known. So far as practicable the mines should be so worked as to make one superimposed vein after the other available. Coal slack should be reduced in amount and utilized. No considerable percentage of coal should be left in the ground as pillars. If these reforms were introduced, the losses could be reduced to half the present amounts and possibly to one-fourth.

"But to ask that any such proposals should be put into operation is purely chimerical. Under the Sherman law there is no opportunity to limit output, divide territory, or regulate prices. Five thousand bituminous operators could produce 200,000,000 tons of coal per annum beyond present demands. If the operators could agree upon limitations of output, and division of market so as to reduce freights, and could arrange for reasonable prices, which would give them no more than their present profits, they would then be able to follow these principles in mining their coal; for they themselves would be gainers in prolonging the life of their mines, and far more important many future generations would be the immeasurable gainers in that they would have an adequate coal supply.

"Under the competitive system, we are recklessly skimming the cream of the natural resources of a virgin continent with no regard for the rights of our children or our children's children. They will have a heavy score against us if we continue to ignore the future and to apply the unrestrained competitive system in total disregard of their rights.

"My proposal to remedy these conditions is neither regulated competition, nor regulated monopoly, but retention of competition, prohibition of monopoly, permission for coöperation, and regulation of the latter. At the present time there are state and national movements to still further extend the advantages of coöperation to the farmers. Since it is unquestionable that the sense of justice of the citizens of the United States will support the courts in prohibiting class legislation, we shall, therefore, I believe, ultimately permit coöperation in all lines of business alike. If we, however, retain freedom of competition, permit concentration sufficient to give efficiency, allow reasonable coöperation, and prevent monopoly, this will require regulation just as it has been necessary to regulate the railroads. This done, the Sherman law will be forgotten. Has there been any prosecution of the railroads for violations of the Sherman law because of collusion in fixing rates? And yet, every one knows that they are just as flagrant violators of the Sherman act as any other class of corporations in the United States. Are the freight rates the same for different roads between any two points? Are the passenger rates between Philadelphia and Chicago identical on all roads? Can you do better in price by traveling over the Pennsylvania, than over any other road? The rate is the same providing the speed is the same. How does it happen that the roads all got together? Just by Providence I suppose. It was doubtless by a providential act that these rates were fixed identically upon all the roads, under the same conditions, all over the country.

"Why is it that nobody proposes to indict the railroads for collusion? Simply for the reason that the rates which they can charge are controlled by commissions, national and state. Nobody any longer wishes to make them further trouble, because the public is protected by its commissions The railroads are just as amenable to attack under the Sherman act as any other combination in the United States, but when the railroads are giving reasonable rates, and are competing in giving reasonable service, even if the law is on the statute book and is the hallowed thing that has been described—the sense of official justice is such that they are not attacked in the courts. Will the Attorney-General of the United States or the Attorney-General of this or any other state, bring suit against the railroads for conspiracy in fixing rates when the public is properly protected? I have not heard the proposal made anywhere.

"However, it is a wrong condition when we have on the statute books a law of a kind which requires the officials of justice to close one eye whenever they pass by the men in control of one great group of industries, and at the same moment see other men not one whit more guilty. We ought to remedy this condition so that honorable business men shall not be in the position, the unfortunate position, of being technically violators of statutes which it is not advantageous from the public point of view to enforce.

"In regard to the Sherman act, it has been assumed that its only violators are the great combinations. This assumption is made in practically all discussion of the question. The Steel Trust, the Tobacco Trust, and a few other large combinations are mentioned; and it is supposed that the small business men and the small producers are not acting in violation of the law. But the principle of coöperation which the Sherman act tries to suppress extends from the great industrial centers, like Philadelphia, to the country cross-roads. Does it make any difference here in Philadelphia, the home of anthracite, whether one buys anthracite of one retail dealer or another? It doesn't make any difference in the country cross-roads either. The price is just the same from all the dealers in the same locality. The same is true of ice, the antithesis of anthracite, and is also true of all standard articles. The principle of coöperation has extended from the great manufacturers and the great dealers of the large cities to the small manufacturers and small dealers of the small cities and even villages. All are coöperating in the same way; the principle is the same for the large and small man; one is violating the law just as certainly as is the other. I am willing to stand for enforcement of law when the law is enforced alike for all; but when somebody is picked out because he is in the front seat, or because it is good politics to attack him, and ninety-nine or nine hundred and ninety-nine are allowed to escape, I say that it is a profoundly immoral situation. And that is exactly the existing situation in this country. The politician who says, 'Break up these trusts; destroy them,' says with the same breath, 'We must have coöperation among farmers.'

"Why, the cranberry growers of Cape Cod, New Jersey, and Wisconsin, sell about 90 per cent of their products through an agency down in Hudson Street, New York. Similarly many products of the farmers, illustrated by cotton, citrous fruits, etc., are marketed through coöperative selling agencies. Have we heard of the Attorney-General prosecuting these farmers? Congress understands the situation and at their two recent sessions they attached to the Sundry Civil bill a clause containing an appropriation of $300,000 for the enforcement of the anti-trust laws, which included the provision 'that none of this money should be spent in prosecuting combinations or agreements of labor, nor spent for the prosecution of producers of farm products, and associations of farmers who coöperate and organize in an effort to and for the purpose to obtain and maintain a fair and reasonable price for their products.' The purpose of this provision is clearly to make the Sherman law class legislation by indirection and in effect to prevent equality before the law of the manufacturer as compared with the farmer. And some of the smarter state legislatures have seen the situation and in order to prevent the farmers from being hit by their anti-trust bills exempted the products of the lands so long as in the hands of the producers. You see, the state legislatures, like Congress, saw that the farmers have so many votes that they have to be dealt with gently when they form a trust. But some of the state laws got into the United States courts, and these courts promptly declared these exemptions unconstitutional as being special legislation. I venture to predict that it will not be so popular a political game to shout, 'Bust the trusts;' when the farmers understand that their trusts are also to be 'busted.' No more pernicious or immoral legislation was ever passed by Congress or by the states. The principles of justice in regard to trusts and combinations are alike for the manufacturers, the farmers and the laborers. In this country we have not a special situation which concerns a few men, but a general, irresistible impulse. There is just as close-riveted an arrangement between the three icemen in the country town as there is in steel; and any solution of the problem of combination, if it be a just solution, must be applied not only to steel, tobacco, etc., but to the small tradesman, the farmer. Just as certainly as the great combinations are violating the Sherman act, as I have no doubt many of them are, so are the small aggregations of wealth violating state anti-trust statutes. This general violation of the trust laws, national and state, is the problem that we have before us."

UNIVERSITY OF WISCONSIN, MADISON

FERTILIZER CHEMISTRY—A REPORT OF PROGRESS[1]

By PAUL RUDNICK

This report is not intended to be a complete or detailed account of the subject with which it deals; the idea has been rather to point out very briefly only the most important developments appearing in the field since the previous report under the same title presented on a similar occasion.

In addition to the process of oxidizing atmospheric nitrogen by means of the electric arc as developed by Birkeland and Eyde and by Schoenherr and the process for converting nitrogen into ammonia by the manufacture of cyanamide (Frank and Caro) and by the manufacture of aluminum nitride (Serpek),[1] we have had the announcement of the process of direct combination of nitrogen and hydrogen to ammonia by means of catalyzers in the process of Haber and Le Rossignol as described in the paper of Professor Bernthsen before the Eighth International Congress of Applied Chemistry.[2] To the original catalyzers, iron, manganese, nickel and cobalt, have been added chromium and cerium and later osmium and uranium. The latter two are said to be superior to all the others, and with them it was possible to work at temperatures of 500° to 600° C. under high pressures at the rate of several kilograms of ammonia per hour and per liter of space occupied by the catalyzer. In the manufacturing process it has been found possible to replace osmium and uranium by cheaper catalyzers based on the improvement produced by certain additions. Electrolytic hydrogen has been replaced by hydrogen made from coal because the impurities which were poisonous to the catalyzers in hydrogen so produced were discovered and eliminated.[3]

It is further announced that the Ostwald process for making nitric acid from ammonia, which attracted considerable attention some ten years ago, has recently been taken up in a commercial way in England. This process is stated to depend upon the oxidation of ammonia to nitric acid by means of the catalytic action of spongy platinum or platinum black. The ammonia needed as raw material is to be obtained from the decomposition of calcium cyanamide.[4]

Recently the market has shown a considerably increased activity in calcium nitrate.

A preliminary research on the fixation of nitrogen by aluminum carbonitride has been announced.[5]

An effort to increase the price of beehive coke may furnish an artificial stimulus to the by-product coke industry and, therefore, to the production of ammonium sulfate.[6] Increased by-product oven facilities now contemplated will, of course, add to the domestic production of sulfate of ammonia to a certain extent. The leading American by-product coke concerns report that the outlook for the industry is bright and that the market could absorb a larger production if it were available.[7]

With reference to the life of the Chilean nitrate beds it is announced that the nitrate existing in all the deposits of Chile which have been prospected, but not all surveyed, is estimated at 1,000,000,000 tons. Large supplies probably also exist on lands now but incompletely prospected. The surveyed and certified tonnage opened up at the present time ready for extracting is fully 250,000,000 tons. The probable life of the surveyed deposits is at least several hundred years, even allowing for a steadily increasing annual rate of consumption.[8] An excellent description of the Chilean nitrate fields by Dr. W. S. Tower has just appeared.[9]

In connection with the many processes proposed for the production of available phosphoric acid from phosphate rock by means other than acidulation with sulfuric acid, it is claimed that a product analyzing 45 per cent of available phosphoric

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[1] Chairman's address delivered before the Division of Fertilizer Chemistry, September 11, 1913, at the 48th Meeting of the A. C. S., Rochester.

[1] THIS JOURNAL, **5**, 335.

[2] *Ibid.*, **4**, 760.

[3] *Chem. Ztg.*, **37**, 584.

[4] *Met. Chem. Eng.*, **11**, 438.

[5] *Am. Fertz.*, **39**, 25.

[6] *Met. Chem. Eng.*, **11**, 427.

[7] *Am. Fertz.*, **39**, 37.

[8] *Ibid.*, **39**, 56d.

[9] *Pop. Sci. Mon.*, **83**, 209.

acid, 12 per cent ammonia, and 5 to 6 per cent of potash is now being produced commercially.[1] The explanation of the process given is that instead of sulfuric acid a plant food is used in the new process. From another source[2] we learn that in this method the phosphate rock is treated in an electric furnace, the phosphoric acid being recovered in vapor form. It is stated that the new method cannot be worked successfully with a higher current cost than $4 per horse power per annum, which is a much lower figure than has ever been attained in this country.

In this connection it must be considered that the utilization of sulfur-bearing gases is undoubtedly increasing right along, chiefly because of the damage which, it is claimed, is being done by these gases. The electrolytic precipitation process of Cottrell[3] and the thiogen process, in which the sulfur is recovered as elementary sulfur, seem to be making satisfactory progress.[4]

An extended review of possible sources of potash in the United States by Cameron has appeared recently.[5] It covers in addition to the minor sources the more important possibilities such as alunite, salines and salt beds, feldspar, green sand marls and kelp. The possibility of recovering potash from the flue dust of cement plants in which potash feldspar is used instead of clay or shale is also described. The manufacture of potash from kelp has apparently reached the commercial stage, judging from a recent advertisement.[6]

The extraction and refining of oil and of the production of ammoniates from the Pacific Coast Fisheries is apparently attracting attention in a commercial way and this may present some interesting chemical problems to the fertilizer chemist for solution.

The controversy between various authorities on the theory of soil fertility, including a satisfactory theory of fertilizer action, is still active, but no important new developments have been recently announced.

Armour and Company
Union Stock Yards, Chicago

FOOD STANDARDS AND THEIR EFFECT UPON FOOD LAW ENFORCEMENT[7]

By Floyd W. Robison

From a standpoint of food law enforcement, there has been quite a constant official pressure toward the creation of food standards. Food standards have had much to do with improving the quality of foods, and it is therefore with full appreciation of this condition that we venture for purposes of discussion a few points bearing on the effect of standards as written in the law on food law enforcement.

Obviously, the analyst when passing upon the purity of a food product must have some standard in mind. It is either an expressed standard or an understood standard. Such a standard, if followed, should be one that will allow the widest liberty to the pure product. Primarily it should be borne in mind that a food product cannot in justice be suited to the limitations of the analyst. With manufactured foods the widest latitude must likewise be given for individuality of manufacture and room should always be allowed for a variation in standard due to actual improvement in process of manufacture.

It has been the aim of many food law officials to incorporate in the laws of the various states as many food standards as possible. In so doing the work of the food analyst and the food department has been very materially simplified. In plain words, a violation of the law may in this way be more clearly and more surely perhaps pointed out to a jury of twelve men. This at first glance may seem very desirable but it is the actual working out of the plan that we should observe. Let us take a specific case, for example, cider vinegar.

Until the present year the Michigan statute required that a fermented vinegar should have not less than 4 per cent of acetic acid, $1^3/_4$ per cent solids and $^1/_4$ per cent ash. It becomes perfectly simple then to sustain a case in court where the solids are $1^1/_2$ per cent or where the ash may be $^1/_5$ per cent without taking into consideration at all the question of the real purity of the product.

On the other hand, it becomes extremely difficult to prove an infraction of the law when the standards set in the law are met by the food product in question. We have had states' attorneys actually refuse to enter complaint in the case of a totally sophisticated product, because so far as its standard was concerned it complied with the figures set in the law.

Food standards in so far as they effect other than the essential constituents of that product when placed in the statute become actually a standard of adulteration instead of a measure of purity.

Another point: improvement of product should always be encouraged by a food law. Many times a set standard in the law works actual hardship upon a manufacturer, who by expensive and painstaking devices and processes has improved his product, and incidentally in so doing disarranged perhaps its several unessential constituents.

Referring again to cider vinegar, we hold that pure cider vinegar should have not less than 4 to $4^1/_2$ per cent of acetic acid, derived from cider. Now the essential requirements concerning cider vinegar are first, that it must be manufactured from cider, and second, that it must have not less than a certain amount of acetic acid. Suppose it becomes desirable in the process of manufacture to clarify a product by any of the methods in use or by other desirable methods not now current. Provided the acid is not disturbed nor the cider value impaired, it is manifestly fair that such improvements should be permitted, yes, encouraged by the law.

In coffee, tea, spices, in fact in nearly all products the inclusion of a standard in the law, other than as indicated above, becomes a source of embarrassment at times to the conscientious official, and at the same time a menace to the business of the wide-awake, progressive manufacturer.

It is convenient for a food official to be able to say to the manufacturer: "Why the law states that your product shall contain a certain ratio of its constituents and it becomes my duty to enforce this law." As we have stated heretofore, this simplifies the duties of the food official. The ratio has been read into the law, not because it bears any relation to the food value or to the food purity, but because perhaps many analyses of the product now on the market or produced heretofore show a certain ratio of these constituents. Actual progress under these conditions is impossible.

Vanilla extract is another example. We are firm in our opinion to date that the very best Vanilla Extract that has been produced has been produced by a method quite similar if not identical with the U. S. P. method, yet it would be absurd to prescribe in the law that besides a certain vanillin content, the extract must contain a certain quantity of resins and other non-valuable constituents of the vanilla bean.

It is not essential, neither is it desirable that a law guarding the purity of maple syrup should state the content of ash, or any standard other than that of sugar content accompanied by the injunction of absolute purity. It is a fact that many farmers priding themselves on the purity and excellence of their maple syrup do actually add clarifying ingredients, etc., for the very purpose of securing greater purity and thereby a more salable product. Such efforts should be encouraged and a law should not prohibit progress of this kind.

[1] *Manuf. Rec.*, July 21, 1913.

[2] *Am. Fertz.*, **39**, 38.

[3] This Journal, **3**, 542.

[4] *Am. Fertz.*, **39**, 55; also This Journal, **5**, 955.

[5] *Com. Fertz.*, **7**, 22.

[6] *Am. Fertz.*, **39**, 20-21.

[7] Presented at the 48th Meeting of the A. C. S., Rochester, September 8-14, 1913.

The standard is most properly the analysts' guide and should be promulgated for that purpose. To incorporate a standard in the law other than to regulate as we have stated above the minimum strength of the essential ingredient or the maximum amount allowable of any specially undesirable constituent is to place a premium upon analytical incompetency.

There are places where the standards can be stated and may be properly incorporated in the law. This includes the fat and solids in milk, but not the ash nor the specific gravity nor the refractive index of the serum. Likewise the acid of vinegar but not the solid, ash, alkalinity, glycerine, nor the other non-valuable constituents. The vanillin content of vanilla extract perhaps; the citral content of lemon extract; the arsenic and lead limits in foods and food colors; and the maximum amounts of preservatives, if permitted, may be made a part of the law with perfect propriety.

The standard laid down in the law should be the minimum quantity permissible of the desired constituent or the maximum quantity allowable of any undesirable ingredient, and for purposes of food law enforcement, it will be found, we think, preferable to limit the standards, in so far as they are read into the law, to practically these two conditions.

Detroit Testing Laboratory
Detroit, Michigan

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

AN AUTOMATIC CHEMICAL FEEDER

According to *Engineering Record*, 68, No. 10, 264, an automatic type of chemical feeder has recently been tested at the hydraulic laboratory of the University of Illinois by the patentee, Ralph Hilscher. The apparatus works in conjunction with a Venturi meter and depends for its action directly on the decreased static head at the restricted section.

Referring to the sketch, the device consists of a box divided into two compartments by a wall which extends from the bottom to within a short distance of the top. At the top of this wall is pivoted a horizontal arm, from which are suspended two floats of equal dimensions, one in each compartment, and at equal distances from the pivot. The arm in compartment B extends beyond the float and connects with a balanced valve on the end of a feed pipe, which supplies chemical from a supply tank. The valve is so made that when the float in B falls below the float in A the downward movement of the arm will cause the valve to open and admit chemical solution to compartment B.

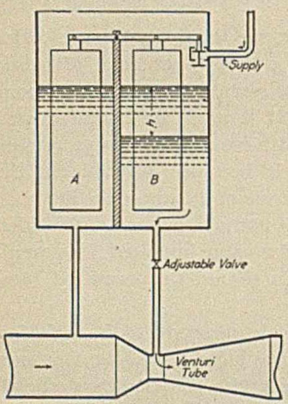

Diagram of Chemical Feeder

Connecting compartment B with the reduced section of a Venturi tube is a pipe in which there is an adjustable valve. Another pipe connects A with the full section of the Venturi tube. The Venturi tube is inserted in the pipe to which it is desired to feed the chemical.

When a flow of water occurs through the Venturi tube unequal pressures at the full and reduced sections will tend to make the levels in A and B different, that in B being lower. This difference in pressure, represented by *h*, is proportional to the square of the rate of flow through the Venturi tube and, if utilized to force chemical solution through an orifice, will produce a flow through that orifice directly proportional to the flow in the main. The adjustable valve acts as an orifice in this device and the desired effective head on it is established by building up the level in B equal to that in A. As already explained, these two levels are kept the same by the float arrangement.

Referring to the test sheet, the figures are for four different tests, each with a different size of opening of the adjustable valve. The first column contains the quantities of water treated, measured in a large tank at the end of each run. Column 2 contains the corresponding quantities of solution fed by the machine, determined by measuring the drop in the supply tank. Column 3 gives ratios of Column 2 to 1, and these figures should all be the same theoretically for a given size of orifice. The ratios are averaged for each test, and in the sixth column are given the per cents by which the various ratios depart from the average. By reference to the fifth column it will be seen that rates at which water was treated varied by about 300 per cent.

TESTS OF AUTOMATIC CHEMICAL FEEDER

Gallons treated	Gallons solution applied	Ratio of Col. 2 to 1	Time of run, in minutes and seconds	Gallons per minute treated	Per cent by which ratio departs from average
639	2.98	214	5.39	113	+6.2
726	3.49	208	6.30	112	+3.2
682	3.58	190	5.12	131	—5.8
1495	8.03	186	10.11	146	—7.7
1382	6.59	210	17.10	80	+4.3
Average..........		202			
1620	5.85	277	9.20	174	+1.8
1014	3.80	267	18.55	54	—1.8
Average..........		272			
1294	2.98	434	19.30	66	—0.2
1680	3.94	426	10.00	168	—2.1
1355	3.04	445	14.30	93	+2.3
Average..........		435			
1365	3.55	384	13.30	101	—4.8
1506	3.58	420	26.00	58	+4.0
1653	4.07	407	10.00	165	+0.8
Average..........		404			

MICARTA AND BAKELITE MICARTA

Micarta is a new material which has been developed by the Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa., to take the place of hard fiber, glass, porcelain, hard rubber, built-up mica, pressboard, rawhide, moulded compounds, etc.; it is used for commutator bushings, brush-holder insulation, as noiseless gear blanks, as conduit for automobile wiring, as spools for spark coil and magnet windings, for refillable fuse tubes, for wireless coil separators, for arc shields in circuit breakers, for water-meter discs, etc.

Micarta is a tan-brown colored, hard, homogeneous material having a mechanical strength about 50 per cent greater than hard fiber. It can readily be sawed, milled, turned, tapped, threaded, etc., if a sharp pointed tool is used, and the work done on a lathe. It can be punched only in thin sheets and cannot be moulded. Micarta is not brittle, and will not warp, expand, nor shrink with age or exposure to the weather, but takes a high polish, presenting a finished appearance.

Two grades of the material are made. The grade known as bakelite micarta will stand a temperature of 150° C. continuously, or 260° C. for a short time. It is infusible and will remain unaffected by heat until a temperature sufficient to carbonize it is reached. Heat will not warp bakelite micarta, and it will stand an electric arc better than hard fiber, hard rubber, built-up mica, or any moulded insulation containing fibrous or resinous materials. Its coefficient of expansion is low, being approximately 0.00002 per degree Centigrade.

Bakelite micarta is insoluble in practically all of the ordinary solvents, such as alcohol, benzine, turpentine, and weak solutions of acids and alkalis, hot water and oils. It is indifferent to ozone—an advantage over hard rubber, resins, etc., for electrical purposes. It is non-hydroscopic and impervious to moisture.

The other grade designated as No. 53 micarta has the same mechanical and electrical properties as the bakelite micarta, but differs in its chemical and thermal properties. The plain micarta behaves toward chemicals and heat very much as an ordinary resin. This grade is not used in plate form.

NEW CENTRIFUGAL PUMP

The *Engineering Record*, Oct. 4, 1913, reports that a new centrifugal pump ranging in size from 2 to 15 inches and suitable for low speeds is being placed on the market by a Philadelphia company. The casing is made solid with a detachable suction head and carries on the top a detachable flange which supports the stuffing box and thrust bearing. By removing the bolts in the upper flange the casing may be opened for inspection of the impeller without disturbing the suction or discharge flanges. The casing is of cast iron and is fitted with removable bronze bushings. The thrust bearing, which is of the radial ball type, is carried on the pump housing and is fitted with a sight feed lubricator. The guide bearings are lubricated automatically. The impeller is of the closed type. The frame is of channel iron with suitable braces which carry the guide bearings, and the motor is supported on a cast-iron base.

TESTING THE LIQUOR IN SULFITE COOKS

Paper 13, No. 4 (Oct. 8, 1913), reports that according to *Papierfabricant* the digesting liquor is not fully utilized in the manufacture of sulfite cellulose because the samples are improperly obtained. Generally the digesting liquor is run off into a copper beaker or a glass vessel, cooled slightly or not at all and then titrated. The SO_2 when heated or agitated is changed from the liquid into the gaseous form, and as the specimen of liquor is agitated and heated very greatly when drawn off, a large part of the SO_2 escapes. If a digester whose total content of SO_2 amounts to $3^1/_2$ to 4 per cent is heated up to 100° C. with gas escaping, scarcely more than 2 per cent SO_2 will be found.

Therefore, if it is desired to determine the correct proportion of SO_2 in the liquor, it is recommended to attach to the delivery outlet pipe a rubber tube or a leaden worm of thin piping, the end of which is provided with a cock, and place the worm in cold water. The liquor should then be run off cold and titrated, when it will be surprising to find how strong it still is.

THE PRESENT STATUS OF THE GLASS BOTTLE AND HOLLOW WARE INDUSTRIES IN THE UNITED STATES[1]

Although the first automatic bottle machine was introduced in 1904, until 1912 its advance was rather slow, owing to the fact that the shops of the Owens Bottle Machine Company were limited to an output of 50 machines per year. In January, 1913, however, this company completed a new plant and it now has a capacity of 100 new-style 10-arm machines a year. These machines, which are said to be complete in general principle, have almost twice the output of the old 6-arm machines, the production being 400 gross per day of $^1/_2$-ounce to 6-ounce bottles, 200 gross of 6-ounce to 32-ounce size, and 100 gross of gallon size. The installations and machines on the order of the Owens type in the United States in 1912, as compared with 1911, were as follows:

	1911	1912
Total installed	103	133
Total ordered	18	33
Total(*a*)	121	166

(*a*) Aggregate annual capacity, 7,000,000 gross of bottles.

The development of automatic lehrs has kept pace with the machines, in order to handle the increased production.

According to Wheeler (*Intern. Soc. Rev.*, November, 1912), it is not likely that the Owens Company will turn out more than 100 more of the 10-arm machines for several years, as the number of machines made and in use by 1914 will be able to supply almost the entire demand for bottles in the United States, Canada and Mexico. The annual consumption will hardly reach 15,450,000 gross in 1914, unless a greater demand can be induced by a greatly lowered price. It is predicted that in two years the bottle industry will belong to the automatic machine, although there are certain classes of ware which may never be taken over by the machine; and it is estimated that by 1914 there will be 250 automatics in operation. At present, the machine is manufacturing almost every type of bottle from $^1/_2$-ounce size to 12-gallon demijohns, and a number of large companies, including firms controlled wholly or in part by the Owens Company, are in a most commanding position in the bottle market. In fact, these concerns are preparing to take over the entire bottle industry. The Fairmont, W. Va., plant of the Owens Bottle Machine Company is the best automatically equipped bottle factory in the world; the production amounts to about 500,000 gross of bottles of all kinds per year.

Among the other types of machines, the Whitall-Tatum automatic machine is said to be capable of competing with the Owens machine.

Notwithstanding the rapid changes constantly going on in bottle-making machinery, at present there is an increase in the number of semi-automatic wide-mouth machines installed. In 1912, 33 plants were equipped with 170 machines of this type; to-day there are 37 factories operating 201 machines. With regard to narrow-mouth machines, it may be noted that 96 United and O'Neill machines, employing 487 journeymen, were in operation in August, 1913. The United machine (semi-automatic) is capable of producing $85^1/_3$ dozen of bottles per man a day.

Owing to the number of blownware furnaces which were constructed and started during the blast of 1912–13, the prospects for the manual blower are somewhat brighter than at any time during the past six years. This is mainly attributed to bringing the cost of production of the blownware bottle closer to that made by the automatic machines. In June, 1913, 609 workmen were reported idle by the Glass Bottle Blowers' Association—801 less than in June, 1912.

As to the visible stocks of blownware on hand at various factories in August, 1913, only 17 per cent of the plants reported heavy stocks. In certain instances, heavy stocks of automatic ware were reported, states *The Glassworker*, August 9, 1913, 12, although the opinion is authoritatively expressed (*National Glass Budget*, **28**, No. 28, 1) that the Owens Company's product is maintaining its pre-eminence in the trade, owing to quality, accurate and uniform weight and capacity, and low cost of manufacture (high productive capacity of the machines and low cost of labor involved).

A list of the manufacturers of glass bottles and hollow ware in the United States follows. The value of the glass bottles and hollow ware produced annually in this country is now approximately $50,000,000.

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[1] For a review of the status of the window glass industry in the United States, see THIS JOURNAL, **5**, 80; and for a discussion of the conditions prevailing in the plate glass industry, see THIS JOURNAL, **5**, 253.

A LIST OF THE MANUFACTURERS OF GLASS BOTTLES AND HOLLOW WARE IN THE UNITED STATES

Including manufacturers of prescription bottles and vials; medicine reagent and liquor bottles; packers' and preserved bottles; beer and mineral water bottles; milk bottles, and fruit jars.

Plants and location B., bottle; G., glass	Method A., automatic; H., hand; M., machine(s)	Continuous tanks	Rings	Furnaces	Pots	Products B., bottle(s); F., flask(s); V., vial(s)
California						
Illinois-Pacific G. Co., San Francisco	M. and H.	4	37	..	...	General line
Pacific Coast G. Works, San Francisco	M. and H.	2	16	..	...	General line
Georgia						
Tallapoosa G. Mfg. Co., Tallapoosa		1	...	..	...	Prescription, medicine, mineral water, and liquor B.; V. and F.
Illinois						
The American B. Co., First National Bank Bldg., Chicago; factories, Streator, Newark and Massillon, O.	A. M. and H.	42	...	..	...	Beer and mineral water B.
Chicago Heights G. Co., Chicago Heights	M. and H.	2	24	..	...	General line
The Headley G. Co., Danville		1	12	..	...	Prescription, mineral water and beer B.; V.
Illinois G. Co., Alton	A. M. and H.	10	...	1	12	General line
Obear-Nester G. Co., E. St. Louis		3	26	1	15	General line
Olney B. Co., Olney		1	10	..	...	Liquor B. and F.
Schram Automatic Sealer Co., Hillsboro	8 semi-A. M. and H.	1	8	..	...	Packers' and preservers' B.
Wilcox G. Co., Inc., Robinson		1	6	..	...	Prescription and liquor B., and F.
Indiana						
Ball Bros. G. Mfg. Co., Muncie	A. M.	14	159	..	...	Packers' and preservers' B. and jars
Bell B. Co., Fairmount		1	16	..	...	Liquor B. and F.
Daleville G. Co., Daleville	M. and H.; 22 shops	..	...	..	...	General line
Fairmount G. Works, Indianapolis	M. and H.	2	28	..	...	General line
Globe G. Co., Arcadia		1	10	..	...	Medicine and liquor B., F., and V.
Graham G. Co., Sales Dept., Majestic Bldg., Indianapolis; factories, Loogootee; Okmulgee, Okla.	17 M.	3	...	..	...	Beer and water B.
Lapel B. Co., Lapel		1	6	..	...	Liquor B. and F.
Marion Flint G. Co., Marion	M. and H.	2	24	..	...	General line
Maring Hart & Co., Dunkirk	M. and H.	2	22	..	...	General line
Model G. Works, Summitville	M. and H.	2	14	..	...	General line
North Baltimore B. G. Co., Terre Haute	O'Neill M. and H.	3	...	..	102	Beer and water B.
Pennsylvania G. Co., Anderson	M.	2	13	..	...	General line
Root G. Co., Terre Haute	M. and H.	3	26	..	...	Beer and water B.
Sims G. Works, Sims		1	8	..	...	General line
Skillen-Goodin G. Co., Yorktown	M. and H.	2	14	..	...	General line
Sneath G. Co., Hartford City	M. and H.	1	5	1	16	Packers', preservers', and milk B.; fruit jars
Standard G. Co., Marion		1	8	..	...	Medicine B. and V.
Thompson B. Co., Gas City	5 A. M. and H.	3	36	..	...	General line
Turner Bros. Co., Terre Haute	M. and H.	2	20	..	...	General line
Upland Flint B. Co., Upland		1	10	..	...	Medicine and liquor B.
Western Flint G. Co., Eaton		2	12	..	...	Liquor B. and F.
Woodbury G. Co., Winchester		3	36	..	...	General line
Kansas						
A. H. Kerr & Co., Altoona	M.	1	10	..	...	Fruit jars
Maryland						
The Buck G. Co., Baltimore	M. and H.	1	7	..	...	General line
Carr-Lowrey G. Co., Baltimore	M. and H.	1	...	3	33	Paste mold ware, stoppers, and a general line of B. and jars
Maryland G. Corporation, Baltimore	M.	3	11	..	...	General line
Swindell Bros., Baltimore	M. and H.	1	...	2	38	General line
Michigan						
Michigan G. Co., Saginaw	M. and H.	1	6	..	...	General line
Monroe G. Co., Monroe	Semi-A. M. and H.	1 continuous; 1 5-ton day; 1 4-ton day; 1 1-ton day	8	..	...	Packers', preservers', and ointment B. and jars
Missouri						
Adolphus Busch G. Mfg. Co., St. Louis		1	25	..	...	Beer B.
New Jersey						
Cape May G. Co., Cape May Court House	M. and H.	2	21	..	...	Prescription, beer, and water B.; V. and F.
Co-Operative G. Co., Barnegat		1	8	..	...	General line
Cumberland G. Mfg. Co., Bridgeton	M. and H.	6	69	..	...	General line; also battery and ointment jars
Gayner G. Works, Salem	M. and H.	2	...	..	22	Battery jars, carboys, water B.; general line of large ware
Hereford G. Co., Cape May Court House (Operated by Cape May G. Co.)		1	9	..	...	Prescription, beer and water B.; V. and F.
More-Jonas G. Co., Bridgeton	M. and H.	4	28	..	...	General line; battery and ointment jars
Parker Bros. G. Mfg. Co., Bridgeton	M. and H.	2 and 1 day tank	14	..	...	Medicine, and packers' and preservers' B.
F. M. Pierce & Co., Clayton		..	...	1	5	Medicine, beer and water B.; V.
Salem G. Works, Salem	M. and H.	3 and 1 day tank	23	3	16	General line
South Jersey G. Works, Swedesboro	M.	..	...	2 of 20 tons each	...	Beer and mineral water B.
Star G. Co., Medford		1	10	..	...	Druggists' supplies, liquor B. and F.

Vineland Flint G. Works, Vineland		1	8	3	27	Glass for gauges, X-ray tubes, vacuum B., electrical ware, etc.
T. C. Wheaton Co., Millville		1 flint tank 1 amber tank	10 8	1	12	Medicine, beer and mineral water B.; V.
Whitall Tatum Co., Millville	M. and H.	3 6 day tanks	41 64	8	71	General line; opal ware
Whitney Glass Works, Glassboro	A. M.	4	...	..	...	General line
Williamstown G. Co., Williamstown	M. and H.	5	46	..	...	General line
Woodbury B. Works, Cons., Woodbury		6	47	..	...	General line
New York						
Acme G. Co., Olean		2	15	..	...	Prescription, beer, liquor and water B.; V. and F.
Bahr Demijohn Co.; office, Brooklyn; factory, Ellenville		1	3	..	...	Demijohns
Binghamton G. Co., Binghamton		1	11	..	...	General line
Bottlers and Mfg.'s Supply Co., Ravenswood, N. Y. City		2	20	..	...	Beer, liquor and water B.; F.
Brookfield G. Co.; office, 2 Rector St., New York City; factories at Brooklyn, N. Y., and Old Bridge, N. J.		3	30	..	...	Medicine, beer and water B.; electrical goods
Clyde G. Works, Clyde	M. and H.	1	9	..	...	General line
Geneva G. Co., Geneva	M.	1	8	..	...	Beer, liquor and mineral water B.; F.
Industrial G. Co., Lancaster		1	6	..	...	General line of B.
Lockport G. Co., Lockport	M.	1	10	..	...	Milk B.
New York G. Works, Alden	M. and H.	3	...	..	...	General line
Olean G. Co., Olean, Port Allegany, Pa.	M. and H.	5	35	..	...	General line
Pierce G. Co., Hamburg	M. and H.	1	16	..	...	Medicine B.
Poughkeepsie G. Works, Poughkeepsie	M. and H.	3	28	..	...	General line
F. E. Reed G. Co., Rochester	M. and H.	2	15	..	...	General line
Ohio						
Bellaire B. Co., Bellaire	M. and H.	2	20	..	...	General line
Chas. Boldt Co., Cincinnati	Owens A. M.	9	...	..	...	Liquor B. and F.; flint, green and amber
Butler B. Co., Butler	M. and H.	1	6	..	...	Milk, packers' and preservers' B.
Coshocton G. Co., Coshocton		2	25	..	...	Beer, water, liquor and packers' B., and F.
Eagle G. Co., Urbana		1	12	..	...	Line of B.
Essex G. Co., Mt. Vernon, O., and Parkersburg, W. Va.	M.	3	19	..	...	Milk B.
Federal G. Co., Columbus	M.	3	45	..	...	Packers' and preservers' B.; fruit jars
G. W. Kearns & Co., Zanesville		2	18	..	...	General line of B.
The Kearns-Gorsuch B. Co., Zanesville and Barnesville	M. and H.	3	27	..	...	Miscellaneous line: pickle, olive, condiment and liquor ware
Nivison Weiskopf Co., Reading	M. and H.	3	24	..	...	Packers', preservers', liquor and grape juice B.; F. and cigar jars
Owens B. Machine Co., Toledo, 2 factories and 1 at Fairmont, W. Va.	Owens A. M.	..	...	8	...	General line of B.
The Rhodes G. & B. Co., Massillon	12 O'Neill semi-A. M.	1 1 day tank	6 6	..	...	Beer B.
The Winslow G. Co., Columbus	M. and H.	2	14	..	...	General line
Oklahoma						
Oklahoma B. & G. Co., Blackwell	M. and H.	1	7	..	...	Packers', milk, water and liquor B., and F.
The Tulsa G. Co., Tulsa		1 and 1 day tank	8	..	...	Water B.
Pennsylvania						
Allentown Flint B. Co., Allentown		1	8	..	...	General line
Berney-Bond G. Co., Bradford; factories at Hazelhurst, Smethport and Clarion		4	32	..	...	General line of B.
Brockway Machine B. Co., Brockwayville	M.	1	10	..	...	Packers', preservers', ink, vaseline, blacking, glue and paste containers
Crescent B. Co., McDonald		..	...	1	12	Pharmaceutical and liquor B.
Cohansey G. Mfg. Co., E. Downingtown		3	30	..	...	Packers', preservers', beer and water B., and F.
D. O. Cunningham G. Co., Pittsburgh		4	24	..	...	Beer and mineral water B.
Diamond G. Co., Royersford		..	...	2	10	General line in special colors
Fidelity G. Co., Tarentum	M. and H.	2	19	..	...	General line
C. L. Flaccus G. Co.; office, Pittsburgh; factory, Tarentum	M. and H.	5	40	1	16	General line; opal ware
H. C. Fox & Sons, Inc., Philadelphia	M. and H.	1	14	3	28	General line
Glenshaw G. Co., Inc., Glenshaw	United M.; narrow and wide mouth	3	15	..	...	General line of flint, green and amber B.
Greensburg G. Co., Greensburg	M. and H.	2	16	..	...	Prescription B. and V.
J. T. & A. Hamilton, Pittsburgh and Butler	M. and H.	2	16	1	8	General line
Hawley G. Co., Hawley		2	14	..	...	Beer and mineral water B.
Hawthorn B. Co., Hawthorn		1	7	..	...	General line of B.
H. J. Heinz Co., Sharpsburg	A. M.	2 and 1 day tank	...	..	...	Packers' and preservers' B. and jars
Imperial G. Co., Charleroi	M. and H.	2	15	..	...	General line of B.
Jeannette G. Co., Jeannette	M. and H.	2	16	..	...	General line
Kane Flint B. Co., Kane		1	4	1	12	General line
Keystone B. Mfg. Co., Inc., Uniontown		2	8	..	...	Beer, water, and liquor B., and F.
Morris G. Co., Point Marion		1	8	..	...	Beer, water and liquor B., and F.
W. H. Newborn & Co., Royersford		1	12	..	...	General line
Puritan G. Co., Shinglehouse	M. and H.; 30 shops	2	...	..	...	General line
Roulette B. Mfg. Co., Roulette	M.	1	8	..	...	General line of B.
Sheffield G. B. Co., Sheffield		2	14	..	...	General line

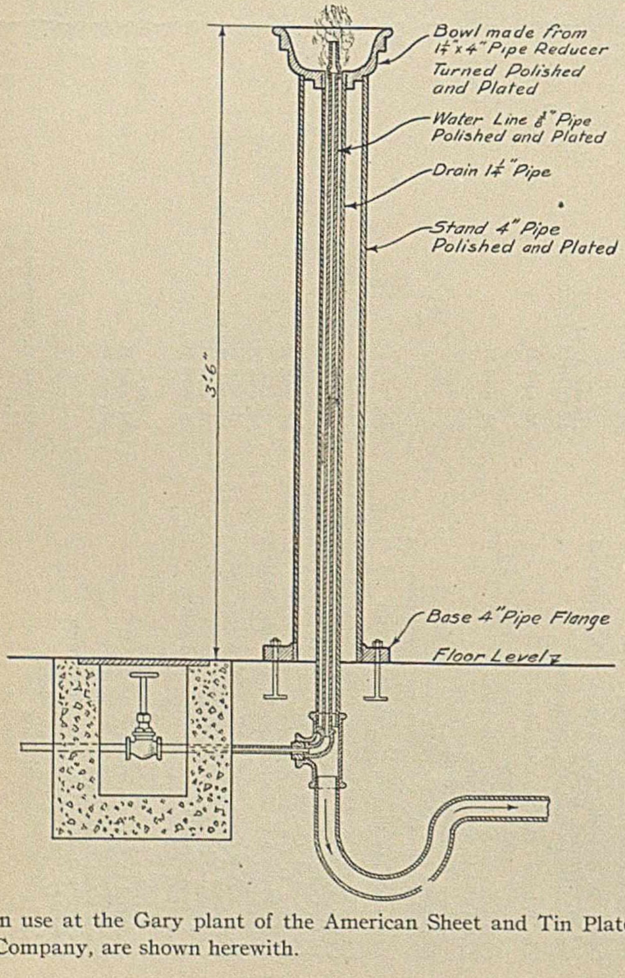
A LIST OF THE MANUFACTURERS OF GLASS BOTTLES AND HOLLOW WARE IN THE UNITED STATES—(*Concluded*)

Plants and location B., bottle; G., glass	Method A., automatic; H., hand; M., machine(s)	Continuous tanks	Rings	Furnaces	Pots	Products B., bottle(s); F., flask(s); V., vial(s)
Spring City G. Works, Ltd., Spring City		1	12	..	...	Prescription, beer and water B., and F.
Thatcher Mfg. Co., Kane, Pa.; Streator, Ill.; Elmira, N. Y.	Owens A. M.	6	...	..	...	Fruit jars and milk B.
Tibby Bros. G. Co., Sharpsburg		..	...	3	30	General line
Wightman G. Co., Parkers Landing		1	8	..	...	Prescription B. and V.
Wilcox G. B. Co., Wilcox		1	8	..	...	Prescription, beer, water, and liquor B., and F.
Wormser G. Co., Pittsburgh		2	12	..	...	General line of B. and jars
South Carolina						
Carolina G. Co., Columbia		1	9	..	...	Prescription and beer B., and F.
Laurens G. Works, Laurens		1	6	..	...	General line
Tennessee						
Chattanooga B. & G. Mfg. Co., Alton Park	M. and H.	3	17	..	...	General line
Texas						
Fort Worth G. Mfg. Co., Fort Worth		1	6	..	...	F.
Virginia						
Alexandria G. Works, Inc., Alexandria		1	9	..	...	General line
American G. Works, Inc., Richmond		1	10	..	...	General line of B.
Belle Pre B. Co., Alexandria	M.	1	8	..	...	Milk B.
Central States G. Co., Bridgeport		2	10	..	...	Prescription and liquor B., and F.
Old Dominion G. Co., Alexandria	M. and H.	2	12	..	...	General line of B.
Piedmont G. Co., Salem		1	6	..	...	Prescription B., fruit jars, F.
Virginia G. Co., Alexandria		1	8	..	...	Packers', preservers' and beer B., and F.
Washington						
Anacortes G. Co., Anacortes		1	4	..	...	Packers' and preservers' jars and B.
West Virginia						
Duquesne G. Co., Paden City		2	8	..	...	Beer and water B., etc.
Fairmont B. Co., Fairmont	M. and H.	1	8	..	...	General line of B.
Hazel-Atlas G. Co. (General offices, Wheeling); factories at Washington, Pa., and Clarksburg, W. Va.	M. and H.	16	...	..	...	Milk, packers' and preservers' B.; fruit jars
Kanawha G. Co., Cedar Grove	M. and H.	1	10	..	...	General line of B.
North Wheeling G. Co., Wheeling	M. and H.	2	12	..	...	General line of flint and amber B.
Owens Eastern B. Co., Clarksburg	6 Owens A. M.	..	...	3	...	Medicine B. and pharmaceutical ware
The Standard Milk B. Co., Parkersburg	Warner M.	1	8	..	...	Milk B.
Travis G. Co., Clarksburg	A. M.	2	20	..	...	Milk B. and jars
Tygart Valley G. Co., Grafton	M.	1	8	..	...	Packers' and preservers' ware, and fruit jars
Wisconsin						
Wm. Franzen and Son, Milwaukee	United M.	3	32	..	...	Beer and mineral water B.

[NOTE—We are indebted to Mr. George B. Kimes, of Pittsburgh, Pa., who courteously furnished much valuable information.—W. A. H.]

A SANITARY DRINKING FOUNTAIN

The details of a sanitary drinking fountain, 52 of which are in use at the Gary plant of the American Sheet and Tin Plate Company, are shown herewith.



THE SCORIA BRIQUETTING PROCESS

Methods that have been developed for efficient means of turning the wasteful expense of handling and recharging flue dust into a productive factory are fairly numerous. According to Ernest Stütz in the *American Institute of Mining Engineers*, the Scoria briquetting process has been in such successful operation for over two years on a daily capacity of 200 tons at the Rheinhausen works of the Friedrich Krupp A. G., that the installation has recently been doubled.

In this method a binder is used, but with the distinction that, between manufacture and use, the material so employed undergoes an essential transformation, being hydraulic until it passes into the furnace, and being there turned automatically into a fusion binder. The metallic oxides are thus free to react during their passage through the region of the top gases, and the binder gives the briquettes the necessary consistency to support the weight of the stock pile.

One briquetting press turns out from 1,800 to 2,000 briquettes per hour. Taking the weight per briquette at 8.8 pounds, this gives 144 to 160 tons per 20-hour working day, about 45,000 tons of briquettes per year.

In this process, granulated slag and lime are mixed with the valuable materials and made hydraulic in rotating drums where they are exposed to moderate-tension steam. When thoroughly mixed, sifted, and ground, the powdery mass is pressed into bricks, which are carried in train-loads of trolleys to cylindrical kilns, in which they are hardened by being exposed to the action of high-tension steam for from 8 to 10 hours. The train-load of hardened bricks goes straight from the kiln to the blast furnace and is there dumped, unless required for immediate use.

The manufacture is almost automatic. If the necessary amount of steam is provided for, there is nothing in the process itself that requires supervision. The transportation is practically all mechanical, the briquettes being handled only in transferring them from the press to the trolleys before hardening. The labor required for an installation of two presses consists of a foreman and fourteen men, including labor for steaming drums, grinding and conveying machinery, presses, hardening kilns, and trolley transportation. The plant operation requires nothing in the way of special experience, skill or supervision. Raw materials are always at hand and the success of briquetting is independent of special conditions of the flue dust.

In the Scoria process no air drying is necessary and this distinguishes it from all other briquetting processes. Savings in space and handling are also considerable factors in its economical advantages.

The hydraulic binder gives the body the necessary consistency at a minimum consumption of binding material, and, being in the nature of a hydrosilicate, leaves the oxides freely accessible to the top gases. It is not necessary in the case of the Scoria binder to have enormous pressure on one side of the briquette to produce an actual flow of gas through the structure. Also the temperature necessary for the destruction of the hydrosilicates is above that where sintering commences, so that there is no possibility of the briquettes crumbling away prematurely.

In practice, a very important coke economy will result from the use of the Scoria process. Working with a homogeneous and naturally piled stock column, gases can circulate and pass up under equal pressure, while combustion will be far more complete and the production of carbon monoxide will be lessened; it has been proved by actual operation in Germany that a saving of from 15 to 20 per cent of coke has been effected. The inventor of the process feels confident that it is quite possible to perfect operating conditions so as to produce one ton of iron per day for every cubic meter of blast-furnace volume.

The Scoria plant may be used to produce excellent slag building brick, and could alternate their manufacture with the production of flue-dust or fine ore briquettes at a moment's notice, the operations being almost identically the same, except that the flue dust or fine ore is left out of the mixture. Such bricks have shown ample strength for all purposes, not only under severe laboratory tests, but also in actual use for building purposes during a number of years.

Cost of production (not counting the slag as having a value) in Germany, on a two-press installation capable of furnishing 24,000,000 brick per year, is about $1.25 per thousand.

EXPOSURE TESTS OF COPPER, COMMERCIAL ALUMINIUM AND DURALUMIN

A paper on the above subject, read by Prof. E. Wilson, before the British Association at Birmingham, described a continuation of tests upon the influence of exposure in London on the electrical conductivity of light aluminum alloys, reports of which have been made from time to time. Each specimen is in the form of wire 0.126 in diam. and 70 feet long. After two years' exposure, the percentages increase of electrical resistance taken on the values in 1911 at 15° C. are as follows:

High conductivity copper	2.0
Commercial aluminum	4.4
Duralumin	8.2

Duralumin is a copper-manganese-magnesium alloy of high tensile strength and exposure has apparently made it more brittle.

ELECTROLYTIC COATING OF IRON AND STEEL WITH LEAD

According to *The Electrician* for September 26, 1913, an English company has acquired a process devised by Mr. Sherard Cowper-Coles for coating iron and steel with lead electrolytically. It is stated that lead can thus be economically deposited up to a thickness of one-eighth inch, and that the method is suitable for protecting iron and steel from corrosion, and for the lining of pipes, tubes and chemical vessels for containing corrosive liquors. Steel plates coated by this process are much smoother than the ordinary terne plate and there is no reduction in tensile strength or ductility. The process can also be used for the coating of earthenware and wood and for the protection of ornamental iron work. The cost is stated to be low.

TANNIC ACID FROM SPENT SULFITE LIQUOR

According to *Tidskrift for Papirindustri* as reported in *Paper* 13, No. 4, 23 (Oct. 8, 1913), Hans Lundmark, Drammen, Norway, has succeeded in reclaiming tannic acid suitable for tanning leather, from waste sulfite liquors. The acid ought, however, to be used only in admixture with some other material, as it is said the tanning process then takes less time. The tannic acid from waste sulfite liquor is said to be very cheap. Some important tanneries in England are now trying out this acid.

Mitscherlich and other chemists have, as is generally known, experimented considerably with the preparation of tanning material from the above source, but with indifferent success.

A NEW DESULFURIZING METHOD

The *Engineering and Mining Journal*, July 5, 1915, describes the Hall process of desulfurizing sulfide ores with eradication of noxious smelter fumes as entirely novel, being based upon the principle of removing the "fixed" sulfur atom of a sulfide by distillation, without permitting any considerable portion of the sulfur thus discharged to pass into any combined forms, such as SO_2 or SO_3.

The distillation of both fixed and free sulfur as such constitutes the advantage this method has over the other sulfur-recovery processes. Eliminating the sulfur as oxide with subsequent reduction means that a large amount of free oxygen must be taken care of before the sulfur reduction begins, thus requiring extra expense for reducing agents, while the fuel expense of removing oxygen combined with sulfur from such association is greater than the fuel expense of direct distillation.

Tests have been made to determine how complete a desulfurizing could be produced in this process; many analyses show less than 1 per cent of total sulfur remaining in the cinder. The distillation is obtained by the direct application to the ore of a burning gas flame of slightly reducing or, at least, non-oxidizing character, accompanied by H_2O, either in the shape of water of formation (from the combustion of hydrogen) or of extraneous water in the shape of steam which is decomposed by the hot ore. The nascent oxygen goes to the metal and the nascent hydrogen combines with any free oxygen that may enter the furnace by means of the atomizer through which the gases are admitted, thus creating a sort of cycle of H_2O decomposition and water formation from the combustion of the hydrogen so derived.

When the furnace burners are properly adjusted, the final discharge of hydrogen appears to be all in the shape of water vapor, *i. e.*, complete balances are easily maintained so that there is substantially neither SO_2, SO_3, COS nor H_2S in the discharge, tests being made on samples taken within a distance of six inches from the furnace.

A large variety of ores have been worked, including pyrites, various pyrrhotites, copper concentrates, crude blende and zinc concentrates. The action appears to be the same on each. In order to prove that the "fixed" atom is removed by distillation, the furnace has been operated on chemically pure FeS; no SO_2 or H_2S was discernible in the discharge, but only yellow elemental sulfur vapor.

The analyses of the cinder show it to be a mixture of Fe_2O_3 and Fe_3O_4. The temperature maintained in the furnace must be slightly above 700° C., as that is about the distilling point of the sulfur of a metallic sulfide, and it must be maintained below 900° C., the fusing point—a large margin of safety.

Although undoubtedly the reaction is somewhat exothermic, no allowance has been made for this in the fuel calculations, fuel required being calculated as if the reaction were entirely endothermic; on such a basis, allowing amply for radiation and for the largest factors of safety, numerous engineers have calculated the amount of coal fuel required (gasified) at less than 10 per cent of the weight of the ore.

The cost of producing sulfur by this method in American smelting works is placed at from $3 to $5 per ton of the crude sulfur derived.

The fumes coming from the smelter are of a heavy yellow appearance with the odor of hot elemental sulfur vapor. The sulfur is extracted from the fumes by simple washing, as it is found that it has great physical affinity for water, due, presumably, to surface tension: when the fumes are agitated with water, the atmosphere is almost instantly clarified, the sulfur settling to the bottom of the apparatus.

This sulfur has been analyzed several times and found to be from 98 to $99^1/_2$ per cent pure, the impurities being flue dust or lead or zinc sulfides. The refined sulfur has been found to be over $99^1/_2$ per cent soluble in CS_2, and is of the octahedral and prismatic types. The fumes have also been run through the Cottrell electrical dust collector, which completely precipitates the sulfur.

The process has been developed principally with a view to attaching it to multiple-hearth roasters, but promising experiments have been made towards its adaptation to blast furnaces.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—FORTY-EIGHTH MEETING, ROCHESTER, SEPTEMBER 8-12, 1913

DIVISION REPORTS

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

After the transaction of the usual routine business and the reading of the papers as presented in the program given in THIS JOURNAL, 5, 868, the following officials were unanimously elected for the ensuing year:

Chairman, Floyd W. Robison; *Vice-Chairman,* R. A. Harcourt; *Secretary,* Glen F. Mason; *Executive Committee,* A. V. H. Mory, L. M. Tolman, H. A. Huston.

G. F. MASON, *Secretary*

FERTILIZER CHEMISTRY DIVISION

The meeting was called to order by Mr. Paul Rudnick, Chairman. After the transaction of the usual routine business, the program was rendered as printed in THIS JOURNAL, 5, 868.

The Executive Committee was authorized to prepare a plan for the future handling of the analytical and research work of the division.

The following officers were elected for the ensuing year:

Chairman, J. E. Breckenridge; *Vice-Chairman,* E. L. Baker; *Secretary,* F. B. Carpenter; *Executive Committee,* Paul Rudnick, F. K. Cameron, C. H. Jones, H. J. Wheeler.

J. E. BRECKENRIDGE, *Secretary*

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

This Division met at Rochester University, with Mr. William Brady presiding.

After the transaction of the usual routine business, the financial condition of the division was reported as follows:

Money received	$234.62
Disbursements	39.00
Balance on hand	$195.62

A report was received on Alum Specifications from a subcommittee of the Committee on Standard Specification and Methods of Analysis. This report will be published later.

The following officers were then elected:

Chairman, George P. Adamson; *Vice-Chairman,* H. E. Howe; *Secretary,* S. H. Salisbury, Jr.; Officers, *ex-officio,* M. C. Whitaker, *ex-officio,* W. F. Hillebrand, C. H. Herty, C. A. Catlin, David Wesson, H. C. Porter.

Participants in discussions of the papers read were the following: Percy H. Walker, A. H. Sabin, Wm. H. Walker, Wm. Brady, N. A. Dubois, G. W. Gray, W. F. Hillebrand, W. A. Noyes, H. C. Porter, A. H. White, Dr. Smith, Mr. Dickinson, I. M. Bregowsky, G. A. Burrell, A. W. Browns, G. W. Gray, E. S. Merriam, and others.

On Friday morning, Dr. W. F. Hillebrand gave a talk on the Composition of the Bureau of Standards Sheet Brass which caused considerable discussion after which the division adjourned.

S. H. SALISBURY, JR., *Secretary*

RUBBER CHEMISTRY SECTION

After the transaction of the usual business, and the rendering of the program, reports were read by the Specification Committee, the Analytical Committee, and the General Rubber Consideration Committee. After discussion the above reports were approved.

The Analytical Committee was instructed to compile and present to the Executive Committee methods of procedure for determinations commonly made in rubber analyses. The Executive Committee was given power to act on such a procedure within its discretion.

The Executive Committee was instructed to appoint a committee to investigate and report with recommendations on the Physical Testing of Rubber and Compounds. This Committee was given power to act within its own discretion.

It was decided (1) to ask the members of the Rubber Section to contribute $1.00 each for the purpose of defraying the expenses of the Section: (2) to request the Council of the American Chemical Society to reappoint or retain in office the present officers of the Rubber Section.

After the reading of papers, a vote of thanks was extended to Mr. Savage for his excellently prepared paper on "Some Refinements of the Ignition Method for the Determination of Rubber in Vulcanized Goods."

DORRIS WHIPPLE, *Secretary*

COMMITTEE REPORTS—FERTILIZER CHEMISTRY DIVISION

COMMITTEE ON PHOSPHORIC ACID

This report is supplementary to the report of this Committee published in THIS JOURNAL, 3, 118. The latter showed that it was possible for the analyst to prepare an ammonium citrate solution which would give the same results as those obtained from a standard citrate prepared by Mr. Jones of this Committee. However, when a comparison was made with other analysts, the differences in some cases were quite large.

The Committee then endeavored to pick out those factors which would most likely influence the insoluble. That the time of filtering had evidently influenced some of the results was evidenced by the fact that the time varied from five minutes to two and one-half hours, this in a sample of complete goods. Another factor was the use of the volumetric method without checking against the gravimetric.

In order to eliminate these factors as far as possible, the following changes were made in the instructions:

(1) In case of complete goods; after insoluble has been placed on filter and flask washed, fold paper containing insoluble in half and transfer to another funnel.

(2) A standard sample in which the Committee had determined the total phosphoric acid was sent with the other samples.

With these exceptions the instructions were the same as those published in THIS JOURNAL, 3, 118.

RESULTS OBTAINED BY THE PHOSPHORIC ACID COMMITTEE OF THE A. C. S. ON THE STANDARD SAMPLE

All Determinations were Made by the Official Gravimetric Method

Analyst	Total P_2O_5	Average
W. J. Jones	3.85 (a)	..
	3.88	3.87
	3.95(b)	3.94
	3.92	
F. D. Fuller	3.90(a)	..
	3.90	
	3.86	3.89
G. Farnham	3.86(b)	..
	3.92	..
	3.86	..
	3.89	3.88
J. Q. Burton	4.00	..
	3.97	3.99
Maximum	..	4.00
Minimum	..	3.86
Average	..	3.91

(a) Sol. made with $H_2SO_4 + HgO$.
(b) Sol. made with $3\ HCl + 1\ HNO_3$.

RESULTS BY OTHER ANALYSTS

Volumetric Method Used throughout unless Otherwise Stated

Sample Analyst	Insoluble P_2O_5 1 Acid phosphate	Insoluble P_2O_5 2 Complete	Total P_2O_5 3 Standard	Time for filtering and washing Minutes 1	Time for filtering and washing Minutes 2
1	0.55	3.15	3.89 (g)	...	..
	0.50	3.10	3.86	2	2
	0.55	3.28	..	...	..
	0.50 (a)	2.98 (a)	..	...	..
	0.50	3.10	..	2	2
	0.48	3.05	..	...	..
2	0.67	3.63	3.89 (e)	...	..
	0.67	3.62	3.91	20	40
	..	3.64	3.89	...	..
3	1.12(i)	1.54(i)	3.86(g)	...	..
4	0.60	3.90	3.93	20	28
5	0.51	3.42 (g)	..	2	4
	0.54	3.62	..	...	..
	0.55	3.52(c)	..	...	5(c)
	0.55	3.54	..	...	..
	..	3.42	..	...	..
6	0.59	3.33 (g)	..	3	3
	0.52	3.40	..	...	..
	0.56	3.33	..	...	..
7	0.57	2.94 (g)	..	...	..
	0.57	2.88	..	...	..
8	0.32	3.02	4.02	...	..
	0.37	3.22	4.05	12–15	30
	0.37 (b)	3.00 (b)	3.97	...	..
	0.35	3.00	..	...	..
9	0.66	3.92	..	...	..
10	0.81	2.68(i)	..	2	5
11	0.48	2.94	4.04	...	..
	0.49	2.95	4.01	15	20
	0.51	2.88	4.00	...	..
	0.49 (b)	3.08 (b)	3.92 (eg)	...	..
	0.51	3.19	3.98	...	..
	0.48	3.20	3.94 (fg)	...	..
	..	..	3.85	...	..
	..	..	4.29 (hg)	...	..
	..	..	4.23	...	..
SUMMARY OF AVERAGES OF INDIVIDUAL ANALYSTS					
Maximum	0.81	3.92	..	...	..
Minimum	0.37	2.91	..	...	..
Average	0.58	3.39	..	...	..

(a) Citrate sol. prepared by method in THIS JOURNAL, 1, 618. Sol. contained 186.3 grams citric acid per liter. Committee method citrate contained 197.4 grams citric acid per liter.

(b) Filtered on funnel with platinum cone.

(c) Filtered and washed without transference.

(e) Silica not removed; allowed to stand two hours in ice water.

(f) Silica removed by dehydration; stood at room temperature over night.

(g) Gravimetric method.

(h) Silica not removed; stood over night at room temperature.

(i) Not included in average.

The variation in the results on acid phosphate is almost exactly the same as that of the previous year. In the case of complete goods the variation has been lowered from one and a quarter to one per cent.

The length of time of filtration has been very materially cut down; some analysts say, however, they can see no advantage that the Hirsch or Buchner funnel has over the glass funnel with platinum cone, providing care is taken not to transfer any of the insoluble matter onto the filter until several washings with hot water have been effected.

The Committee thinks that this work should be continued along these lines with the hope that a suitable method may be worked up which will give more concordant results.

COMMITTEE ON PHOSPHORIC ACID
J. Q. BURTON
W. J. JONES
J. R. POWELL
G. FARNHAM, *Chairman*

COMMITTEE ON PHOSPHATE ROCK

The Committee on Phosphate Rock continued their investigations during the past year. Three sub-committees were appointed to take charge of the different determinations—moisture, iron and alumina and phosphoric acid. The only report received, however, was from the sub-committee on phosphoric acid. A brief abstract of this report is as follows: "The work of the sub-committee on phosphoric acid for 1913, was done by members of the committee and a few other analysts on a sample prepared by mixing together four different kinds of phosphate rock including Tennessee brown and blue, South Carolina and Florida rock. The sample was prepared by mixing the finely ground individual samples, each of which had been previously passed through a 100-mesh sieve. The samples, with instructions, were sent out to eleven analysts, and reports were received from seven, including results in two case from two analysts each, some of the members of the committee and some of the other analysts referred to being unable to find time for this work. The results received varied so widely that your committee considers it inadvisable to average them. As the results began to come in it seemed probable that the wide variations showing up might possibly be laid to the difference among the samples themselves rather than to differences between the analysts. An investigation made with two remaining samples seemed to bear this out, and your committee inclines to the opinion that the sample sent out was not suitable for this work, and that the same work should be repeated on a sample made up of only one type of rock, and that this point be carefully observed in the making up of any future samples. Aside from this point, there is no definite tendency apparent either in the direction of abnormal results by any one of the methods tried by all of the analysts or by any one of the analysts in all of the methods tried."

The announcement published in the *Industrial Journal* in the early part of the year of a tentative standard of phosphate rock having been adopted by the committee, has resulted in a surprising number of requests. Nearly all of the laboratories interested in the fertilizer work in this country as well as in some other countries have been supplied with this sample.

COMMITTEE ON PHOSPHATE ROCK
W. D. RICHARDSON
S. W. WILEY
C. F. HAGEDORN
W. P. HEATH
F. B. CARPENTER, *Chairman*

COMMITTEE ON FERTILIZER LEGISLATION

Your committee have, during the past year, endeavored to keep up with the new legislation in the various states and used their influence as far as possible to prevent unwise or unjust enactments, but as to bringing about a uniformity of laws they have been able to accomplish very little; in fact there is less uniformity at the present time than there was a few years ago. In this connection I have considered it desirable to review briefly some of the efforts which have been made towards bringing about uniform laws in the different states.

As far as I can learn from the records, the first fertilizer law in this country worth considering was enacted by the Massachusetts Legislature in 1869; this proved inadequate for the reason that there was no provision for its execution and was amended in 1873, in which form it remained for a number of years. This served as a model for other states and we find in the early laws a striking similarity to the Massachusetts law. In the subsequent years additions and changes have been made so that at the present time the laws in the different states are far from uniform. This lack of uniformity does not lie so much in the general principles of the law, but rather in the elaboration of these principles and the mode of expressing the details.

The Association of Official Agricultural Chemists, recognizing the disadvantages of having the laws unlike in different states, not only from the standpoint of inspection and analysis but also on account of the hardships imposed on the manufacturers, appointed a committee "on uniform methods of fertilizer control." A like committee was also appointed by the "Association of American Agricultural Colleges and Experiment Stations." These committees did a considerable amount of work on the subject and finally after consulting with manufacturers drew up a statement of principles which was quite satisfactory to all parties concerned and made a report to the Association of Official Agricultural Chemists at their Annual Meeting in 1897. This committee was continued as a standing committee, taking up different phases of fertilizer laws, including questions relating to national legislation, reporting annually to the association.

In 1909, the committee presented to the Association, for their endorsement, a proposed form of National Fertilizer law. This, however, did not meet with their approval, it appearing that there was no necessity for such a law as the different states were prepared to attend to the inspection work in a satisfactory manner. On a motion of the chairman the committee was discharged and since that time there has been no Committee on Fertilizer Legislation either in the Association of Official Agricultural Chemists or the Association of American Agricultural Colleges and Experiment Stations.

At the organization of the Fertilizer Division of the American Chemical Society a Committee on Fertilizer Legislation was appointed, which has used its influence against the passage of unwise and unjust laws, but has been unable to accomplish much along the lines of uniform fertilizer legislation. The National Fertilizer Association maintains a legislative committee and points out in their last report the futility of hoping for the adoption of a uniform fertilizer law by the various states as illustrated by the fact that not a single state has taken the law proposed by the Association of Official Agricultural Chemists as a basis of revision.

The most that has been accomplished along the line of uniformity was effected when, about fifteen years ago, some ten of the southern states practically agreed on a uniform law, which was framed by the state chemists and Commissioners of Agriculture in an Association known as the Cotton States Association of Commissioners of Agriculture. Since this time, however, these states have so modified and amended their laws that there is, at the present time, no more uniformity than in other parts of the country.

From the efforts which have been made and the results attained it would appear that there is little hope of ever having a uniform fertilizer law which will be effective in the different states. The question of federal legislation has been suggested as a means of bringing the individual states in line, it being argued that if a model law were passed by Congress there would be little difficulty in having this enacted by the different states. If this could be effected there is no doubt that manufacturers would favor federal legislation, but there are so many obstacles to be overcome and so much doubt of ultimate success that they prefer to let the matter stand as it is rather than to take chances in having additional complications in the already complex system of legal requirements, which applies especially to those who do an interstate business.

Notwithstanding the fact that there appears to be no hope of uniform laws there is no doubt that the various committees and organizations, which have been referred to, have done much to bring about reasonable legislation as well as to maintain some points in common in different state laws. It is to be regretted that any of these committees have been discharged, especially that of the Association of Official Agricultural Chemists, and I hope at their next meeting a standing committee may be appointed to direct our law-makers when a change in the state laws is contemplated. Many fertilizer bills which are presented to the legislatures are drawn by parties who have no knowledge of the fertilizer business or the necessary requirements to safeguard the interests either of the manufacturer or consumer. Often these bills are prompted by some personal grievance and if enacted would work hardships on both manufacturer and consumer. It is important, therefore, for those who are interested in fair and impartial legislation and in enactment of uniform laws to work together in an effort to bring about the desired results. Our laws are enacted for the protection of both producer and consumer and it is the duty of our agricultural departments to use their influence, as far as possible, in behalf of fair and impartial legislation.

While it may appear that our committee and the other committees, which have been mentioned, have accomplished little in bringing about uniformity, under the existing conditions, it is only through organized effort that anything can be accomplished and I am not only strongly in favor of maintaining a standing committee in our division, but also of urging the appointment of similar committees in the organizations interested in the welfare of the fertilizer manufacturing and agricultural industries.

F. B. Carpenter, *Chairman*

AMERICAN CHEMICAL JOURNAL TO BE COMBINED WITH THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

The Directors of the American Chemical Society have entered into an agreement with Dr. Ira Remsen, Editor of the *American Chemical Journal*, whereby, at the completion of its fiftieth volume, the *American Chemical Journal* will be discontinued as a separate publication and will be incorporated from January, 1914, with the *Journal of the American Chemical Society*.

AMERICAN PETROLEUM SOCIETY

The American Petroleum Society was organized September 10th, at the Experiment Station of the U. S. Bureau of Mines, Pittsburgh, Pa. This organization is the result of an effort of the Bureau for the past seven years to bring together the men interested in the petroleum industry.

Invitations were sent out in July to the secretaries of twenty-four of the great National Societies of the United States, inviting them to be present and coöperate in this organization. Eighteen of these societies responded at a meeting on August 1st at the Bureau of Mines. A similar invitation was sent out in August to eight additional societies, making a total of thirty-two societies that were invited to attend the September conference. A large number of these were represented when the final organization was completed.

This society will concern itself with the study of all phases of natural gases and petroleum, including the origin, statistics, conservation, drilling methods, production, transportation, storage, refining and specifications for refined products.

When it is considered that each year, within the United States alone, there is produced crude petroleum and natural gases having a value in excess of $200,000,000, it is reasonable to suppose that the future of this society is assured. There is to-day a tremendous waste of natural gases which, by proper methods of drilling, could be prevented. Also there is a great waste of crude oil itself by improper methods of production, since in the fields producing paraffin oils the paraffin is allowed to congeal around the well, sealing in the oil strata and thus preventing the recovery of the oil. The necessity for a critical study of petroleum and gas production and conservation is evident.

At the meeting on September 10th at the Bureau of Mines the constitution and by-laws were adopted, and officers were elected as follows:

President, C. D. Chamberlain, National Petroleum Association, Cleveland, O.

Vice-President, R. Galbreath, Independent Oil and Gas Producers Association of Oklahoma, Tulsa, Okla.

Secretary, Irving C. Allen, U. S. Bureau of Mines, Pittsburgh, Pa.

Treasurer, Warren C. Platt, Independent Petroleum Marketers' Association, Cleveland, O.

Acting Past President, Frank B. Fretter, Western Petroleum Refiners' Association, Coffeyville, Kan.

Executive Committee

Ralph Arnold, Los Angeles, Cal.
C. F. Clarkson, Soc. Automobile Eng., N. Y.
G. M. Swindell, Chamber of Mines and Oil, Los Angeles, Cal.
Edmund O'Neill, Univ. of Cal., Berkeley Cal.
E. B. Rich, Gasoline Producers' Assoc., Parkersburg, W. Va.
Geo. H. Taber, Gulf Refining Co., Pittsburgh.

The first annual meeting will probably take place in the spring of 1914, and the second annual meeting will be held at the Panama Pacific Universal Exposition in San Francisco in 1915. At the 1915 meeting it is hoped that all the petroleum societies in the country will meet in one great congress where many things of interest and of value will be presented.

An official invitation has been sent from the president of the Exposition at San Francisco to the president of the International Petroleum Commission, which convenes in January, 1914, in Bucharest, Roumania, to hold its annual meeting for 1915 in San Francisco. Plans are already being formulated for this great 1915 meeting, which will be part of the great assembly of the petroleum industries of America, where the foremost petroleum technologists and scientists of the world will congregate.

OBITUARY—JULIUS LEWKOWITSCH

Dr. Julius Lewkowitsch, consulting and analytical chemist and chemical engineer, of London, England, died September 16th at Chamonix, Switzerland, after only a brief illness. Dr. Lewkowitsch was born at Ostrovo, Prussian Silesia, in 1857.

After a brilliant university career at Breslau, he graduated as Doctor of Philosophy. He carried out a considerable quantity of original investigation under Professor Victor von Richter at Breslau. Afterwards he took a position under Professor Hans Landolt in the Chemical Laboratory of the Berlin Agricultural High School, and later was assistant to Professor Victor von Meyer in the University of Heidelberg. During these early years he published much original experimental work on stereochemistry, which was at that time a new and undeveloped subject.

Dr. Lewkowitsch went to England about 25 years ago and, becoming naturalized, took up the study of the industrial technology of fats and oils. By assiduous labor he achieved the position of one of the foremost authorities on vegetable and animal fats and oils. A large number of processes which are widely employed in the utilization and valuation of these important raw materials were devised by him, and his writings on these subjects are regarded as standard works of reference. He also won a considerable reputation as a chemical engineer, while his linguistic attainments were truly remarkable, for he could converse fluently on scientific subjects in most current European languages. These gifts were placed unstintingly at the service of the various scientific societies to which he belonged.

Dr. Lewkowitsch was a fellow and a past member of the Council of both the London Chemical Society and the Institute of Chemistry, and a past member of the Council of the Society of Public Analysts. He was a vice-president and at the time of his decease honorary foreign secretary of the Society of Chemical Industry. He had acted with conspicuous success as chairman of the London Section of this Society and was one of the most active members of the Society's Publication Committee.

He published numerous papers (over 120) on oils, fats and waxes during the last thirty years. His "Chemical Technology and Analysis of Oils, Fats, and Waxes" has passed through four editions as well as appearing in German and French. The first volume of the fifth edition was published on Sept. 4, 1913, and the remaining volumes are now in the press. He also wrote a "Laboratory Companion to Fats and Oils Industries" (English edition, 1901, German edition, 1902), the article "Oils and Fats" in "British Encyclopaedia," and articles on various oils, and fats in Thorpe's "Dictionary of Applied Chemistry."

Dr. Lewkowitsch found his chief recreation in mountaineering, being particularly attached to the Swiss Alps among which he died. He was married in 1902, and is survived by his widow, a son and a daughter.

NOTES AND CORRESPONDENCE

ON THE INFLUENCE OF THE RATIO OF LIME TO MAGNESIA ON PLANTS

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, **5**, 564, a second article by P. L. Gile and C. N. Ageton appeared concerning the lime-factor, but no convincing evidence was brought forward to show that my objections (This Journal, **5**, 257) to their first article would not be tenable. In New York, last October, I received full information about the calcareous soils near Ponce from Mr. Ried, former auditor of the Guanica Co. in Porto Rico. He stated that these soils must receive a very heavy dressing of pen manure in order to produce a moderate harvest of cane. Also the proprietor of the Mercedita Cane plantation near Ponce stated to me, on inquiry by letter, that his cane soil receives heavy doses of pen manure. Pen manure, however, is relatively rich in lime and magnesia.

As regards the pineapple plant, it is a lime-loving plant in Florida, but even if it would not be so in other countries this plant can precipitate the excess of lime absorbed abundantly as oxalate. I would like to know those gramineae which can accomplish that in the same measure as pineapple or citrus. I have never stated that soils with a very unfavorable ratio of lime to magnesia should be corrected to the standard ratio, but I have repeatedly pointed out that such soils should be improved by adding one or the other as the case may demand, as far as practicable. See *Landw. Jahrbücher*, **1910**, 1008.

I have further never stated that the lime-magnesia ratio in the soil would also be found in every part of the plant. It is a well established fact that seeds show a ratio of mineral nutrients quite different from that of leaves. In seeds, the amount of magnesia exceeds that of lime while in leaves just the reverse condition is observed. On such determinations see also a communication of mine in the *Landw. Jahrbücher*, 1912, 186.

For the general information of the reader I may be allowed to add the "General Conclusions" to which *Dr. Augustus Völcker*, of the Woburn Experiment Station, near London, has arrived in several years' study on the question of the lime factor. In his recent report on his experiments to the Royal Agricultural Society of England (London, John Murray, Albemarle Street, W. 1913) his conclusions are:

1. That magnesia may, with advantage to the wheat plant, be added to a soil poor in magnesia, so long as the amount of magnesia in the soil does not exceed that of lime.
2. That, as the ratio of lime to magnesia approaches 1 : 1 a benefit will continue to accrue, but that if magnesia be in excess, a toxic influence will be exercised and the crop be diminished.
3. The soils in which magnesia is in excess of lime will not give fully satisfactory results as regards corn growing, but will be benefited by the addition of lime.
4. That lime used in excess does not possess the toxic influence which magnesia, similarly used, has.

These conclusions agree perfectly with those of my co-workers and myself, of *Bernardini* and his co-workers, *Warthiadi*, *Portheim* and *Samec*, and *Hansteen*.

Oscar Loew

Hygienic Institute, Munich, Germany
September 8, 1913

NOTE ON DETERMINATION OF FAT IN ICE CREAM

Editor of the Journal of Industrial and Engineering Chemistry:

In This Journal, 5, 786, there appears a rapid method for the determination of fat in ice cream, by Mr. H. F. Lichtenberg.

The method appears to be practically the same as one developed by Prof. H. E. Ross, of the Department of Dairy Industry, of the New York State Department of Agriculture, at Cornell University, and published in the *New York Produce Review and American Creamery*, December 28, 1910, and republished by the same paper in a recent issue, the only special difference in the two methods being that Mr. Lichtenberg uses a little more acetic acid and a little less sulfuric acid than originally advised by Prof. Ross. According to the date of publication, it appears that Prof. Ross first developed the method.

Hugh C. Troy

N. Y. State College of Agriculture
Cornell University, Ithaca
September 24, 1913

DESIGN OF SURFACE COMBUSTION APPLIANCES—CORRECTION.

In my article printed under the above title, This Journal, 5, 801, the section "That this statement" (bottom of p. 824) to the end of the paragraph should be omitted, and the following discussion substituted for it:

"That this statement is justified is indicated by the following, assuming the inefficient fan and motor that costs 0.9 cent per hour to operate is replaced by a better set, more suitable in size and design. If the service of a standard 15 cubic foot Bunsen top burner is equal to a 10 foot surface combustion burner (ratio 1.5) the gas saving is 5 cubic feet per hour, which is worth $5 \div 1000/100 = 0.5$ cent per hour. If the range had four top burners, one jumbo and two broiler oven burners, and the ratio 1.5 applied to the whole consumption, then for the Bunsen range the hourly gas would be $(3 \times 15) + (3 \times 20) = 105$ cubic feet, against $(3 \times 10) + (3 \times 13.3) = 70$ cubic feet for the surface. For this gas the latter would require $6 \times 70/60 = 7$ cubic feet per minute at 4 inches water pressure. This corresponds to an air horse power of $4 \times 5.2 \times 7/33000 = 0.0044$. With a fan efficiency of 50 per cent the motor horse power is $0.0044/0.5 = 0.0088$, and for 75 per cent motor efficiency the electrical horse-power input is $0.0088/0.75 = 0.0117$. This is equivalent to $0.0117 \times 746 = 8.76$ watts which at 10 cents per 1000 is worth 0.0876 cent. Thus the electric cost for the whole range is only 0.0876 cent per hour while one top burner saves in gas 0.5 cent per hour. This shows how conservative is the general estimate above, that the gas saving at one burner will more than defray the expense for current for the entire range, for under the conditions named the gas saving at one burner is five times the cost of current for all of them. The vacuum cleaner fan used on the first range consumed ten times the current that was really necessary, yet even so, two top burners save enough gas to pay for all the current."

Charles Edward Lucke

October 20, 1913

NOTE ON QUANTITATIVE DETERMINATION OF ROSIN IN PAPER

Editor of the Journal of Industrial and Engineering Chemistry:

I have read with much satisfaction Mr. C. Frank Sammet's paper on "Quantitative Determination of Rosin in Paper," This Journal, 5, 732.

In order to extract all the rosin present, it is necessary to set free all the combined rosin, a part of which is in combination with the basic cellulose hydrate and a larger part with the base of the alum used.

Instead of using an acidified mixture of alcohol and ether of about 83 per cent which will partially dissolve out on extraction any substances soluble in water, from which the rosin must later be separated by evaporation and extraction with ether, as Mr. Sammet proposes, I prefer to cut the paper for test into strips and wet them out in a very weak solution of hydrochloric or acetic acid. I then air-dry them and place in Soxhlets and extract with absolute alcohol, when the extract may be evaporated and weighed. The extract will be free from water-soluble impurities and give very satisfactory results. Alcohol is the normal solvent for rosin and I prefer it to ether for this work. My suggestion shortens the process and is equally accurate.

Martin L. Griffin

Rumford, Maine
September 24, 1913

PLATINUM PRODUCTION INCREASES

While the high price of platinum in the United States in 1912 encouraged prospecting for this rare metal, the production in that year was but slightly larger than that of the preceding year. According to David T. Day, of the United States Geological Survey, in an advance chapter from Mineral Resources for 1912 on the production of platinum and allied metals, the output of crude platinum in 1912 was 721 ounces, compared to 628 ounces in 1911. With the exception of a small yield from the New Rambler copper mines, in Albany County, Wyo., the entire domestic production came from California and Oregon. The greater part of the California platinum was obtained as a by-product in gold dredging in Butte, Yuba, Sacramento, and Calaveras counties.

The United States supply comes chiefly from the unmanufactured and manufactured platinum imported indirectly from Russia. In addition, 45,280 ounces of platinum sand were imported into the United States in 1912 which, by the usual estimate of 80 per cent fine metal, would yield 36,224 ounces of refined platinum. In all, the refined platinum produced in domestic refineries from both domestic and foreign sources amounted to approximately 38,029 fine ounces, valued at $1,732,221, compared with 29,140 fine ounces similarly obtained in 1911. The total value of our platinum importations in 1912—both raw material and manufactured products—was $4,503,682 against $4,866,207 in 1911.

BOOK REVIEWS

Electro-Plating and Analysis of Solutions. By HERMAN H. REAMA. 12mo., 101 pp. The Metal Industry Print, New York. Price, $5.00.

This book is evidently intended by an electro-plater as a help to others in the same line of business.

Science does not enter into the make of it to any great extent which is unfortunately the case with many other books on the same subject. In the actual description of plating operations such as nickel or copper, the author gives the composition of the baths and leaves the reader to find out elsewhere how to use them, no mention being made of current density, time of plating, or character of the metal deposit with which he is working.

The author's statements often leave much to be desired in the way of clearness as the following passage on conductors, page 2, shows: "It has been stated by competent and qualified people that using bus-bars of the type shown in Fig. 1 (rectangular) will give better service than the ordinary round bar. This is strictly a matter of opinion and is still up to the man in charge or in ownership of the said factory or shop. As heretofore stated, many means of operating can be and are used at the present writing, and it is quite difficult to meet all requirements and all classes of trade and still meet the approval of the majority. Nevertheless, facts are facts, and the above are true."

In the analyses of solutions we find that sulfuric acid is determined in an acid copper sulfate solution by titration with standard alkali, using methyl orange as indicator.

The book is illustrated by cuts from catalogues of various apparatus used in electro-plating establishments with no explanations of their use.

The price of $5.00 is charged for this book of which there are 101 pages in all, with very little to the page; in fact it is rather absurd to call it a book at all, and it seems to us as if 30 cents would be a high price to pay for it.

SAMUEL A. TUCKER

General Index to the Chemical News, Vols. 1 to 100 (1860–1909). Pp. viii + 712. Price, $10. Chemical News Office, 16 Newcastle Street, Farringdon Street, London, E. C.

This index covers all material in the issues of *Chemical News* for the first fifty years and should be of inestimable value to every working chemist, whether a subscriber to *Chemical News* or not. The plan of the index, as explained in the preface, is comprehensive yet quite simple and examination shows that, indeed, "every effort has been made to enable readers to find quickly and easily any subjects which have appeared." It is to be hoped that the immense amount of labor involved in the preparation of this reference volume will be appreciated by those for whose benefit it has been prepared.

LEOLA E. MARRS

Calcium Cyanamid. By E. J. PRANKE. Price, $1.25. The Chemical Publishing Co., Easton, Pa.

There can be no doubt that the use of artificially prepared "fertilizers" for the management of soils and control of crop production is rapidly increasing and must continue to increase. It is also apparent that to maintain an adequate supply of nitrogen carriers, "fixation" of atmospheric nitrogen is a quickly coming necessity. This condition is the main stimulus to pronounced activity in research and invention which is bringing to light various processes or suggestions of immense interest and importance to the scientific and technical world alike. It is not yet possible to predict with any great assurance or conviction what processes are ultimately going to survive the test of experience. So far, the production of calcium cyanamide probably outranks commercially all the nitrogen fixation processes yet tried. Over a dozen factories abroad are now producing the material and at Niagara Falls there is an important plant whose annual capacity has recently been raised from 25,000 to 50,000 tons. Calcium cyanamide has, moreover, other possible commercial uses than as a fertilizer.

The adoption of this material as a fertilizer by the manufacturer and farming public has on the whole been rapid, and its place is now assured, pending the possible introduction of a satisfactory nitrogen carrier more cheaply prepared. But its present position has not been won without a struggle, with attendant controversies, sometimes acrimonious, which have had good fruit as well as bad, however, in stimulating study and investigation so that now a fairly large body of information exists regarding the chemistry of the substance.

In the volume before us, Mr. Pranke has brought together the main facts that have been established in a systematic arrangement. His attitude toward the value of this material as a fertilizer in comparison with nitrates and ammonium salts impresses the reader as being decidedly biased in spite of an evident effort to maintain a judicial attitude. Nevertheless, he has produced a very interesting and readable book, and a very valuable one, in which even the expert and specialist will probably find new material. The proof-reading seems to have been carelessly done in some parts of the book.

The meagreness of detail in describing the actual technique of manufacture is a disappointment, justified only by the well-known but mistaken policy of manufacturers in maintaining secrecy regarding their factory practice. And to the reviewer the discussion of the effect of soil zeolites and colloids appears unsatisfactory and unconvincing. The very doubtful assumptions as to the presence and the particular properties of these hypothetical substances are not necessary to explain the phenomena of surface action in soils, and invoking their aid, a common practice these days among soil chemists in difficulties, merely makes against clear thinking.

FRANK K. CAMERON

The American Fertilizer Handbook. 1913 Ed. 356 pp. Price, $1.00. Ware Bros. Company, 1010 Arch Street, Philadelphia.

It would be difficult to estimate the service rendered to those interested in fertilizers by these annual handbooks. This particular issue contains four noticeable sections:

(1) A very comprehensive advertising section, consisting of a classified directory of the allied fertilizer trades including manufacturers of fertilizer machinery and factory equipment; manufacturers of and dealers in fertilizer materials and supplies; brokers, importers and exporters, chemists, phosphate miners, sulfuric acid plants, etc.

(2) Directories of the cottonseed oil mills and of the fertilizer manufacturers of the U. S.—arranged by states.

(3) Valuable tables, such as sulfuric acid and fertilizer formulae tables; a list of agricultural experiment stations; an annual review of the fertilizer materials market, etc.

(4) A series of interesting and instructive articles on special topics, prepared by experts especially for this volume. These include: "Fertilizer Materials in the U. S.," Frank K. Cameron; "The Year's Progress in the Fixation of Atmospheric Nitrogen," T. C. Pinkerton; "Middle West Soil Improvement Committee," H. G. Bell; "The Menhaden Industry," J. W. Turrentine; "Some Analyses of Fish Scrap," J. R. Lindemuth and E. G. Parker; "Sampling of Fertilizers," J. S. Brogdon; "The Sulfuric Acid Industry," A. M. Fairlie; "Fertilizers for Hay and Pastures," E. B. Voorhees; "Cyanamid," E. J. Pranke; "Definitions of Fertilizer Materials," T. C. Pinkerton; "The Chicago Ammoniate Market," J. B. Sardy; "On Tennessee Phosphate Mining Practice," L. P. Brown; "Florida Phosphate Rock—1912," E. H. Sellards; "Production of Phosphate Rock in 1911," F. B. Van Horn.

LEOLA E. MARRS

NEW PUBLICATIONS

By D. D. Berolzheimer, Librarian The Chemists' Club, New York

Alumina, The Manufacture of. By A. Berge. 8vo. 70 pp. Price, $0.75. M. Knapp, Halle. (German.)

Analysis, Laboratory Manual of Testing Materials. By William K. Hatt and Herbert H. Scofield. 8vo. 130 pp. Price, $1.25. McGraw-Hill Book Co., New York.

Analysis, Qualitative Chemical. By Wilfred Welday Scott. 8vo. 167 pp. Price, $1.50. D. Van Nostrand, New York.

Analysis, Technical Gas and Fuel. By Alfred H. White. 8vo. 276 pp. Price, $2.00. McGraw-Hill Book Co., New York.

Arsenic Compounds, Organic, Handbook of the. By A. Bertheim. L. 8vo. 238 pp. Price, $2.00. F. Enke, Stuttgart. (German.)

Asphalts, Natural Rock, and Bitumens. By A. Danley. 8vo. Price, $2.50. D. Van Nostrand Co., New York.

Celluloses, Production of, for Paper Manufacture other than those from Wood. By Henrv de Montessus de Ballore. 8vo. 294 pp. Price, $2.50. Bernard Tignol, Paris.

Cement, Portland, its Manufacture, Testing and Use. By D. and B. Butler. 3rd edition. 8vo. 470 pp. Price, $4.00. Spon & Chamberlain, London.

Chemistry, A New Era in. By Harry C. Jones. 8vo. 326 pp. Price, $2.00. D. Van Nostrand Co., New York.

Chemistry, Textbook of. By William A. Noyes. L. 12mo. 602 pp. Price, $2.25. Henry Holt & Co., New York.

Chemistry, The Theories of. By Edgar F. Smith. 8vo. 188 pp. Price, $1.15. John C. Winston Co., Philadelphia.

Color Chemistry, Textbook of. Vol. I. By E. Grandmougin. 4th edition. 8vo. Price, $3.75. F. Deuticke, Vienna. (German.)

Coal Tar Dyes and Allied Industries, Progress in the Manufacture of. Part X. 1910-1912. By P. Friedländer. L. 8vo. 1422 pp. Price, $18.75. Julius Springer, Berlin. (German.)

Dyestuffs, Synthetic, and the Intermediate Products from which they are Derived. By John C. Cain and J. F. Thorpe. 2nd edition. 8vo. 440 pp. Price, $5.00. London.

Electrochemistry, Elements of. By Edgar F. Smith. 8vo. 200 pp. Price, $0.90. John C. Winston Co., Philadelphia.

Encyclopedia, New, of Scientific, Technical and Industrial Chemistry. Vol. II. By I. Guareschi. 4°. 1116 pp. Price, $6.00. Umiore Tip.-Ed. Torinese, Turin. (Italian.)

Fats, Animal, and Butters. By Albert Brum. 8vo. Price, $1.25. Ch. Beranger, Paris. (French.)

Food, Text-book on the Chemistry of. Vol. II. H. Roettger. 4th edition. 8vo. Price, $4.00. Johann Ambrosius Barth, Leipzig. (German.)

Gases, The Influence of Inert, on Inflammable Gaseous Mixtures. By J. K. Clement. 8vo. 24 pp. U. S. Bureau of Mines, Technical Paper 43.

Iron Ores, The Titaniferous, in the United States, their Composition and Economic Value. By Joseph T. Singewald, Jr. 8vo. 145 pp. U. S. Bureau of Mines, Bulletin 64.

Kaolin and Feldspar, Mining and Treatment of, in the Southern Appalachian Region. By A. S. Watts. 8vo. 170 pp. U. S. Bureau of Mines, Bulletin 53.

Liquid Air, The Production, Application and Storage of. By O. Kausch. 4th edition. 8vo. 463 pp. Price, $3.75. C. Steinert, Weimar. (German.)

Metal Casting. By Ernst A. Schott. 8vo. 285 pp. Price, $3.00. Bernhard F. Voigt, Leipzig. (German.)

Metallurgical Analysis. By Nathaniel W. Lord and Dana J. Demorest. 3rd edition. 8vo. 330 pp. Price, $2.50. McGraw-Hill Book Co., New York.

Mineral Deposits. By Waldemar Lindgren. 8vo. 882 pp. Price. $5.00. McGraw-Hill Book Co., New York.

Minerals, The Useful, with the Exception of Ores, Potash Salts, Coal and Petroleum. Vol. I. By B. Dammer and O. Tietze. 2 vols. L. 8vo. 501 pp. Price, $4.00. F. Enke, Stuttgart. (German.)

Nitrogen Industry, The Air. By A. Perlick. 8vo. Price, $1.50. W. Klinkhardt, Leipzig. (German.)

Oils, Fats and Waxes, Chemical Technology and Analysis of. Vol. I. By J. Lewkowitsch. 3 vols. 5th edition. 8vo. Price, $6.25. Macmillan & Co., New York.

Peroxid, Hydrogen, Production of, by the Cathodic Reduction of Oxygen. By O. Priess. 8vo. University of Erlangen. (Dissertation.) (German.)

Physico-Chemical Theory, The Application of, to Technical Processes and Manufacturing Methods. By R. Kremann. 8vo. 205 pp. Price, $2.25. Constable & Co., London. (Translation.)

Plant Products, An Introduction to the Chemistry of. By Paul Haas and T. G. Hill. 8vo. 404 pp. Price, $2.25. Longmans, Green & Co., New York.

Rare Earths, Utilization of the. By C. R. Boehm. 8vo. Price, $1.25. Veit & Co., Leipzig.

Reagents, Merck's Index of Chemical. By Merck & Co. 3rd edition. L. 8vo. 446 pp. Julius Springer, Berlin. (German.)

Rubber, The Chemistry of. By B. D. Porritt. Cr. 8vo. Price, $0.50. Gurney & Jackson, London.

Spectro-Chemistry, Introduction to. By G. Urbain. 8vo. Price, $2.50. Theodor Steinkopff. Dresden. (Translation.) (German.)

Steel, The Manufacture of. By H. Noble. 2nd edition. 8vo. Price, $5.25. Dunod & Pinat, Paris. (French.)

Sulfur, Colloidal. By S. Oden. Let. 8vo. 193 pp. Price, $4.00. Akademische Buchhandlung, Upsala. (German.)

Technical Processes and Manufacturing Methods, The Application of Physico-Chemical Theory to. By R. Kremann. 8vo. Price, $2.25. Constable & Co., London. (Translation.)

Temperature Measurement, Methods of. By Bruno Thieme. 8vo. 160 pp. Price, $1.00. M. Krayn, Berlin. (German.)

Zinc and Cadmium and their Production from Ores and By-products. By R. G. Max Liebig. 8vo. 598 pp. Price, $8.00. O. Spamer, Leipzig. (German.)

RECENT JOURNAL ARTICLES

Alloy, A New Osmium-Platinum. By F. Zimmermann. *Chemical Engineer*, Vol. 18, 1913, No. 3, pp. 99–107.

Asphalt Paving Cements and Road Binders. By J. W. Howard. *Engineering Record*, Vol. 68, 1913, No. 13, pp. 345–347.

Cellulose, Obtaining, from Wood and Textil Fibers as well as Abolition of the By-product Lyes. By Hasenbacumer and Braun. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 73, pp. 481–485.

Cement, Composition Flooring. By H. M. Hooker. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 6, pp. 305–338.

Cement Materials and the Manufacture of Portland Cement in Montana. By W. H. Andrews. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 81, pp. 2383–2389.

Cereals, The Chemical Composition of South African Maize and other. By C. F. Juritz. *South African Agricultural Journal*, Vol. 6, 1913, No. 2, pp. 189–197.

Coke Oven Plant, The Modern, Recovery of By-products in. By C. A. Meissner. *American Gas Light Journal*, Vol. 99, 1913, No. 13, pp. 199 and 202–203.

Cyanid, Sodium, Manufacture of. By M. A. Vasseur. *Reone de Chemie Industrielle*, Vol. 24, 1913, No. 285, pp. 221–226.

Formic Acid as a Solvent. By Ossian Aschan. *Chemiker Zeitung*, Vol. 37, 1913, No. 112, pp. 1117–1118.

Indicator for Oxidizing Agents, An Electrochemical. By E. K. Rideal and U. R. Evans. *Analyst*, Vol. 38, 1913, No. 449, pp. 353–363.

Inorganic Manufacturing Industry, Progress in the, 1905-1912. By Bruno Waeser. *Chemiker Zeitung*, Vol. 37, 1913, No. 110, pp. 1097–1098.

Lime-Nitrogen Industry. By E. O. Siebner. *Chemiker Zeitung*, Vol. 37, 1913, No. 106, pp. 1057–1058.

Organic Chemistry, The Spectroscope in. By James J. Dobbie. *American Chemical Journal*, Vol. 50, 1913, No. 4, pp. 231–243.

Paper, A New Source of Pulp Supply. By Frederick F. Strong. *Paper Makers' Monthly Journal*, Vol. 51, 1913, No. 9, pp. 397–399.

Refractories for the Modern Boiler Plant. By Kermeth Seaver. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 6, pp. 339–362.

Sewage-Sludge Utilization. By Hermann Back and Leslie C. Frank. *Engineering Record*, Vol. 68, 1913, No. 12, pp. 331–333.

Smoke Prevention. Anonymous. *Industrial World*, Vol. 47, 1913, No. 37, pp. 1093–1101.

Steel, Over-Oxidation of. By W. R. Shimer and F. O. Kichline. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 81, pp. 2361–2377.

Steel, Volumetric Determination of Phosphorus in, According to Macagno's Method. By H. Wdowiszewski. *Chemiker Zeitung*, Vol. 37, 1913, No. 107, pp. 1069–1071.

Tanning Effluents, Valuation and Fixation of. By J. W. Phelan and J. H. Cohen. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 10, pp. 426–438.

Thermocouples, Base Metal, Some Observations on. By O. L. Kowalke. *Chemical Engineer*, Vol. 18, 1913, No. 3, pp. 93–96.

RECENT INVENTIONS

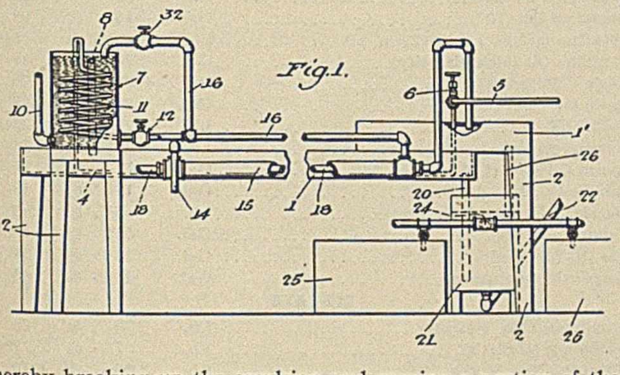
By C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Preparation of Catalytic Substances in a Minutely Divided State. H. Kast, Aug. 12, 1913. U. S. Pat. 1,070,138. Heavy metal salts of the trinitrophenols are heated in a weakly oxidizing atmosphere until the salts burn off by themselves leaving behind their ashes in a very voluminous and spongy form.

Sulfate of Potash and Alumina. H. F. Chappell, Aug. 12, 1913. U. S. Pat. 1,070,324. Sulfate of potassium and aluminum oxid are obtained from natural deposits of alum stone, alum rock and alunite by heating them to a temperature of about 800–1000° C. until the aluminium compounds present are converted into insoluble aluminum oxid and the potassium compounds present are converted into potassium sulfate; the potassium sulfate is separated by lixiviation.

Extracting Oils from Fuller's Earth and Like Materials. L. Felizat, Aug. 19, 1913. U. S. Pat. 1,070,435. Oil is recovered from Fuller's earth and like materials used in refining oils by adding water and a soluble alkaline carbonate to form a fluid mass. This is heated and carbonic gas is then liberated from the carbonate by means of acid to free the oil from the earthy material and permit it to rise to the top of the mass.

Cleaning and Refining Oil. C. W. Stone, Aug. 19, 1913. U. S. Pat. 1,070,555. Free water, emulsified water and oil having a lower boiling point than water are removed from crude petroleum by heating it in a stationary condition to a temperature sufficient to cause the free water to settle. The petroleum is then drawn off and caused to flow rapidly over a metallic surface heated to a temperature above the boiling point of water, thereby breaking up the emulsion and causing a portion of the water content to separate in a liquid condition and another portion of the water to vaporize together with the volatile oil having a lower boiling point than water. The oil is then allowed to stand to settle out the separated water. The vapors of water and oil arising from the rapidly flowing body of oil are collected and condensed.

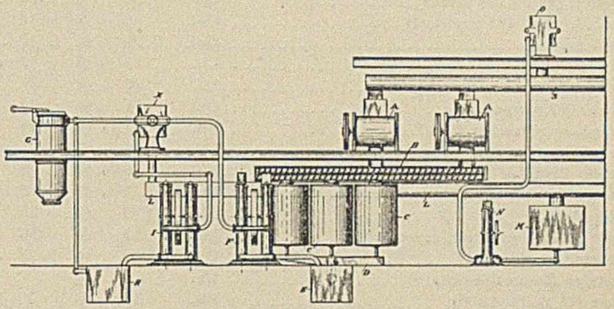


Making Oxalates. A. Hempel, Aug. 19, 1913. U. S. Pat. 1,070,806. Oxalates are produced from formates by heating to from 360° to 440° C. in an atmosphere of the waste gas which is produced in the manufacture of formates from carbon monoxid and caustic alkali.

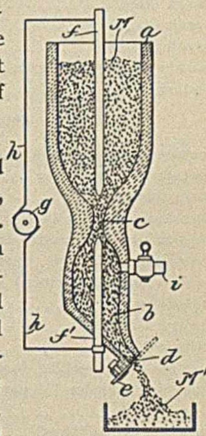
Soluble Barium Salts. F. F. Hunt, Aug. 19, 1913. U. S. Pat. 1,070,810. Soluble barium salts are obtained from residues containing barium in an acid-soluble form by adding a sufficient quantity of an acid to solubilize the acid-soluble barium compounds. The treated residues are then dried and leached with water to obtain a solution of the barium salts.

Explosive. J. F. O'Brien, Aug. 19, 1913. U. S. Pat. 1,070,836. The mixture consists of potassium chlorate, starch and silica.

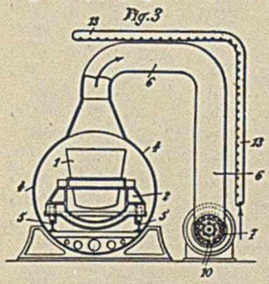
Manufacturing of White Sugar Direct from Raw Sugar-Juices. Wijnberg and Sauer, Aug. 19, 1913. U. S. Pat. 1,070,654. Raw sugar juices are refined by adding about 1 per cent of normal sulfur dioxid. The treated juices are then mixed with decolorizing carbon and kieselguhr, the latter being afterwards removed by filtering.



Granular Carbon. J. C. Lee, Aug. 26, 1913. U. S. Pat. 1,071,442. Finely divided anthracite coal is heated in the apparatus illustrated by means of an electrical current of definite intensity, the particles of coal being controlled so that each particle is exposed to the action of the current for a definite period of time.



Treating Melted Metals, Alloys and Steels. L. M. V. H. Baraduc-Muller, Aug. 26, 1913. U. S. Pat. 1,071,632. Molten steel in a vacuum chamber is subjected to a reduced pressure of approximately 1 mm. of mercury. The air and gases evacuated from the chamber are rapidly refrigerated to below 0° C. before reaching the evacuating apparatus whereby the volume and temperature of the air and gases coming from the vacuum chamber are greatly reduced.



Improving the Condition of Flour. J. A. Wesener, Sept. 2, 1913. U. S. Pat. 1,071,977. Flour is treated with anhydrous chlorine (diluted with an inactive gas) in order to mature and whiten it.

Explosive. F. Raschig, Sept. 2, 1913. U. S. Pat. 1,072,032. The explosive comprises sodium nitrate and the alkali soluble constituents of waste products of the soda pulp process.

Bleaching Solid and Semisolid Fats of All Kinds. F. Richter and L. von Orth, Sept. 2, 1913. U. S. Pat. 1,072,034. The fat is melted and filtered through a layer of aluminium oxid obtained from aluminium amalgam. This oxid is stated to have a much higher absorptive power than aluminium oxid produced by other processes as by heating trihydrate of aluminium. The aluminium oxid after use may be regenerated by calcining.

Potash Salts from Feldspar. H. P. Bassett, Sept. 9, 1913. U. S. Pat. 1,072,686. Feldspar or similar potassium-containing rock is heated to a red heat with one-half its weight of sodium chlorid and the potassium salts thus rendered soluble are extracted with water.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF OCTOBER, 1913

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	1.75	@	1.90
Acetone (drums)	Lb.	13½	@	14½
Alcohol, denatured (180 proof)	Gal.	35	@	38
Alcohol, grain (188 proof)	Gal.	2.50	@	2.52
Alcohol, wood (95 per cent)	Gal.	46	@	48
Amyl Acetate	Gal.	2.20	@	2.30
Aniline Oil	Lb.	10⅛	@	10⅝
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	21	@	23
Camphor (refined in bulk)	Lb.	42½	@	44
Carbolic Acid (drums)	Lb.	8½	@	11
Carbon Bisulfide	Lb.	6½	@	8
Carbon Tetrachloride (drums)	Lb.	7½	@	8
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	55	@	56
Dextrine (corn)	C.	3.02	@	3.23
Dextrine (imported potato)	Lb.	6	@	7
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8½	@	9½
Glycerine (dynamite)	Lb.	19¾	@	20¼
Oxalic Acid	Lb.	7½	@	7¾
Pyrogallic Acid (bulk)	Lb.	1.20	@	1.40
Salicylic Acid	Lb.	25	@	30
Starch (cassava)	Lb.	3¼	@	4
Starch (corn)	C.	2.34	@	3.00
Starch (potato)	Lb.	4½	@	5
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2⅜	@	2¾
Starch (wheat)	Lb.	5¼	@	6½
Tannic Acid (commercial)	Lb.	35	@	36
Tartaric Acid, crystals	Lb.	31½	@	32½

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7¾	@	8
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.	3⅛	@	3¾
Barium Chloride	C.	1.67½	@	1.90
Barium Nitrate	Lb.	5¼	@	5½
Barytes (prime white, foreign)	Ton	19.00	@	23.50
Bleaching Powder (35 per cent)	C.	1.25	@	1.30
Blue Vitriol	Lb.	5	@	5¼
Borax, crystals (bags)	Lb.	3¾	@	4¼
Boric Acid, crystals (powd.)	Lb.	7	@	7½
Brimstone (crude, domestic)	Ton	22.00	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	85	@	1.10
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.	8	@	8¼
Litharge (American)	Lb.	6¾	@	7
Lithium Carbonate	Lb.	65	@	70
Magnesia (powdered)	Lb.	5½	@	6
Magnesite (raw)	Ton	30.00	@	35.00
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.	3.30	@	3.50
Potassium Chlorate, crystals	Lb.	8¼	@	9½
Potassium Cyanide (bulk), 98–99%	Lb.	19	@	24
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.	9¾	@	10
Quicksilver, Flask (75 lbs.)		38.00	@	40.00
Red Lead (American)	Lb.	7	@	7⅛
Salt Cake (glass-makers')	C.	55	@	65
Silver Nitrate	Oz.	38¾	@	40¼
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.	8¼	@	9½
Sodium Hydroxide, 60 per cent	C.	1.55	@	1.57½
Sodium Hyposulfite	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	2.32½	@	2.40
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6⅞	@	7⅝
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.	44	@	45
White Lead (American, dry)	Lb.	5¾	@	6
Zinc Carbonate	Lb.	9	@	10
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.	42	@	45
Black Mineral Oil, 29 gravity	Gal.	13½	@	14
Castor Oil (No. 3)	Lb.	8⅞	@	10
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6.35	@	6.40
Cottonseed Oil (crude), f. o. b. mill	Gal.	42	@	42½
Cottonseed Oil (p. s. y.)	C.	6.80	@	6.90
Cylinder Oil (light, filtered)	Gal.	21½	@	32
Japan Wax	Lb.	9	@	9½
Lard Oil (prime winter)	Gal.	93	@	95
Linseed Oil (double-boiled)	Gal.	48	@	49
Menhaden Oil (crude)	Gal.	33	@	35
Neatsfoot Oil (20°)	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.)	Lb.	3½	@	3¾
Paraffine Oil (high viscosity)	Gal.	26	@	28
Rosin ("F" grade)	Bbl.	4.00	@	4.10
Rosin Oil (first run)	Gal.	27	@	28
Shellac, T. N.	Lb.	21½	@	23½
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.	8¾	@	9
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	43½	@	45

METALS

Aluminum (No. 1 ingots)	Lb.	20	@	21
Antimony (Hallet's)	Lb.	7½	@	7¾
Bismuth (New York)	Lb.	2.05	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	16⅝	@	—
Copper (lake)	Lb.	16¾	@	—
Lead, N. Y.	Lb.	4.35	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43.50	@	44.50
Silver	Oz.	61⅛	@	62⅛
Tin	C.	40.50	@	43.50
Zinc	C.	5.30	@	5.40

FERTILIZER MATERIALS

Ammonium Sulfate	C.	3.07½	@	3.10
Blood, dried	Unit	3.15	@	—
Bone, 4½ and 50, ground, raw	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian)	C.	2.05	@	2.10
Castor meal	Unit		3.30	
Fish Scrap, domestic, dried	Unit	3.25	@	3.35 & 10
Mowrah meal	Ton		nominal	
Phosphate, acid, 16 per cent bulk	Ton	—	@	6.75
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	38.55	@	—
Pyrites, furnace size, imported	Unit		0.13¼	
Tankage, high-grade	Unit	3.12½ & 10		