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## EDITORIALS.

### FIREPROOF MATERIALS.

RECENT developments indicate an approaching general awakening to the crying need for fireproof buildings and methods of construction. The lessons taught by the Baltimore, San Francisco and Chelsea fires have borne and are bearing fruit. Large buildings, office and factory buildings, in and near the larger cities—especially those that have suffered greatly by fire—are being designed and built with the most careful attention to the minimizing of fire risks. Materials of construction are receiving more attention and actual tests of their fire-resisting qualities are multiplying; and while the adherents of concrete and terra cotta tile are waxing warm in the discussion of their respective merits both these materials are finding a place in real fire-proof construction that cannot be seriously damaged by any ordinary conflagration.

We have brick, stone or concrete walls and rein-

forced concrete or tile-covered columns, floors and stairs, so that there is little combustible material in the average modern office building, but the furniture, and even this and the door- and window-frames and trimmings may be obtained in metal or other non-combustible material. With such fire-proof material at hand, even to doors, window-frames and sashes and flooring, and with fire-proof construction thoroughly tested and approved by competent authorities and by fire underwriters, it is a serious reflection on our intelligence as communities that we continue to build school-houses, theaters, hotels and other public buildings with wooden floors, partitions and stairs even when the outside walls (which is not always the case) are not themselves combustible.

But, as has already been intimated, capital is now awake and humanity is also slowly awakening to the necessity of protecting human life; of rendering impossible such calamities as the Collingwood school disaster and others equally familiar, and of making the wholesale destruction of property a thing of the past by the use of materials that will not burn. That such buildings can be built has been established beyond any doubt. The problem now is to so finish and furnish them that the possibility of fire and the amount of material on which it might feed shall be reduced to a minimum.

A test was recently made at the Columbia University fire-testing station of a fire-proof hollow block of a new material passing under the trade name of "Sagax," consisting of 60 per cent. ground straw with a magnesium cement as a binder. The material is said to be 25 per cent. lighter than terra cotta of the same size and strength and fully as fire-resisting, and it has had the added advantage that it may be cut, painted or nailed to like wood.

There is a large field for further experiment and exercise of inventive genius in the improvement of and addition to the fire-proof materials and processes now in use.

The relation of the industrial chemist to the problems involved is self-evident; it is chiefly to him that the world is indebted for all that has thus far been achieved, and it is to him that the world looks for the improvements that are bound to come,

—satisfactory substitutes for wood and efficient methods for fire-proofing fabrics that must be used in furnishings as well as the improvement and cheapening of existing methods and materials of construction.

ERNEST B. MCCREADY.

## ORIGINAL PAPERS

### THE MANUFACTURE OF CARBON ELECTRODES.

By G. A. ROUSH.

Received December 26, 1908.

The manufacture of carbon electrodes is each year becoming a more important industry, as it must necessarily keep pace with the constantly increasing number of electrochemical processes, both electrolytic and electrothermic, in which electrodes of carbon or graphite are parts of the apparatus. The amount of carbon used as electrode material is increasing immensely every year. In 1900 the value of the furnace carbons reported for the United States Census, was approximately \$11,000.<sup>1</sup> Now electrodes to that value are used every month in the smelting of aluminum alone. Large quantities are also used in the manufacture of caustic soda, calcium carbide, carbon disulfid, phosphorus, ferro-alloys, etc., and after graphitization by the Acheson process, in many other processes. The production of carbon electrodes of various sorts, for 1906, was probably in the neighborhood of 10,000,000 pounds, not including large quantities of battery carbons, for electrodes in dry and wet primary batteries.

The manufacture of electrodes for furnace work, of course, is simply an adaptation of the process for making arc light carbons. The dynamo and arc light not having been perfected until 1877–1880, the demand for carbon electrodes of all kinds was very limited, and all that were made before this time were for experimental purposes only, and were made by hand. With the introduction of the Brush dynamo and arc light, a demand was created and the supplying of carbons for these lamps then became a problem of importance.<sup>2</sup>

The development of the American carbon industry is largely due to Chas. F. Brush and W. H.

<sup>1</sup> Twelfth Census Report of the U. S., Vol. 10, p. 70.

<sup>2</sup> A fairly good historical account of the development of the manufacture of carbons can be had from "The Manufacture of Carbons for Electric Lighting and Other Purposes," by Francis Jehl, pp. 3–17 (The Electrician Printing and Publishing Co., London), and the Twelfth Census Report, Vol. 10, p. 170–1.

Lawrence, of Cleveland, Ohio, and to them belongs the credit for the discovery of the fitness of petroleum coke as the basic raw material for the manufacture of carbons. The experiments then made to ascertain the grain best adapted for burning in the electric arc, and the most suitable adhesive material to bind the carbon particles together laid the basis of the industry which has continued to the present day, with such additions as experience has shown advisable and the invention of the automatic and labor-saving machinery has made possible.

The raw materials used in the manufacture of carbon electrodes for electrochemical and electro-metallurgical work are:

1. Coke.
2. Hard pitch.
3. Soft pitch.
4. Tar.
5. Oil.

These materials will be taken up and discussed in the order named.

*Coke.*—For some purposes where a relatively high amount of ash is not objectionable, a seventy-two hour Connelsville coke or a calcined anthracite coal might be used. These make a very hard, dense carbon, but their high ash content prohibits use in all electrolytic processes where the ash freed by the disintegration and consumption of the carbon would contaminate the electrolytic bath.

Methods have been devised for purifying such materials by the removal of the ash<sup>1</sup> but so far as is known none of these are in commercial use.

For these reasons except in special cases, the material used is petroleum coke—the residue left in the still in the refining of crude oil. After calcining to remove volatile matter this gives a hard, dense material, low in ash, admirably suited for the purpose. For the manufacture of electrodes a coke from sulphur-bearing oil is generally used, since it is considerably cheaper than coke from a non-sulphur-bearing oil, and the presence of the sulphur in the electrodes is not objectionable as it is in the case of lighting carbons.

The coke as purchased contains 6–10 per cent., and sometimes as high as 14 per cent. of volatile matter which must be removed by calcination before the coke can be used. If the volatile matter

<sup>1</sup> Process for removing silica from coke, U. S. P. 733,389, July 14, 1903; C. M. Hall, abstracted in *Electrochem Industry*, Vol. 1, p. 467 (1903). Method of purifying electric lighting carbons, U. S. P. 542, 982, July 23, 1895. "The Manufacture of Carbons for Electric Lighting and Other Purposes," Jehl, pp. 87–93.

is over 10 per cent., the coke cakes together in the calcining retorts, and is very difficult to remove. The coke usually carries 0.02-0.06 per cent. of ash.

The raw coke costs about \$12.00 per ton including the freight, from the refineries at Philadelphia, and Bayonne, N. J., to West Virginia.

In some cases, to impart better mechanical wearing properties to the material, a small portion of the coke is replaced by lampblack.

*Pitch.*—The coke forms the main body of the electrode. The material next in importance is the binder which is used to hold the coke particles together. For this purpose coal tar pitch is mainly used. Both hard and soft pitch are used, either singly or together, depending on the fineness of the coke and the kind of electrode being made.

The hard pitch should soften at 160-170° F., and contain 40-45 per cent. of residue insoluble in benzol. It usually carries about 0.10 per cent. of ash, mostly oxid of iron.

The soft pitch is soft enough at ordinary temperatures to be easily dented with the finger nail.

The cost of the pitch is about \$10.00 per ton.

*Tar.*—For the sake of special properties in the electrode, to be discussed later, a part of the pitch is sometimes replaced by coal tar.

*Oil.*—A small quantity of summer oil, the last distillate in the refining of crude oil, is used simply as a lubricant.

The process of manufacture may be divided as follows: (1) calcining, (2) milling, (3) mixing, (4) plugging, (5) forcing, (6) baking, (7) cleaning and sorting, (8) testing.

*Calcining.*—As has been said, the coke, when received, contains a considerable percentage of volatile matter, which, to avoid a large and uneven shrinkage in the baking, must be removed before the coke can be used.

The raw coke is crushed to about three-fourths inch size in an ordinary gyratory crusher, and is elevated to a storage bin over the calcining retorts, into which it is fed by gravity. The retorts consist of circular pockets of fire-brick, so arranged that the fire plays all around them. Figs. 1 and 2<sup>1</sup> show diagrammatic sections of a retort. The retort is charged at B and discharged at D by means of gate valves.

The calcined coke is discharged into wheelbarrows and spread out on the floor to cool, when it is

shoveled into screw conveyers and carried to the milling department.

The coke as it comes from the retorts should contain less than 0.2 per cent. of volatile matter; a higher percentage than this calls for re-calcining. The ordinary run of coke can be reduced to this point in forty-eight hours, but a coke running extra high in volatile matter may require more time.

Counting fuel, labor, loss in weight, etc., it costs approximately \$5.00 a ton to calcine the coke.

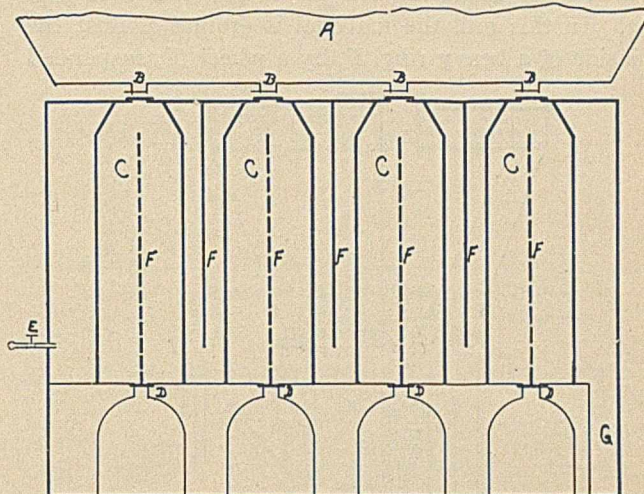


Fig. 1.—Coke retorts.

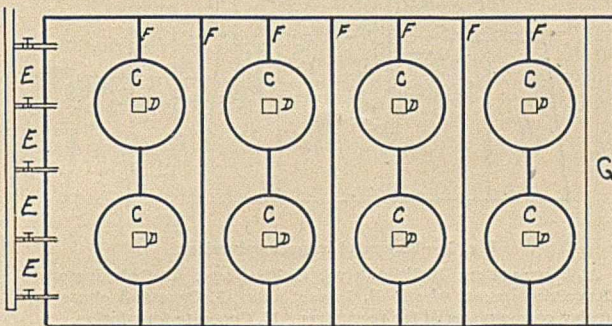


Fig. 2.

- |                                |                   |
|--------------------------------|-------------------|
| A, Coke bin.                   | E, Gas valves.    |
| B, Gate valve for charging.    | F, Flue walls.    |
| C, Retort.                     | G, Flue to stack. |
| D, Gate valve for discharging. |                   |

*Milling.*—The calcined coke is very porous and in order to make a compact carbon, must be reduced to a flour. Varying degrees of fineness are used for different sizes of carbons, the coarser flour being used for the larger sizes, and the finer for the smaller sizes.

A hard, dense carbon is at all times most desirable, and the finer the flour, the lower the porosity of the carbon made from it, but in the larger sizes, low porosity is sacrificed to a certain extent, since

<sup>1</sup> All the illustrations accompanying this article are merely diagrammatic, and are not intended to adhere strictly to proportions or show details and dimensions.

a somewhat coarser flour lessens the liability of the carbon to crack across the end in baking. Following are three typical analyses of the flours used in the various sizes:

	For small sizes, per cent.	Medium sizes, per cent.	Large sizes, per cent.
On 100 mesh.....	0.8	5.0	10.0
On 140 mesh.....	7.7	17.3	20.5
On 200 mesh.....	27.5	21.7	19.0
Through 200 mesh.....	64.0	56.0	50.5

The finest flour is produced most satisfactorily in the Raymond impact pulverizer, shown in Fig. 3. In this mill the material is ground against the inside of a heavy ring, F, by a wheel, E, suspended

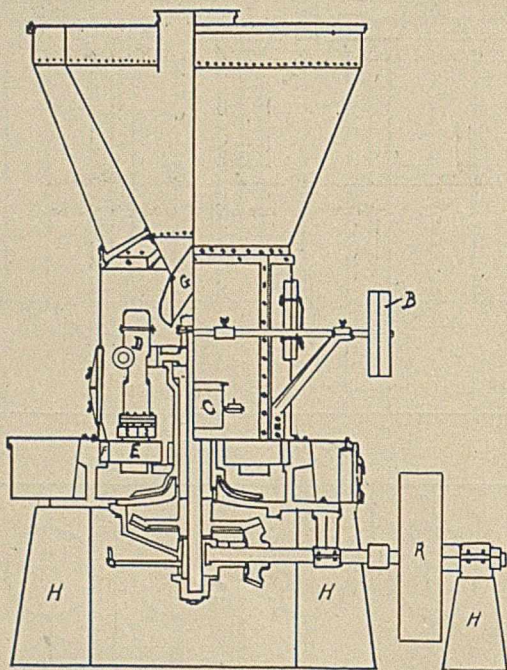


Fig. 3.—Raymond impact pulverizer.

A, Drive pulley; B, Feed drive; C, Feed box; D, Swinging arm; E, Revolving impact wheel; F, Impact ring; G, Cone and chute for returning coarse material for regrinding; H, Concrete foundation.

at the end of a rotating arm D, the wheel being forced against the ring by the centrifugal force of the rotation. The crushed material, falling through to the bottom of the mill, is elevated by a stream of air from a fan. The coarser particles, of course, require a heavier blast of air to raise them than the fine material, and thus, by regulating the speed of the fan, the fineness of the material can be controlled, the coarser matter being allowed to drop back and be crushed again.

With this mill, it is a simple matter to get material of such a fineness that 98 per cent. will pass a 100-mesh sieve, and 92 per cent. will pass a 200-mesh sieve, without the expensive operation of bolting.

The current of air carrying the pulverized material is passed through a settling chamber where all but the finest dust settles out. The air from the settling chamber goes through a dust collector where it is filtered through muslin, and the last of the dust removed and returned to the settling chamber.

If for any special purpose, an exceptionally fine flour is desired, the fines from the dust collector may be saved separate, giving a material too fine to classify by sifting, 100 per cent. passing through a 200-mesh sieve.

The coarse flours are produced either in the Raymond mill with a higher speed on the fan, or in the ordinary Buhr mill with or without bolting, according to the fineness desired. Only the coarsest flour can be used from the Buhr mill without bolting.

The bolters used for this purpose are the same type as ordinarily used in flour mills.

The hard pitch is crushed to approximately one-half inch size in a gyratory crusher, and the soft pitch is melted in a steam jacketed kettle.

The various grades of flour and the hard pitch are stored in bins directly over the mixing room. The soft pitch and the supply of summer oil should be in the mixing room.

*Mixing.*—It may be stated as a general rule that the hardness of a carbon increases with the fineness of the flour and the increasing fluidity of the binder used in it. By properly controlling these conditions, carbons of different hardness may be produced according to requirements. This rule, however, cannot be worked at pleasure since the nature of the substance in hand sometimes prohibits. For exceedingly fine flours, soft pitch or tar or a mixture of the two must be used, since it is very difficult to coat the very fine particles with a binder of such a high melting point, and low degree of fluidity as the hard pitch.

The finer flours require more pitch to bind them together than do the coarser ones. The amount also varies with the melting point of the pitch and the size of the carbon to be made, a small carbon requiring a softer composition than a large one. With an ordinary grade of hard pitch it will require 30-40 per cent. of the weight of the coke. For the ordinary medium grade of electrode, hard pitch is used almost entirely.

Following is given the composition of some of the more common "mixes:"

(1) For ordinary electrodes.

Coke, 325 pounds.

Hard pitch, 110 pounds.

Oil, 1 gal.

(2) For a somewhat finer flour or a pitch of a higher melting point.

Coke, 325 pounds.

Hard pitch, 115 pounds.

Oil, 2 gal.

(3) For a coarse flour.

Coke, 325 pounds.

Hard pitch, 40 pounds.

Soft pitch, 4 gal.

Oil, 1 gal.

(4) For a carbon to stand heat and wear but not used as electrode.

Coke, 325 pounds.

Lampblack, 20 pounds.

Hard pitch, 30 pounds.

Tar, 10 gal.

A variation of two pounds of pitch in a batch can be detected in forcing the carbon by one experienced in handling it.

The materials weighed out in the proper proportions are run into steam-jacketed mixing kettles (Fig. 4) with revolving blades and mixed for about twenty minutes. The mix comes from the kettles as a very stiff dough, every particle of coke being covered with a thin coating of melted pitch. The mixing must be sufficient to insure a uniform

is shoveled into heavy cast iron hoops, and by means of hydraulic presses,<sup>1</sup> pressed into cheeses about six inches thick, and the same diameter as the opening in the press in which the carbons are to be formed. This may vary from four to twenty

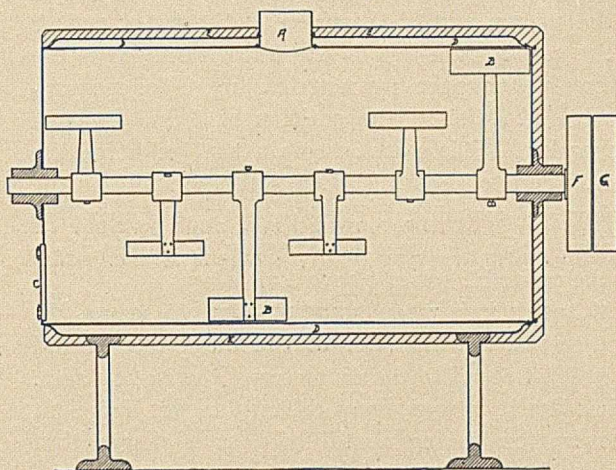


Fig. 4.—Mixer with one-half of casing removed.

A, Charging aperture; B, Mixing paddles; C, Discharge door; D, Steam jacket; E, Magnesia covering; F, Drive pulley, G, Idle pulley.

four inches, depending on the size of the carbons to be made.

The plugging puts the mix into a compact form easily handled, and presses out most of the air, thus avoiding the presence of large air bubbles in the carbon.

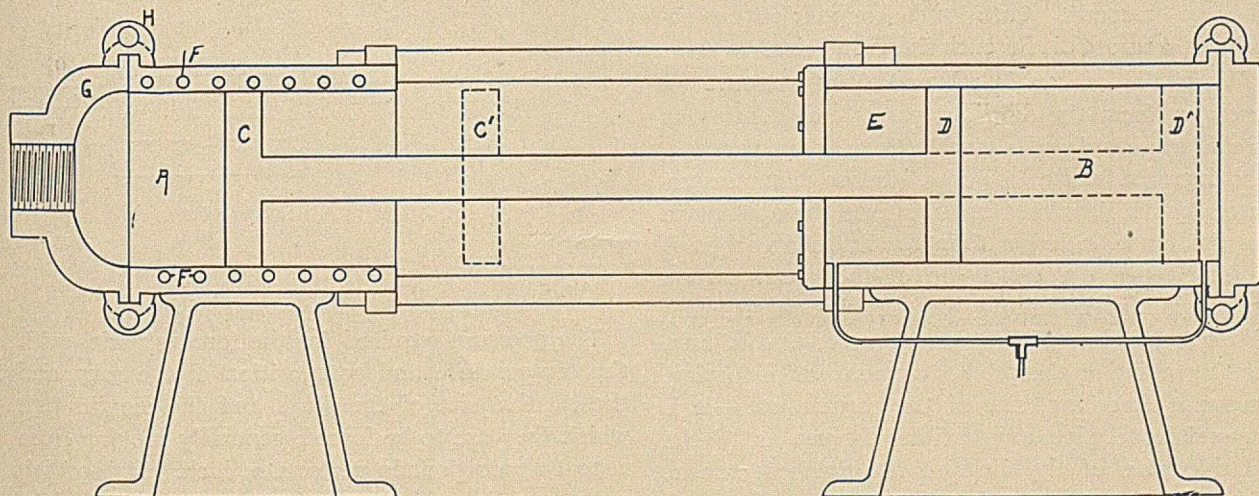


Fig. 5.—Carbon press, sectional view.

A, Carbon end; B, Water end; C, Carbon ram; D, Water ram; E, Reverse water space; F, Steam coil; G, Die head; H, Collar; C' and D' show the positions of C and D when charging.

product, or unequal shrinkage and cracks will result on baking. The hot mix has a temperature of 265–275° F.

*Plugging.*—The hot mix from the mixing kettles

*Forcing.*—These cheeses, or “plugs,” are then forced by hydraulic pressure through a die the size

<sup>1</sup> An illustration showing the style of press used for this work may be found in *Electrochem. Industry*, Vol. 1, p. 51 (1902).

and shape to make the carbons of the desired cross section, various sizes of round and square dies being kept in stock.

The press for the forcing, generally known as a "Jumbo," is shown in cross section in Fig. 5. A is the carbon end of the press, B the water end; C is the carbon ram and D the water ram. E is the reverse water space, for withdrawing, C for recharging C' and D' show the position of C and D when recharging. F is a steam coil in the jacket of the carbon end to keep it the same temperature as the carbon it contains. The head G, carrying the desired die in the threaded opening, is held in place by the collar H, bolted above and below.

Although it is often made smaller, to secure the best results the diameter of the water ram should be at least equal to the diameter of the carbon ram. Otherwise it is sometimes difficult to get sufficient pressure for forcing a stiff mix, or a charge that has accidentally been left to cool too long.

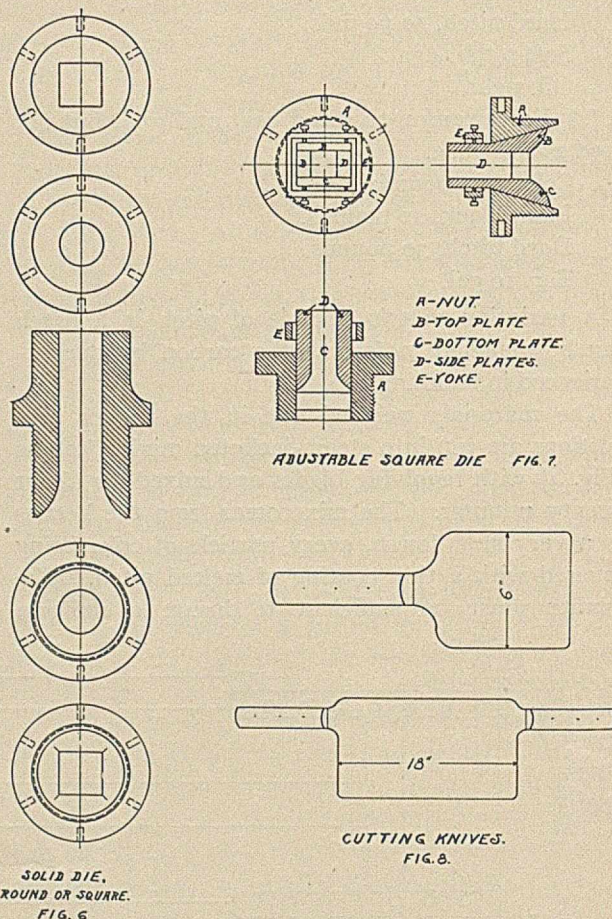
Dies for all sizes in common use are kept in stock. Fig. 6 shows a solid die for round or square carbons. A die of this kind is, of course, of a fixed size, and a separate die must be had for each size of carbon made. Fig. 7 shows an adjustable die for rectangular carbons. By supplying extra side plates, D, of varying width and thickness, rectangular carbons of any size up to the extreme limit of the die may be made. Carbons of irregular outline require a separate die for each shape and size.

When the carbon is released from pressure on emerging from the die, it expands considerably in size, in smaller sizes, as much as four or five per cent. This increase in size, however, is more than counteracted by the shrinkage in baking, so the opening in the die must be larger than the finished carbon is to be. Since the expansion of the green carbon and shrinkage in baking both depend on so many different factors—size of flour, composition of mix, melting point of the pitch, temperature of forcing, pressure of forcing, size of the carbon, etc.—it is impossible to give any definite figures as to the relative sizes of the die and the finished carbon. This must be more or less a matter of "cut and try." The diameter of the die is usually about 3-5 per cent. greater than the diameter of the desired carbon.

The plugs fresh from the plug presses are usually too soft to work well in the jumbo, and must be allowed to cool for a time. If run too hot, the pressure required to force the mix through the die is not sufficient to press the separate plugs into one co-

herent mass. The plugs entering the jumbo vary in temperature from 200-240° F., according to the composition of the mix, the size of the plugs, and the size of the carbons to be made.

The jacket of the jumbo should be kept at a temperature about 5-10° higher than the plugs, to prevent the formation of a hard shell around the outside of the mass of carbon.



The pressure required for the forcing varies with the temperature and composition of the mix, and the relative size of the plugs and the die through which they are to be forced, generally ranging from 1000 to 3000 pounds per square inch. If too high a pressure is used, the carbon expands so rapidly and so much on emerging from the die as to cause it to split radially from end to end.

The carbon as it comes from the die is caught in wooden or iron forms, and while still warm and plastic, is cut to the proper length by hand with heavy knives (Fig. 8) and left in the forms to cool and harden. After hardening so they can be handled without losing their shape, they are loaded

into trays and carried into the furnace room on trucks.

A large percentage of the mix is lost in the forcing, as scrap, consisting of spoiled and defective carbons, trimmings, etc. This frequently amounts to 25 per cent. of the mix handled. A portion of this scrap is used in the furnace room, as will be explained later; the remainder, after cooling and hardening, is crushed to a flour and mixed again as a part of a new batch, correction being made for pitch it contains.

*Baking.*—The green carbons, being composed argely of pitch, are nonconductors of electricity and require baking to render them conducting. This removes the volatile portions of the pitch, and leaves the particles of coke-flour bound together by the coke thus formed. The carbons must be protected from the action of the air while being baked, and this is done by burying them in the furnace in fine sand.

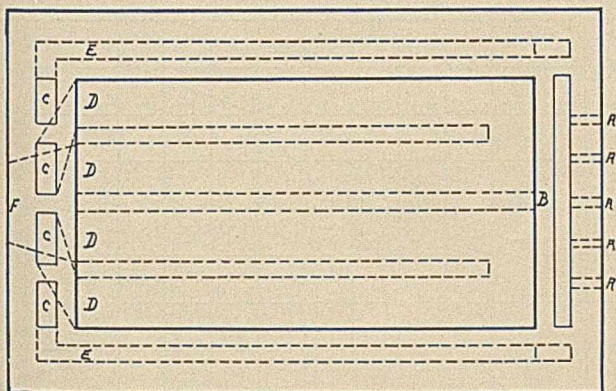


Fig. 9.—Baking furnace, top view.

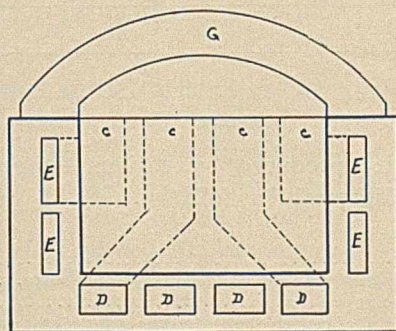


Fig. 10.—Cross section.

A, Opening for gas burners; B, Distributing wall for gas; C, Distributing flues; D, Flues in bottom of fce.; E, Flues in sides of fce.; F, Flue to stack; G, Fce. top.

Figs. 9 and 10 show the construction of the baking furnaces. Flues are so arranged in the walls and bottom that the space inside the furnace is completely surrounded by fire. The inside dimensions

of a furnace such as shown, are 12'8" × 7' × 3'. The furnaces are gas-fired.

Patents have been granted<sup>1</sup> for an electric furnace for baking electrodes, but from the best information at hand, it is believed that the process was never in commercial use.

In filling a furnace the bottom is covered with a layer of sand; on this is placed a layer of carbons, care being taken that they do not touch each other, the space between being filled with sand. Over this is placed another layer of sand, then another of carbons, and so on until the furnace is full. If there is not sufficient space between the carbons, the volatile matter boiled out of the pitch will cake the sand together around them. This space varies from one-eighth inch or less for carbons one inch in diameter, to two or three inches for a twelve-inch carbon. The top layer of sand is three or four inches thick, and is covered with brick or tile, forming the seal of the furnace.

Great care must be taken that the layers of sand on which the carbons are packed are perfectly smooth and level, and that the sand is packed firmly around them at every point. In firing the furnace when the melting point of the pitch is reached, the carbon becomes very soft and plastic and will assume any shape allowed by the sand in which it is packed. A small leak in the floor of the furnace allowing the sand to trickle through into the flues during the firing is liable to cause crooks and cracks in all the carbons immediately above it.

After the fire is turned out and the furnace begins to cool off, enough air usually enters through the seal of the furnace to considerably damage the top layer of carbon by oxidation. For this reason the top layer is usually green carbon scrap, brought from the furnace room for this purpose, which after baking is ground up and used in making battery carbons.

The number of carbons packed in a furnace depends entirely on their size. The following table gives the number that will pack in a furnace, for some of the common sizes:

1 <sup>1</sup> / <sub>4</sub> × 15 inches <sup>2</sup> .....	10900
7 <sup>7</sup> / <sub>8</sub> × 2 × 30 inches.....	3600
1 <sup>3</sup> / <sub>4</sub> × 3 × 36 inches.....	1408
3 <sup>3</sup> / <sub>8</sub> × 18 inches.....	1396
4 × 4 × 13 <sup>1</sup> / <sub>2</sub> inches.....	1086
5 <sup>1</sup> / <sub>4</sub> × 19 <sup>1</sup> / <sub>2</sub> inches.....	564

<sup>1</sup> U. S. P. 705,076, July 22, 1902; C. M. Hall, abstracted in *Electrochem. Industry*, Vol. 1, p. 30 (1902) and Vol. 2, p. 7 (1904).

<sup>1</sup> Where only two dimensions are given, the carbon is round, the smaller being the diameter.

4 × 30 inches.....	470
4 × 8 <sup>3</sup> / <sub>4</sub> × 15 inches.....	305
12 × 49 <sup>1</sup> / <sub>4</sub> inches.....	10
12 × 12 × 50 inches.....	10
12 × 60 inches.....	5

With the smaller sizes the number varies somewhat according to the size of the scrap packed on top of the furnace. With the larger sizes, more could be packed were it not for certain rules that are followed in packing. Whenever possible carbons are packed with the long way of the carbon running the long way of the furnace, and if rectangular in shape, with the narrow edge up. As can be seen from the construction of the furnace, most of the heat is received from the top, bottom and sides, rather than from the ends. This method of packing permits the heat to pass through the carbon, through its shorter dimensions, so that, as near as possible, all parts of a single carbon are at the same temperature at the same time, thus giving less liability of uneven shrinkage, which causes warping and cracking.

The proper firing of a furnace requires considerable experience. At its best this operation requires such a large amount of time and fuel, that it must be accomplished with as great an economy of both as possible. Yet just as great care must be taken not to force a furnace too fast, or its entire contents may be ruined. If the pitch in the green carbon is volatilized faster than the gas can escape through the pores of the carbon, it will cause bubbles in the carbon and uneven shrinkage with its attendant warping and cracks. The firing throughout must be steady and even, and must be judged from the appearance of the fire, the amount of pitch gas escaping through the seal, and the temperature measured in a test pipe leading through the walls about two feet into the contents of the furnace. A furnace of small goods can be fired faster than one of heavy goods.

A furnace begins to "gas" after three or four days' firing; seven to seven and a half days should see the gassing practically over. The total firing requires ten to fourteen days according to the size of the material and the rapidity with which it can be forced. Figs. 11 and 12 show the temperature curves of two furnaces, showing the rate of firing.

Most carbons are baked to a final temperature of 1020° C., although some need be taken only to 950°. Practically all electrodes are baked to 1020°, since the higher the temperature of baking, the higher the density and conductivity of the carbon. The carbon should have a resistance of 0.0016

ohm for a one-inch cube,<sup>1</sup> and have a safe carrying capacity of 25 amperes per square inch of cross section.

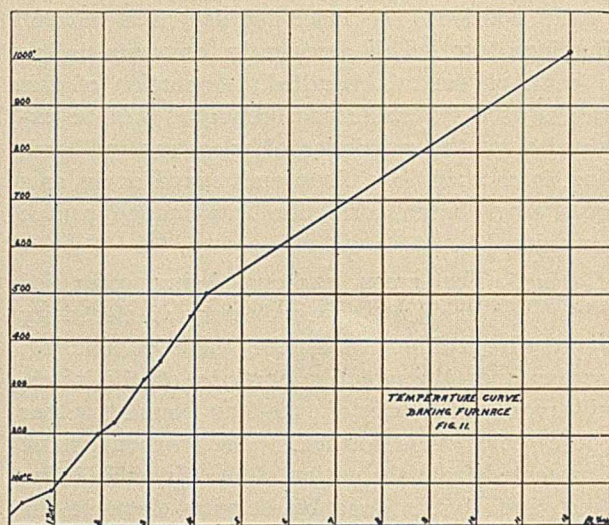


Fig. 11.

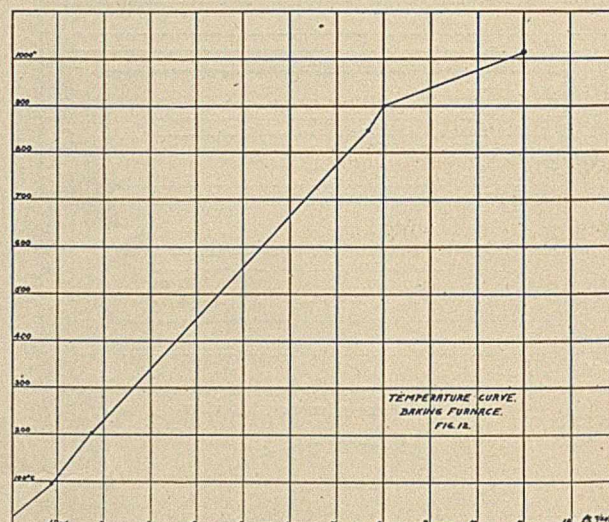


Fig. 12.

The density produced by various temperatures is given by Fitzgerald<sup>2</sup> as follows:

Temperature.	Density.
Dull redness.....	1.9141
Above melting point of CaCl <sub>2</sub> —below melting point of silver....	1.9612
Above melting point of silver.....	1.9853
Above melting point of copper—below melting point of cast iron	2.0061
Above melting point of cast iron.....	2.0363
Heated in platinum crucible over blast lamp.....	2.0585

The variations in temperature in the various parts of the baking furnace were shown by the following experiments:

<sup>1</sup> "On Carbons for Electrometallurgy," Fitzgerald and Forsell, *Trans. Amer. Electrochem. Soc.*, 11, 321 (1907).

<sup>2</sup> *Trans. Amer. Electrochem. Soc.*, 6, 33 (1904); abstracted in *Electrochem. Industry*, 2, 415 (1904).



1. Samples were tested for density from the center of each layer in a furnace containing nine layers, with the following results:

No. of layers (from top).	Density.
1.....	2.00
2.....	2.00
3.....	1.995
4.....	2.00
5.....	2.00
6.....	2.00
7.....	1.99
8.....	1.974
9.....	1.96

2. In another furnace samples were taken:

(1) From the end of the furnace next to the burners.

(2) In the middle of the furnace.

(3) From the end of the furnace next to the distributing flues (see Fig. 9).

Sample No.	Density.
1.....	2.026
2.....	2.005
3.....	2.018

The baking out of the pitch from the green carbon causes a considerable shrinkage in both weight and dimensions, varying somewhat with the composition of the mix, and the size of the carbon. The longer the dimension, the smaller the percentage of shrinkage. Rough figures on the shrinkage between green and baked carbons are given in the following table:

Approximate length of dimen- sions of inches.	Per cent. shrinkage.
1.....	5.5
2.....	4.9
3.....	4.0
4.....	3.4
6.....	3.2
12.....	2.3
24.....	2.2
48.....	2.0

Shrinkage in weight averages 13.4 per cent. loss.

The final temperature is judged by an alloy of gold and silver in such proportions that it melts at 1020° C. When the furnace reaches such a temperature that a small square of the alloy melts readily when placed in the test pipe, the fire is turned off and the furnace allowed to cool.

It requires four or five days for the furnace to cool sufficiently for it to be opened and the contents removed. If a furnace is opened too soon and its contents exposed to the air at too high a temperature, oxidation and cracking will result.

When the furnace is opened the sand is shoveled out, run through a small gyratory crusher, screened through a trommel screen and is then ready for use again.

*Cleaning and Sorting.*—The carbons are taken out of the furnace, and adhering sand removed by brushing with a wire brush. The cleaning is almost all done by hand, no very satisfactory machine for this purpose having been devised. A furnace of five 12 × 60 carbons or even one of ten 12 × 12 × 50's is not a particularly difficult proposition, but one containing eleven thousand 1 1/4 × 15's is another story.

While the carbons are being cleaned, all defective ones are thrown aside, leaving only the perfect ones, ready for shipment, if the laboratory tests on the lot are favorable.

The culls are either used for making battery carbons or may be ground up and the flour used the same as the regular coke flour. It however requires somewhat less pitch in mixing and makes a carbon that shrinks less in baking, and is slightly harder.

*Testing.*—While the furnace is being emptied, samples are taken to give an average of the lot by chipping from carbons in all parts of the furnace, and taken to the laboratory for examination. The tests made include apparent density, real density, and ash.<sup>1</sup>

The apparatus for the density determinations consists of a volumeter tube<sup>2</sup> graduated to 100 cc. in divisions of 0.2 cc. fitted with a rubber stopper, through which passes a glass tube connected to a vacuum pump.

For ordinary carbon, it has been found that the size of the pieces in the sample has no effect on the results, and in general, there is no practical difference between the center and outside of an electrode. The essential thing is to see that there is no sand adhering to the sample. Temperature does not affect the results, and the pressure need be reduced only to two inches of vacuum. These conditions give results checking to hundredths.

*Apparent Density.*—The sample—30 grams or more—is weighed and given a coating of shellac by covering it for a few minutes with a light solution of a good grade of shellac in wood alcohol, and drying. The tube is carefully filled to about 50–60 cc. with water free from air bubbles. Read the tube, and introduce the sample, using care not to spatter the sides of the tube. Jar the tube slightly to remove adhering air bubbles, and read again. The difference between the two readings,

<sup>1</sup> "Testing Carbon Electrodes," Fitzgerald, *Trans. Amer. Electrochem. Soc.*, Vol. 2, p. abstracted in *Electrochem. Industry*, 1, 68 (1902).

<sup>2</sup> Eimer and Amend Catalog, No. 7179, p. 395 (1905).

divided into the weight of the sample, gives the apparent density.

*Real Density.*—For the real density instead of water, use coal oil of 0.78 sp. gr. If new, exhaust in a vacuum for fifteen minutes. Fill the tube to 50–60 cc., allow to stand a few minutes and read. Introduce the weighed sample—30 grams or more—and apply the exhaust gradually. After most of the bubbling has ceased, it can be increased to the limit, and the tube jarred slightly to help free any bubbles. Care must be taken that no oil escapes through the connecting tube to the pump. The action is complete in 6–10 minutes. Remove the exhaust, allow to stand a few minutes and read again. The difference between the two readings, divided into the weight of the sample, gives the real density.

For ordinary, or purely comparative results this method is sufficient, but where greater accuracy is desired, the pycnometer method should be used. The pycnometer is weighed empty, full of water, and full of oil, the bottle being filled each time to 25° C. in a thermostat. The weight of the oil divided by the weight of the water, multiplied by the factor of contraction, to convert water at 25° to water at 4°, gives the density of the oil.

A sample of about 30 grams of carbon is ground to 100-mesh; ten grams of this are weighed into the pycnometer which is then filled half full of oil and exhausted under a bell jar, or in a vacuum desiccator until all bubbles cease. Then more oil is added and further exhaustion continued. Finally the bottle is completely filled and placed in the thermostat till it comes to 25° C., and is then dried and weighed.

The calculation for the density of the carbon is as follows:

D = density of carbon.

d = density of oil.

W = weight of sample in grams.

b = weight of pycnometer.

O = weight of oil in pycnometer containing no sample.

O' = weight of oil in pycnometer containing the sample.

0.0012 = density of air.

0.997071 = factor of contraction of water from 25° C. to 4° C.

Then  $D = \left( \frac{W}{(W+b+O) - (W+b+O')} \times d \right) + 0.0012$ .

This method gives results which average 0.025 higher than the volumeter method.

*Ash.*—Five grams of the sample are burned in a muffle in a porcelain crucible, and weighed.

$$\frac{\text{Wt. ash} \times 100}{5} = \text{per cent ash.}$$

With ordinary electrodes, the apparent density varies from 1.55 to 1.70; the real density from 1.95 to 2.05; and the ash, from 0.10 to 0.30 per cent.

As can be seen from the apparent density, carbons will approximate 100 pounds per cubic foot in weight.

*Carbons for Graphitization.*—A large percentage of the electrodes used in the various electrochemical processes are of graphite. Acheson's process of converting amorphous carbon into graphite<sup>1</sup> makes possible the conversion of formed carbon electrodes into graphite. It is not necessary to describe this process here, since it can readily be found in the literature.<sup>2</sup> We shall consider only the production of the electrodes of amorphous carbon ready for graphitization. This is just the same as the production of ordinary electrodes except the composition of the mix, which is as follows:

Coke.....	325 pounds
Hard pitch.....	103 pounds
Soft pitch.....	½ gal.
Oil.....	1 gal.
Oxid of iron.....	5 pounds

According to Danneel,<sup>3</sup> aluminum oxid is more suitable for this purpose than iron oxid, but iron oxid is the one that is used. The presence of some metal in the carbon is necessary, since the conversion into graphite depends on the formation of a metallic carbide, and its subsequent decomposition by a higher temperature, volatilizing the metal, and leaving the carbon in the form of graphite.

All scrap and culls, both green and baked, must be worked back into the process, since carbon containing iron cannot be used for battery purposes.

The finished carbon for graphitization should have an ash content of approximately 1.5 per cent., and a real density of 2.00. A density below this point calls for the re-baking of the material, at a heavy cost for labor, time and fuel.

Some idea of the possibilities of growth in the

<sup>1</sup> U. S. P. 542,982, July 13, 1895, abst. in *Electrochem. Industry*, 3, 416 and 482 (1905); U. S. P. 568,323, Sept. 29, 1896, abst. in *Electrochem. Industry*, 3, 482 (1905); U. S. P. 617,979, Jan. 17, 1899, abst. in *Electrochem. Industry*, 3, 417 (1905) and 4, 42 (1906); U. S. P. 645,285, March 13, 1900, abst. in *Electrochem. Industry*, 3, 416 (1905) and 4, 42 (1906); U. S. P. 702,758, June 17, 1902, abst. in *Electrochem. Industry*, 3, 417 (1905) and 4, 42 (1906); U. S. P. 711,031, Oct. 14, 1902, abst. in *Electrochem. Industry*, 1, 130 (1902) and 3, 417 (1905).

<sup>2</sup> *Electrochem. Industry*, 1, 52 (1902) and 3, 417 (1905), and above patents, note (1).

<sup>3</sup> *Zeit. Elektrochemie*, Sept. 25, 1902, abst. *Electrochem. Industry*, 1, 106 (1902).

carbon industry can be had from the patent statistics. During the year 1907, over eighty patents were granted on processes or apparatus using carbon or graphite as electrodes—about 40 per cent. of the total electrochemical patents granted, exclusive of battery patents.

### THE DETECTION OF PIN HOLES IN TIN PLATE.

By WILLIAM H. WALKER.

Received March 14, 1909.

It is very generally contended among the users of modern tin plate, though not conceded by the makers of the same, that the product now offered upon the market is not so durable as that obtained some twenty years ago. At that time all of our tin plate was imported; but since 1892, or soon after the McKinley Tariff Act was passed, domestic manufacture has steadily grown, until now very little foreign plate is to be found. It is interesting to note that dealers who were previously large importers of tin plate, while maintaining that our present supply is inferior, are willing to admit that even in the "good old times" they were greatly annoyed by the so-called "pin holes" in their goods.

A study of deteriorated tin plate reveals the fact that invariably the tin surface breaks down at a great number of distinct points, and not in continuous patches or zones. The cause of this deterioration is easily seen to be the rusting of the iron (including hereunder steel) base or foundation upon which the tin coating has been placed. These minute bare spots on the iron surface, or small channels through the tin coating down to the iron base are technically called pin holes, and are generally so small as to be undetected by the unaided eye. While unquestionably the number of these holes is greater upon a sheet which carries a very thin coating of tin than upon the triple or quadruple plate, yet upon the heaviest and most expensive plate such as the "dairy stock" used in making large milk cans, the occurrence of these imperfections in the coating is so frequent as to seriously impair the life of the can. Generally the most careful inspection of a heavily coated sheet fails to indicate any lack of continuity of the tin coating, and yet cans made from such stock show rust spots within a few days after being put into service. Contrary to what might be expected, experience demonstrates that the very rough places and apparent imperfections on the bright tin surface are not centers of

corrosion, but that rust spots appear at places where the tin coating is seemingly most perfect.

As has already been shown,<sup>1</sup> before iron can form rust it must pass into water solution in the shape of iron ions, and there must at the same time separate from the water or film of moisture an equivalent number of hydrogen ions. Tin is a metal which has a negligible solution pressure, on the one hand, and presents a surface upon which hydrogen can separate and be readily oxidized, on the other. Hence, tin and iron in the presence of water form what is spoken of as a "galvanic couple" or "cell," and an electric current flows from the iron to the tin induced by the solution of the iron and the plating out or precipitation of the hydrogen.

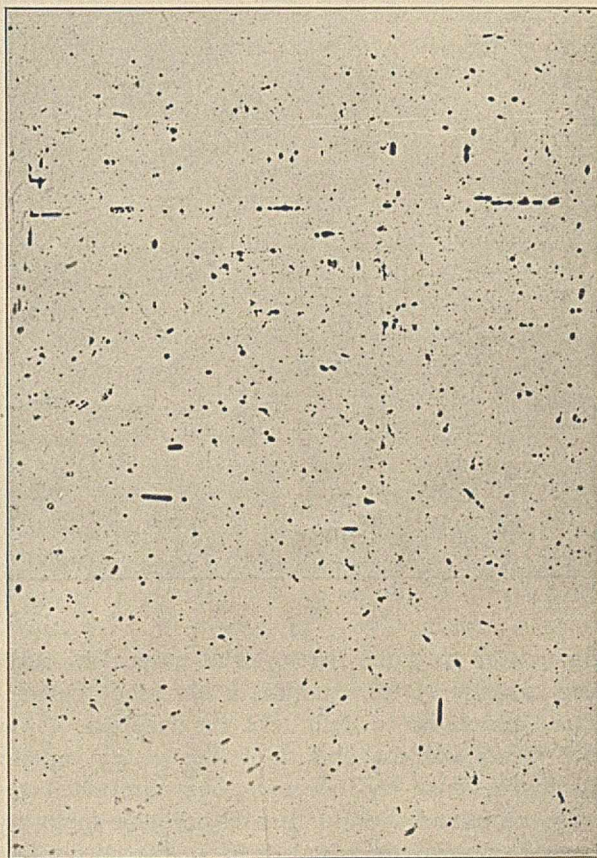


Fig. 1.

In accordance with this theory, when rust spots form upon the surface of a tin plate, the iron must dissolve at the bottom of the pin holes, and pass in this dissolved condition up through the channels to the surface of the tin where it is oxidized by the air and precipitated as rust. But the oxidation and precipitation by the air is not sufficiently rapid to

<sup>1</sup> *Jour. Am. Chem. Soc.*, 29, 1257.

be easily followed experimentally. Potassium ferricyanide, however (red prussiate of potash), is a reagent which immediately forms with these iron ions an insoluble precipitate and which is bright blue in color. Hence, if at the opening of these

is needed; owing to the gradual reduction of the ferricyanide and the action of the acid on the gelatine, the acid should be added only when the gelatine has cooled to about 40°C., and only so much of the reagent prepared as can be used within a few hours. If a large number of plates are to be examined, the sensitiveness of the reaction may be increased by soaking the plates over night in a dilute ammonium chloride solution, or by dipping them for one-half minute in 5 per cent. sulphuric acid. Either of these treatments loosen the material at the bottom of the pin holes, and allows the iron at these points to dissolve more rapidly.

The number and distribution of the pin holes as found upon an average sheet of "coke plate" is shown in Fig. 1, while a sheet of extra heavy dairy stock appears as in Fig. 2. Not infrequently the holes appear to be on lines, indicating that they

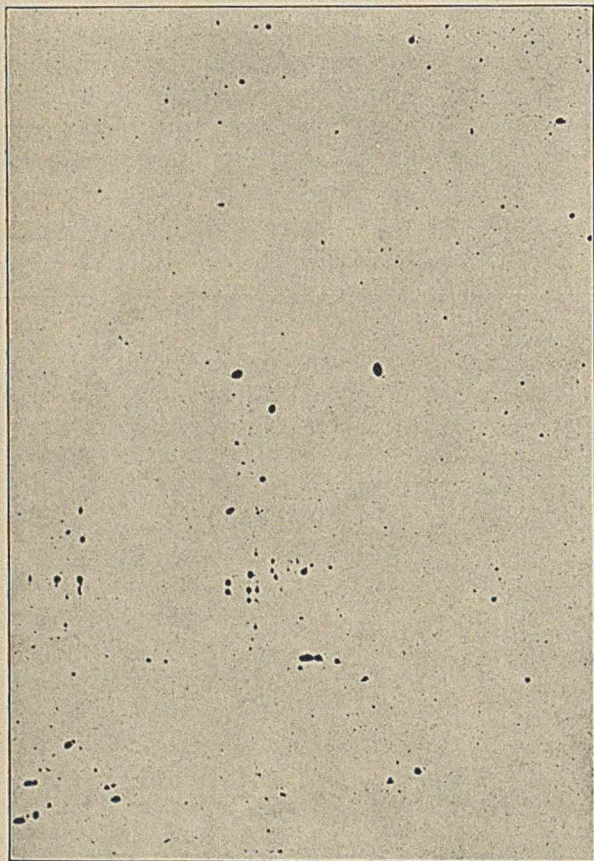


Fig. 2.

channels or pin holes through the tin coating there be a solution of ferricyanide, a blue spot will develop, and indicate definitely the location of the hole. This solvent action of the water can be greatly hastened by increasing the number of the hydrogen ions, which in turn is brought about by the addition of a very little acid. Disturbances on the surface due to convection currents may be eliminated by stiffening the solution with ordinary gelatine. The proportions which have been found to develop the majority of the pin holes within thirty minutes or so, are as follows:

Gelatine.....	50 grams
Water.....	450 "
$K_3Fe(CN)_6$ .....	1 "
$H_2SO_4$ .....	1 "

The gelatine is dissolved in the water by the aid of heat and the ferricyanide added as the reagent

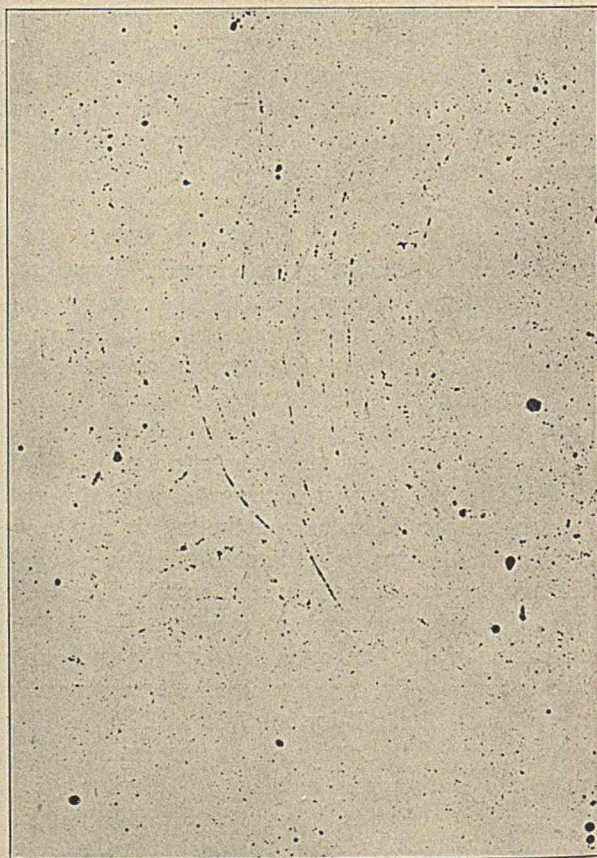


Fig. 3.

may have been caused by a scratch which at places pierced the tin coating, extending down to the iron base. This is well shown in Fig. 3 where the scratches are in curves, suggesting that they were due to the rotating brush used in cleaning the

grease or tallow from the plates, or by moving one plate over another with a twisting motion. Such injuries are seen to be ready centers of corrosion.

In order to determine what proportion of the imperfections brought out by the reagent were due to holes incident to cleaning and handling the plates after tinning, some regular coke sheets were obtained just as they emerge from the tin bath, still covered with the tallow used on the top of the bath. While the number of the holes was reduced, the improvement was not such as to warrant a radical change in the customary method of cleaning. This experiment, however, emphasizes the softness of the tin coating and the great care which must be given to handling tin plate if the centers of corrosion are to be kept at a minimum.

With this easy and accurate method of locating the pin holes or other points on the tinned surface where the iron base is exposed, it is hoped that something more definite may soon be learned regarding the cause of these imperfections and a possible method of preventing them be suggested.

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## THE CONSUMPTION OF NITRATE OF SODA IN THE UNITED STATES.<sup>1</sup>

By CHARLES E. MUNROE.  
Received March 8, 1909.

On November 10, 1904, I had the honor of calling the attention of the members of the Washington Chemical Society to the fact that as the statistics for the chemical manufactures had come to be taken by the Bureau of the Census they could be made use of in solving many problems of interest and value, provided only that they were properly used, and I pointed out that one of these problems was that of ascertaining the principal industries in which a given material was used and the extent of its use in each industry. The results of this process as applied should prove to be not only of general scientific and economic interest, but also of special value in legislation and litigation where the rule of "principal use" obtains; in determining tariffs and levying taxes; in fixing freight rates; in manufacturing and other operations where the question of substitution may arise; and in other special instances. In the investigation work of the census itself such data furnishes additional checks on the returns.

<sup>1</sup> Read at the Baltimore meeting of the American Chemical Society, December 31, 1908.

The application of this method<sup>7</sup> was illustrated by taking sulphuric acid as an example, since this is the substance of fundamental importance in the chemical industries, and there was presented, in tabular form, the results obtained. These results, after further checkage, have been published on page 23 of "Chemicals and Allied Products for 1905," this being Bulletin No. 92 of that census of manufactures.

Attention having been called to the proper use of the statistics of the census it may be well to state here that, where the chronology is of importance one should be careful to ascertain the period of time to which any given census statistics refer, because, in a census of manufactures, the data record transactions already completed at the time the investigation was made, and, because of changes in the law, as enacted by the Congress, the yearly periods covered may not be similar and the intervals between the successive censuses may not be of precisely the same length. In illustration we have the census of 1900, covering the operations for the year ending May 31, 1900, and the census of 1905, covering the operations for the calendar year ending December 31, 1904, except for the State of Michigan, where, for the purpose of coöperation with the State authorities, and to avoid duplicate enumeration in the same year, the statistics were collected for the year ending June 30, 1904.

Also it may be proper to point out the chance of error which may arise from making use of census data without consulting the text carefully so as to ascertain to what the data applies. Thus, if one wishes to obtain the statistics for the chemical industries of this country at the census of 1905 he might consult Table CX on page clxxi, of Part I, and find the value of the products given as \$1,031,965,263, or he might consult Table 1, on page 398 of Part IV and find the value of the products given as \$323,997,131 or a difference of over \$707,000,000 in the value of products for the same period of time. But on investigating the tables and their accompanying text we find the first to cover the "Chemical Group" and to embrace a large part of those substances found in chemical technologies, while the second table treats only of those substances styled in the census classification, "Chemicals and Allied Products." Also, to take another example, we find from Table 8, page 404 of Part IV, that the sulphuric acid produced at the census of 1904 was 467,614 tons, while from Table II on page 405 of the same part, the sulphuric acid

produced is reported for the same census as 1,869,437 tons, both being for 50° B $\acute{e}$ . acid. From inspection of the text we find there is no discrepancy between these figures, but that the first table treats only of the products of those establishments which are included in the census class of "sulphuric, nitric and mixed acids," while the second table gives the total sulphuric acid produced not only for sale, but for consumption also, by establishments of all kinds.

What is true of products is also true of materials used in manufacture. They may appear in different reports represented by different numbers and yet each of the statements may be correct. Such a condition of affairs may be repeatedly met with in the Reports on Chemicals and Allied Products, and it is here especially, that the text should be scrutinized, since each of the Special Reports for 1900 and 1905 embraces nearly two score of classes and some thousands of industries and, in order to present the true condition of each of several industries, it has been necessary to duplicate some of the data.

Thus if we examine the statistics of the class styled "Fertilizers," we find nitrate of soda enumerated as one of the materials used in this manufacture, and that it is used in this industry not only as a direct component of mixed or compounded fertilizers, but also in the manufacture, within fertilizer factories, of sulphuric acid by the chamber process. Again if we examine the report on the class styled "Explosives," we find that nitrate of soda, as a material used, is used not only as a component of blasting powder and of dynamite, but also in the manufacture, within explosive factories, of nitric acid and also of saltpeter or potassium nitrate. In order then to completely set forth the sulphuric acid, or nitric acid, or saltpeter industries, the quantities of these substances produced in fertilizer or explosives establishments, and of the materials used in their production, must be reassembled and presented anew.

Two methods for presenting the statistics of the consumption or distribution of the materials of manufacture are thus indicated. (1) By the classes of products in the manufacture of which the material is consumed both directly and indirectly. (2) By the products in the manufacture of which the material is consumed directly only though some of these products may constitute the raw material of further manufacture. The data under the first category is that which is reported by the establish-

ments in gross, and may be taken directly from the published census tables. The data under the second category must, on the other hand, be obtained by analyses of the data returned for each class, assigning the proportion of the material consumed in the manufacture of each intermediate and each final product, and then assembling that consumed in the direct manufacture of each single product.

Proceeding in this manner for nitrate of soda, I find:

(1) NITRATE OF SODA CONSUMED IN THE UNITED STATES BY ESTABLISHMENTS CLASSES AS FOLLOWS:

Class.	1900.	1905.
	Short tons.	Short tons.
Fertilizer industry.....	19,518	42,213
Dyestuffs " .....	223	261
General chemicals industry.....	35,990	38,048
Glass industry.....	10,770	11,915
Explosives industry.....	88,924	133,034
Sulphuric, nitric and mixed acids ind... ..	27,406	29,301
	<hr/>	<hr/>
	182,431	254,772

(2) NITRATE OF SODA CONSUMED IN THE UNITED STATES CLASSED BY PRODUCTS IN WHICH IT IS DIRECTLY USED.

Products.	1900.	1905.
	Short tons.	Short tons.
Compounded fertilizers.....	13,058	34,795
Dyestuffs.....	223	261
General chemicals.....	30,287	31,324
Glass.....	10,770	11,915
Explosives.....	76,696	100,985
Nitric acid.....	30,213	50,301
Saltpeter.....	5,703	6,724
Sulphuric acid.....	15,481	18,467
	<hr/>	<hr/>
Total.....	182,431	254,772

An attempt has been made to check these totals by comparing them with the quantities of nitrate of soda reported by the Bureau of Statistics as having been imported for consumption in the United States during the fiscal years 1899 and 1904 and 1905, taking the average of this latter two-year period. These quantities are reported in long tons, while the census quantities are given in short tons. As reduced we have 206,357 short tons as being available at the Census of 1900 and 322,709 short tons as being available at the Census of 1905. There is therefore 23,926 short tons of nitrate of soda for 1900 and 67,937 short tons for 1905 not accounted for in the tables which may be charged up to all other uses and products, such as enameling, metallurgical flux, pickling and the manufacture of minor chemicals. These last figures must be regarded as mere approximations, since stocks of nitrate are frequently hoarded and then brought out when there is a specially active demand for them, and it may therefore happen that the consumption in this country for a given year may exceed or fall below the imports for that year.

The results set forth in the tables, though not exhaustive are of interest, especially in the item of fertilizers, for there is a wide-spread belief that nitrate of soda is most largely consumed in agriculture, yet such does not appear to hold true in this country. But the conditions which obtain in this industry in the United States vary widely from those which obtain in European practice, for, in the United States, besides nitrate of soda and ammonium sulphate, large quantities of other nitrogen-containing substances are used in compounding fertilizers. Thus the statistics of the census of 1905 show that in that census year there was used for this purpose, besides the nitrate of soda, 10,540 tons of ammonium sulphate, 923,305 thousand fish, 125,888 tons of ammoniates, 1,160 tons of saltpeter, \$2,376,448 worth of cotton-seed meal and \$5,094,149 worth of bones, tankage and offal.

The menace to an extension in the use of nitrate of soda in the United States is found:

(1) In the increased use of by-product ovens for coking coal, it having been shown<sup>1</sup> that but 3,317,585 tons of the 37,376,251 tons of coal coked in this country in the census year 1905 were coked in by-product ovens and that if all had been so treated there would have been produced 359,560 tons of ammonium sulphate instead of 15,773 tons which was the actual yield from this source.

(2) In the substitution of contact processes for chamber processes in the manufacture of sulphuric acid.

(3) In the discovery of calcium cyanamid or lime-nitrogen because an extensive plant is now being erected at Niagara Falls for its production, and

(4) In the introduction of electric processes for the manufacture of nitrates from atmospheric nitrogen.

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## CHANGE IN THE COMPOSITION OF UNGROUND CEREALS DURING STORAGE.<sup>2</sup>

By SHERMAN LEAVITT AND J. A. LECLERC.

Received March 14, 1909.

The purpose of this investigation was to find out if there is any change in the chemical composition of cereals and to what extent these changes take

place when they are stored in their natural state (unground) for a period of months or years. Where many hundreds of samples are to be investigated it is not always convenient to analyze all of the samples when fresh, and as a result some samples are analyzed after they are months and in some cases even a year or more old.

It would seem possible that a deterioration or a transformation of some of the organic compounds such as carbohydrates or proteins might easily take place either due to the direct loss through respiration of carbon dioxide producing simpler compounds or to an actual conversion of one compound into another, such as starch into sugars due to enzymic action.

The authors are not aware that very much work along this line has been carried out in the past. The effect of ageing has been studied in connection with the gluten content of the grain<sup>1</sup> (good wheats maintaining their gluten content better than poor wheats), but as far as we know the study has not been applied to the different combinations of nitrogen in the grain such as the proteins and amids nor to the content of sugars.

In the fall of 1906 large samples were collected of the season's crop of four cereals, *i. e.*, field corn, Swedish select oats, Kubanka wheat and Minnesota No. 6 barley, all grown at the State Experiment Station at Brookings, South Dakota, and were sent to the Bureau of Chemistry for experimentation. Small samples of these were ground and analyzed immediately for the following substances: Water; ash;  $P_2O_5$ ; total nitrogen; albuminoid nitrogen; 70 per cent. alcohol-soluble nitrogen; 5 per cent.  $K_2SO_4$ -soluble nitrogen; water-soluble nitrogen; water-soluble nitrogen coagulable on heating; water-soluble nitrogen precipitated by cupric hydroxide (Stutzer's reagent); invert sugar; cane sugar as dextrose; weight per 1000 kernels; and weight per bushel. All results with the exception of the last two have been calculated to the *dry basis*. The samples have been ground and analyzed at intervals of six months and the results compared. In the fall of 1907 additional samples of wheat, oats and barley were collected at College Park, Maryland, at the Experiment Station. Rye was also taken as an additional cereal. The record of corn is a continuous one for two years involving five separate periods of analysis. A sample of ground corn was allowed to stand for one year and its

<sup>1</sup> Bulletin No. 65. Census of Manufactures, 1905. Coke.

<sup>2</sup> Read before the Baltimore meeting of the American Chemical Society on December 30, 1908 and published by permission of the Secretary of Agriculture.

<sup>1</sup> "La Dégénérescence des Blés," L. Vuafart, *Jr. Agr. Prac.*, 1908, No. 40, page 429.

analysis compared with the sample that had stood unground for one year.

TABLE I.  
Ground October, 1906.  
Analyzed October, 1906.  
Sugars.

Cereal.	Invert, per cent.	Cane, per cent.	Total, per cent.
Corn.....	0.43	1.73	2.16
Barley.....	0.63	2.26	2.89
Oats.....	0.50	1.05	1.55
Wheat.....	0.55	2.21	2.76
Rye.....	..	..	..

Nitrogen soluble in

Cereal.	70% alcohol, per cent.		5% K <sub>2</sub> SO <sub>4</sub> , per cent.		Water.	
	70% alcohol, per cent.	5% K <sub>2</sub> SO <sub>4</sub> , per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn....	0.65	0.24	0.17	0.09	0.17	0.09
Barley...	0.62	0.46	0.28	..	0.28	..
Rye.....	..	..	..	..	..	..
Wheat...	1.07	0.51	0.14	..	0.14	..
Oats....	0.47	0.42	0.36	..	0.36	..

Ground October, 1907.  
Analyzed October, 1907.  
Sugars.

Cereal.	Invert, per cent.	Cane, per cent.	Total, per cent.
Corn.....	0.26	0.10	0.36
Barley.....	0.94	1.70	2.64
Oats.....	0.38	0.96	1.34
Wheat.....	0.53	2.16	2.69
Rye.....	..	..	..

Nitrogen soluble in

Cereal.	70% alcohol, per cent.		5% K <sub>2</sub> SO <sub>4</sub> , per cent.		Water.	
	70% alcohol, per cent.	5% K <sub>2</sub> SO <sub>4</sub> , per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn....	0.58	0.21	0.20	0.14	0.20	0.14
Barley...	0.62	0.51	0.35	0.18	0.35	0.18
Rye.....	..	..	..	..	..	..
Wheat...	0.98	0.48	0.10	0.23	0.10	0.23
Oats....	..	..	..	..	..	..

Ground October, 1907.  
Analyzed October, 1907.  
Sugars.

Cereal.	Invert, per cent.	Cane, per cent.	Total, per cent.
Corn.....	0.35	0.41	0.76
Barley.....	0.66	1.37	2.03
Oats.....	0.52	0.82	1.34
Wheat.....	0.32	2.17	2.49
Rye.....	0.62	4.39	5.02

Nitrogen soluble in

Cereal.	70% alcohol, per cent.		5% K <sub>2</sub> SO <sub>4</sub> , per cent.		Water.	
	70% alcohol, per cent.	5% K <sub>2</sub> SO <sub>4</sub> , per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn....	0.52	0.21	0.17	0.11	0.17	0.11
Barley..	0.45	0.33	0.32	0.23	0.32	0.23
Rye....	0.59	0.56	0.70	0.43	0.70	0.43
Wheat..	0.92	0.55	0.14	0.31	0.14	0.31
Oats....	0.40	0.34	0.32	0.22	0.32	0.22

Ground in October, 1908.  
Analyzed October, 1908.  
Sugars.

Cereal.	Invert, per cent.	Cane, per cent.	Total, per cent.
Corn.....	0.40	0.29	0.69
Barley.....	0.66	1.42	2.08
Oats.....	0.61	0.88	1.49
Wheat.....	0.40	1.91	2.31
Rye.....	0.86	4.24	5.10

Nitrogen soluble in

Cereal.	70% alcohol, per cent.		5% K <sub>2</sub> SO <sub>4</sub> , per cent.		Water.	
	70% alcohol, per cent.	5% K <sub>2</sub> SO <sub>4</sub> , per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.	Total, per cent.	Coagulated by Stutzer reagent, per cent.
Corn....	0.34	0.18	0.12	0.08	0.12	0.08
Barley...	0.43	0.35	0.32	0.14	0.32	0.14
Rye....	0.61	0.65	0.58	0.24	0.58	0.24
Wheat...	0.91	0.55	0.13	0.24	0.13	0.24
Oats....	0.36	0.35	0.32	0.18	0.32	0.18

In studying these two sets of analyses in Table I, giving yearly results, we notice that the change in the sugar content of the ground corn is more marked than in the unground sample. The total sugar content of the original sample was 2.16 per cent.; after standing ground one year it was 0.36 per cent., whereas the sample that was freshly ground showed 0.76 per cent. We see from these results that about 80 per cent. of the total sugar in corn is lost in one year's time when ground, while about 60 per cent. of the total sugar content is lost on standing even without grinding.

We also notice that the alcohol- and water-soluble nitrogen compounds of corn both show a tendency to decrease with age, the alcohol-soluble decreases 50 per cent. in two years, whereas the total nitrogen remains practically constant. This would seem to indicate a slight change in the protein bodies themselves, involving some rearrangement of these complex molecules.

The alcohol-soluble protein bodies of wheat seem to indicate the same tendency to decrease with age as is exhibited in the case of corn but not to so great an extent. The sugar content of the wheat behaves quite differently from corn in many cases, although the sample of wheat which has been specially preserved for the ageing process indicates a slight falling off in the sugar content at the end of the first and second years. After the first year the tendency in many instances is to increase. This tendency to increase was shown by regrinding and reanalyzing fourteen samples of wheat which had been analyzed two years previously; in all but one a marked increase in the content of total sugar was observed, this being from 1-24 per cent. in the total sugar content.



TABLE II.

Cold extrac-  
tion.Dry basis,  
cold extraction.

Sample.	Moisture content, 1906.	Moisture content, 1908.	Cold extrac- tion.		Dry basis, cold extraction.		Percentage increase in sugar content
			Total sugar, 1906.	Total sugar, 1908.	Total sugar, 1906.	Total sugar, 1908.	
742	11.17	9.17	2.90	3.34	3.27	3.68	11.1
743	10.31	8.70	3.17	3.88	3.53	4.25	17.0
747	11.11	9.75	2.36	2.45	2.65	2.71	2.0
752	7.91	9.37	3.42	3.34	3.71	3.69	-0.5
757	9.55	8.90	2.70	2.90	2.98	3.18	6.3
760	9.31	9.46	2.40	3.14	2.65	3.47	23.6
763	9.02	9.86	2.37	3.09	2.61	3.43	24.0

In studying the sample of oats (see Table I) we find a similar change to that of corn but a more gradual one. The total sugar content has fallen off about 12 per cent. of the total sugar originally present. In barley we observe a tendency of the alcohol-soluble, salt-soluble, and the water-soluble protein bodies precipitated by Stutzer's reagent to decrease.<sup>1</sup> The total sugar also shows an appreciable loss.

Rye in the course of one year shows a very slight tendency to increase its alcohol- and salt-soluble protein,<sup>1</sup> while its water-soluble protein coagulated by Stutzer's reagent has lost about 50 per cent. The total sugar has remained practically constant, the only apparent change being an increase in the invert sugar.

At this point the authors did considerable work to determine the best method of extracting sugars from grains with the least amount of enzymic action. Extraction with boiling water kept at the boiling temperature for one hour although very troublesome on account of the gelatinization of the starch and its difficult filtration was referred to as the standard method. Assuming that the treatment with boiling water inhibits enzymic action and using this method as a standard we find that extraction with water previously cooled to 5-7° C. and kept at this temperature during the entire extraction gives results for total sugar almost identical with the ones obtained by the boiling water extraction. The results obtained by this method for total sugar are three or four tenths of 1 per cent. lower than by extraction with water at room temperature, the high results being probably due to diastatic action.

At the suggestion of Dr. C. S. Hudson, of the Bureau of Chemistry, we tried extracting the sugars with a 0.2 per cent. solution of sodium carbonate at room temperature. The results for total sugar agreed excellently with those obtained by the cold

<sup>1</sup> The changes in the protein combinations of barley, rye, wheat and oats in two years' time is so small that we do not wish to lay stress upon them. Corn, however, is an exception.

extraction, the latter method being used for all sugar determinations on ageing.

The presence of a 0.2 per cent. solution of sodium carbonate seems to entirely stop enzymic action in water infusions of cereals. The samples examined did not show the slightest trace of reducing sugars when sodium carbonate was used. (Care must be observed to see that the solution be not acidified during the process of digestion and clarification.) The total sugars, however, were the same as by the cold extraction. Water at 5-7° C. seems to be unfavorable to diastatic action.

Germination tests were made of all of these grains in December, 1908, by Dr. E. Brown, botanist of the Seed Laboratory of the Bureau of Plant Industry, U. S. Department of Agriculture, in which he obtained the following results on one hundred seeds of each of the grains submitted:

TABLE III.

	Duration of test	Per cent. germination.
Corn.....	5 days	0.0
Oats.....	6 "	55.0
Barley.....	6 "	29.5
Rye.....	6 "	0.0
Wheat.....	6 "	0.0

The germination tests are included as they may possibly help to explain some of the changes that have taken place. It has been suggested that loss of germination power by cereals during storage may bear some relation to its sugar content.

In conclusion, we would say that our results for the period of time they represent (two years) seem to indicate that there is more or less change in all cereals under the influence of ageing. These changes seem to take place whether the cereal is stored in the whole grain or is ground to a fine powder before storage. In the latter case, however, the changes take place more rapidly. We notice that the principal products which seem most susceptible to change are first the sugars and then the 70 per cent. alcohol-soluble proteins, the 5 per cent. K<sub>2</sub>SO<sub>4</sub>-soluble proteins and the water-soluble proteins coagulated by so-called Stutzer's reagent.

Corn, barley and oats are most subject to loss of sugar during ageing. On the other hand, many samples of wheat show a slight loss the first year and then quite a rapid gain in the sugar content, in some cases a gain of 24 per cent. of the total sugar present being noted at the end of two years.

Considering the grains most susceptible to protein change we have in the order given corn and to a very slight degree barley, rye, wheat and oats. As we should expect, there seems to be no

change in the mineral constituents of the grain or in the total nitrogen, the weight per bushel and the weight per 1000 kernels remaining practically constant.

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### A RAPID METHOD FOR THE DETERMINATION OF TOTAL POTASSIUM IN SOILS.

By O. M. SHEDD.

Received March 8, 1909.

The method herein described was devised for the rapid determination of total potassium in soils, but is applicable to silicates generally. It is a combination of the J. Lawrence Smith<sup>1</sup> method with the cobaltinitrite method of W. A. Drushel,<sup>2</sup> the potassium being brought into solution by the former method and determined by the latter, without previous separation of the calcium.

The procedure recommended is as follows: One gram of finely ground soil and an equal weight of C. P. ammonium chloride are well mixed by grinding them together in a mortar and these intimately mixed with 8 grams of C. P. calcium carbonate. The mixture is transferred to a platinum crucible of 25-50 cc. capacity, in which a thin layer of calcium carbonate has been sprinkled to prevent sticking of the fused mass to the bottom, and the contents compacted by gently tapping the crucible. The crucible is then covered with a well-fitting lid and supported upright over a good burner by means of a square of asbestos board through which a round hole has been cut of such size that about one-third of the crucible projects below the board and will be exposed to the heat. The heating is conducted as recommended by Smith as given in the detailed description of the process already cited. By this arrangement only the part of the crucible containing the mixture is exposed directly to the flame, while the upper part and cover are kept relatively cool, thus reducing to a minimum the chance of losing potassium chloride by volatilization. After the heating has been finished and the crucible is cool, the sintered mass is transferred to a porcelain evaporating dish, rinsing lid and crucible into the dish with hot water, adding, finally, about 50 cc. It is best to let the mass slake a few minutes with only enough water to moisten it, after which it should be well ground up with a pestle, more water added and allowed to

digest on the water-bath two or three hours. The liquid is now decanted through a filter and the mass stirred up with another portion of hot water, allowed to settle a few moments, decanted again and this operation repeated two or three times, after which it is transferred to the filter and well washed, using about 200 cc. of hot water. It is not necessary or practicable to wash free of chlorides. Indeed, in one experiment a faint test for chlorides was still obtained after washing with a liter of boiling water. The liquid, or an aliquot containing about 0.01-0.02 gram of K, is put into a porcelain casserole or dish, acidified slightly with acetic acid and evaporated to a volume of about 10 or 15 cc.<sup>1</sup> Ten cc. or a liberal excess of the cobaltinitrite reagent, prepared according to Adie and Wood,<sup>2</sup> are added slowly, so that the precipitate may not be too finely divided, and the liquid evaporated on the water-bath to a syrupy consistency becoming solid on cooling. It is important not to heat longer than is just necessary. After cooling, the soluble matters are dissolved in about 25 cc. of cold water which should give a brown solution, showing excess of reagent, and the solution decanted through a carefully prepared Gooch filter<sup>3</sup> and this operation repeated until the dish and any precipitate remaining in it have been thoroughly washed.<sup>4</sup> After washing the filter, the felt with the precipitate is returned to the dish in which the precipitation was made and well broken up by stirring with a glass rod in a little water. If any of the precipitate adheres to the Gooch crucible so that it cannot be washed off, the crucible also is to be put into the dish. A measured excess of N/10 potassium permanganate solution (usually 20-40 cc.) is now run in and the whole diluted to about 8 or 10 times the volume of permanganate added, the dish covered and its contents heated nearly to boiling over free flame or hot plate, with frequent stirring, for about ten minutes, or until the potassium cobaltinitrite is thought to have been completely oxidized. It was found that the oxidation requires a somewhat longer time than the five to eight minutes recommended by Drushel, apparently because it is hard to separate the yellow potassium precipitate from

<sup>1</sup> When the reagent is added to a dilute solution, it is decomposed before the potassium salt is precipitated. In small volumes, this does not happen.

<sup>2</sup> Sutton's "Volumetric Analysis," 9th edition, p. 62.

<sup>3</sup> The asbestos pulp for making the felt should be just fine enough to hold the precipitate and free from very fine particles.

<sup>4</sup> A half-saturated solution of common salt may be used instead of water, if there is trouble in filtering the precipitate.

<sup>1</sup> Fresenius' "Quantitative Analysis," Am. edition, page 426.

<sup>2</sup> Adie & Wood, *J. Chem. Soc.*, 77, 1076. Drushel, *Am. J. Sci.*, 24, 433. *Chem. News*, 97, 124.

the asbestos, so that the permanganate can come in contact with it. When the oxidation is thought to be complete, as indicated by the darkening of the solution and separation of manganese hydroxide, about 15 cc. of dilute sulphuric acid (1:7) are added and allowed to act three or four minutes to favor oxidation of the last traces of cobaltinitrite.<sup>1</sup> A measured excess of N/10 oxalic acid containing 50 cc. of concentrated sulphuric acid to the liter is then run in and the liquid kept at the same temperature until all the manganic hydrate has been dissolved and the solution is colorless. At this point it will be seen by the absence or presence of the yellow potassium compound, whether the oxidation of the cobaltinitrite precipitate was complete. The excess of oxalic acid is now titrated with N/10 permanganate solution. The total volume of permanganate solution used, less that equivalent to the oxalic acid added, gives the amount used up in oxidizing the cobaltinitrite and this, multiplied by the appropriate factor, gives the weight of potassium obtained. One cc. of N/10 permanganate solution is equivalent to 0.000711 gram K, or 0.000856 gram K<sub>2</sub>O. It is necessary, also, to carry out a blank experiment, under the same conditions as the analyses, using the same quantities of the reagents, and to subtract the small amount of permanganate solution consumed from that found in the analyses. The following determinations have been corrected in this way. The permanganate used was standardized by means of Kahlbaum's special C. P. sodium oxalate and also by iron wire, the two methods giving identical results. The soils analyzed were the two samples sent out for coöperative work in 1908 by the Referee on Soils of the Association of Official Agricultural Chemists, and were selected for testing this method because a number of determinations had already been made upon them in this and other laboratories by the J. Lawrence Smith method and by Pettit and Ystgard's modification of that method.<sup>2</sup> The following table gives the results obtained by the new method, in the columns headed "volumetric," in comparison with determinations by the J. L. Smith method and the average of some twelve to fourteen determinations by Association chemists, in the columns headed "gravimetric."

PERCENTAGE OF K, CALCULATED ON THE WATER-FREE SOIL.

		Sample No. 1.		Sample No. 2.	
		Volumetric.	Gravimetric.	Volumetric.	Gravimetric.
1	1 gram of soil taken.....	1.14	..	1.47	..
2	1 gram of soil taken.....	1.14	..	1.46	..
3	1 gram of soil taken.....	1.22	..	1.47	..
4	½ gram of soil taken.....	1.17	..	1.43	..
5	½ gram of soil taken.....	1.23	..	1.46	..
6	1 gram taken, solution divided... 1.12	1.12	1.07	1.60	1.45
7	1 gram taken, solution divided... 1.12	1.12	1.07	1.65	1.46
8	1 gram taken, solution divided... 1.10	1.10	1.14	1.37	1.44
9	1 gram taken, solution divided... 1.12	1.12	1.10	1.50	1.50
Average.....		1.15	1.10	1.49	1.46
A. O. A. C. average, Smith method..		..	1.18	..	1.56
A. O. A. C. average, Pettit and Ystgard modification.....		..	1.17	..	1.56

In Experiments 6, 7, 8 and 9, 1 gram of soil was treated by the Smith method as far as obtaining the solution. This was then divided into two equal parts, one-half being used for determination of potassium, as already described, and the other by the regular gravimetric method. In this way irregularities in the decomposition of the silicates would be eliminated from the comparison.

A good degree of concordance is found in the average results of all the determinations by the three methods, though there is not as close agreement as could be desired between the several findings by the new method, especially in soil No. 2, the difference between the lowest and highest being 11 per cent. of the average in soil No. 1, and 19 per cent. in soil No. 2. The low result in Experiment 8 of soil No. 2 has not been accounted for, but it is believed that the high results in Experiments 6 and 7 on the same soil were caused by too long heating of the residue after evaporation with the nitrite reagent. In these two instances the dishes were, through oversight, left on the water bath two or three hours. When the residue is heated too long, especially when the solution has not been sufficiently concentrated before the nitrite reagent is added, the yellow potassium precipitate becomes contaminated with small quantities of a bluish-green substance probably containing cobalt, which washing with water does not remove. Under these circumstances, the results appear to be too high. This source of error should be carefully guarded against also in the blank experiments. The potassium equivalent to permanganate reduced in 9 blank experiments with reagents only ranged from 0.10-0.23 per cent. K, calculated for 1 gram portions, the average being 0.1567 K, a variation great enough to introduce a very considerable error, showing that the greater

<sup>1</sup> The sulphuric acid is not to be added first, along with the permanganate, as the action would be very rapid and some cobaltinitrite might escape oxidation.

<sup>2</sup> Proceedings A. O. A. C., 1906 (Bureau of Chem., Bull. 105) page 147, also U. S. Dept. Agr., Bur. of Chemistry, Circular No. 34, p. 4.

part of the reduction was not due to potassium in the reagents.

Two control experiments made with the quantities of reagents used for 1 gram of soil, dividing the solutions from each into two equal parts and adding 0.0175 gram of C. P.  $K_2SO_4$  to each of two of these portions gave, in the halves to which no potassium had been added, 3.2 cc. and 1.65 cc. of permanganate solution reduced. In the corresponding halves, after subtracting the equivalent of the potassium added from the total volume of permanganate solution reduced, there remained 1.51 cc. and 1.24 cc. respectively, a much more satisfactory result. The plan of adding a known quantity of potassium to the control will probably give more reliable results than are obtained without this addition. These and other points affecting the accuracy of the method will be investigated further.

It is believed that these sources of error can be controlled and that the method is a promising one for rapid work, where many determinations are to be made at the same time. It has the advantages of easy manipulation, rapidity, requiring only about half the time necessary for the Pettit-Ystgard modification, and cheapness of reagents used as compared with platinum chloride.

It is self-evident that the method is of as general application to silicates as that of Smith, but it has only been tried upon soils.

POTASSIUM, AS PER CENT. OF THE WATER-FREE SOILS.

Analyst.	Sample 1.		Sample 2.	
	Pettit-Ystgard modification.	Smith method.	Pettit-Ystgard modification.	Smith method.
A. W. Gregory, Illinois...	1.156	1.205	1.568	1.582
	1.157	1.175	1.547	1.598
	1.182	1.164	1.566	1.594
	1.156	1.208	1.552	1.586
	1.158	1.223	1.547	1.566
W. B. Ellett, Virginia....	1.068	1.183	1.495	1.564
	1.081	1.121	1.487	1.536
S. D. Averitt, Kentucky.	1.190	1.162	1.552	1.491
	1.185	1.170	1.546	1.541
	1.214	1.202	1.531	1.565
O. M. Shedd, Kentucky..	...	...	...	1.510
	...	...	...	1.630
R. F. Trowbridge, Missouri	1.177	1.186	1.512	1.357 <sup>1</sup>
A. A. Wells, Iowa.....	1.271	1.121	1.608	1.751 <sup>1</sup>
	1.275	1.134	1.702 <sup>1</sup>	1.760 <sup>1</sup>
I. O. Schaub, Iowa.....	1.320 <sup>1</sup>	...	1.656	...
	1.440 <sup>1</sup>	...	1.678	...
Average.....	1.175	1.166	1.560	1.563

As the proceedings of the Association of Official Agricultural Chemists for 1908 may not appear for several months, it will be of interest to publish here

<sup>1</sup> Not included in the average.

in detail the results obtained on these soils by the several chemists coöperating, using J. L. Smith method and the Pettit-Ystgard modification.

The difference between the highest and lowest result, included in the averages, is 18 per cent. of the average in No. 1, and 12 per cent. in No. 2, by the modified method and 9 per cent. in each sample by the regular Smith method.

The author desires to express his thanks to Dr. A. M. Peter, of this Station, for many valuable suggestions made during the progress of the work.

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### LOSS OF POTASH IN COMMERCIAL FERTILIZERS.<sup>1</sup>

By F. B. PORTER AND E. G. KENNY.

Received January 15, 1909.

It is a well-known fact that at the present time there is an apparent loss of water-soluble potash, added to commercial fertilizers, when determined by the method of the A. O. A. C. This is due to the fact that acid phosphate, like clays and soils, has a certain power of withdrawing certain soluble compounds from solution. It was with the hope of learning more about this retention of potash that the following work was attempted. Our thanks are due to Mr. G. S. McDaniel for a part of the analytical work here reported.

The loss is purely a laboratory matter, being due to the solvent used in the analytical method. The Lindo-Gladding method<sup>2</sup> recognized as official by the Official Association of Agricultural Chemists requires "with potash salts and mixed fertilizers" the boiling of "10 grams of the sample with 300 cc. water thirty minutes."

A short review of the recent work of the association is to the point here. The 1901 and 1902 reports of the potash referee showed a loss of 8 per cent. and 7 per cent. respectively of the water-soluble potash added in making mixed fertilizers when the official method was used.

The addition of 5 cc. of hydrochloric acid was suggested as a means of freeing the potash. This was tried by the association for two years and recommended as an addition to the official method by the referee at the 1904 meeting. The modified method gave results much nearer the calculated amount added as shown by the following table:

<sup>1</sup> Presented before the Division of Fertilizer Chemists, Baltimore, December 31, 1908.

<sup>2</sup> Bureau of Chem., Bull. 107, p. 11.

Average of the work of seventeen analysts.<sup>1</sup>

	Sample No. 1 phosphate potash.	Different from theory.	Sample No. 2 ammoniated fertilizer.	Different from theory.
Calculated potash.....	4.31	..	4.30	..
Official method.....	3.90	-0.41	4.05	-0.25
Modified method.....	4.23	-0.08	4.33	-0.03

Action on the recommendation was postponed until the next year. At the 1905 meeting the referee reported similar results and investigated the possibility of the use of the acid solvent opening up the way for the use of potash silicates as fillers. His conclusion was "the amount of potash that could be so added is insignificant."<sup>2</sup> He also found that the laws of twenty-seven states require and specify water-soluble potash and largely because of this fact the motion to make the addition of 5 cc. of acid official, was lost.

Since that time Mr. Cushman's work on potash in feldspars has been made public and he has suggested to the association that it make a study of what really constitutes available potash in soils and fertilizers and ground mineral products so that we may have a definition of available potash.<sup>3</sup> No work has to our knowledge been done along this line as yet although the work of the Bureau of Soils on Absorption of Phosphates and Potassium by Soils<sup>4</sup> will be valuable material when the work is begun.

Our work besides confirming the loss above reported comprises a study of the conditions affecting the retention of the soluble potash and a study of the ease with which the retained potash is liberated.

The results given above which Mr. F. B. Carpenter as referee reported to the A. O. A. C. indicate that the retention of potash is a property inherent in the acid phosphate as retention is highest in phosphate and potash goods. We have found this to be the case as will be clearly shown by the results given later which also show the effect of various kinds of phosphate. Practically all the results given are confirmatory of the fact that potash is retained, so to avoid duplication they will not be given at this point.

A study of the factors affecting the retention of potash reveal the following points:

1. Acid phosphates of different ages and from different kinds of rock so far as tested show practically the same retention. The figures given are

the average of duplicate determinations. The weighed phosphate and muriate of potash were introduced into 500 cc. flasks, a little water added, allowed to stand for about an hour and then the determination completed according to the official method, boiling thirty minutes with 300 cc. water, etc.

Wt. in grams.	Potash present in.	Kind of rock used in making.	Acid phosphate.		Potash theory.	Potash found.	Retained, per cent.
			Age in months.	Potash retained.			
7.00	0.19	Blue Tenn.....	6	9.97	9.71	0.26	
7.00	0.11	Brown Tenn.....	4	9.89	9.66	0.23	
7.00	0.12	Fla pebble.....	2	9.90	9.64	0.26	
7.00	0.10	Low-grade Tenn.....	5	9.88	9.65	0.23	
7.00	0.14	Low-grade Tenn.....	18	9.92	9.70	0.22	
7.00	0.11	Low-grade Tenn.....	4	9.89	9.61	0.28	

The approximate factory guarantee for the above would be 10-0-10.

2. The amount retained increases with high percentages of potash.

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	Approx. factory guarantee. <sup>1</sup>
6.45	1.10	1.07	0.03	10-0-1
6.45	2.10	2.08	0.02	10-0-2
6.45	4.10	3.98	0.12	10-0-4
6.45	6.10	5.91	0.19	10-0-6
6.45	10.10	9.81	0.29	10-0-10

In these experiments the flasks stood one hour after the dry phosphate and muriate had been thoroughly mixed. 200 cc. water was then added and the test allowed to stand another hour. A comparison of these results with the table immediately following, shows that this procedure gave less retention than was obtained when the 200 cc. water was replaced by 10 cc. as was the case in the latter table.

3. The amount retained increases with the amount of acid phosphate present.

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	Approx. factory guarantee.
2.58	4.04	3.99	0.05	4-0-4
5.16	4.08	3.92	0.16	8-0-4
6.45	4.10	3.85	0.25	10-0-4
7.24	4.12	3.80	0.32	12-0-4
9.04	4.14	3.81	0.33	14-0-4

4. Acid-free dried phosphate still retains potash. Acid phosphate was extracted with absolute alcohol to remove free acid and moisture and then dried to remove alcohol. Seven grams of this material in a flask as above reduced a theoretical percentage of 5.45 to 5.28 or a retention of 0.17 per cent. This figure may be low, as the theoretical percentage was calculated on the supposition that the alcohol

<sup>1</sup> In the factory guarantees, the first figure refers to available phosphoric acid, the second to ammonia, the third to water-soluble potash.

<sup>1</sup> Bull. 90, p. 109, Bureau of Chem.

<sup>2</sup> Bull. 99, p. 137, Bureau of Chem.

<sup>3</sup> Bull. 105, p. 194, Bureau of Chem.

<sup>4</sup> Bull. 32, Bureau of Soils.

extracted the small amount of soluble potash contained in the original acid phosphate,

5. The higher the concentration of potash the quicker the retention takes place. Parallel tests in flasks as above, allowing three hours' contact with 10 and 100 cc. of water, gave the following results:

Grams acid phos.	Potash theory.	Potash found.	Potash retained.	cc. water.	Approx. factory guarantee.
7.13	10.11	9.65	0.46	10	11-0-10
7.13	10.11	9.78	0.33	100	11-0-10

6. Ground phosphate rock retains potash. Ten grams of brown Tenn. rock retained 0.18 per cent. potash. The percentage found was 9.65, while the percentage added was 9.83. This rock contains some clay, so it remains an open question whether either the fluoride or phosphate of calcium in the natural state retains potash.

7. A part of the loss of potash is due to the precipitate produced by ammonia and ammonium oxalate. 7.13 grams acid phosphate were boiled with 300 cc. water and filtered into a 500 cc. flask, the potash was then added and to the filtrate the usual precipitants were also added.

	Per cent.
Potash present.....	10.10
Potash found.....	9.95
Potash lost.....	0.15

8. Number 1 tankage shows practically no tendency to retain potash. Ten grams were boiled with the muriate of potash as above.

Potash present.....	10.19
Potash found.....	10.18
Potash lost.....	0.01

9. Number 1 tankage partially prevents the retention of potash. Four grams of tankage added to determinations which were in all other ways duplicates of those given under (1) gave a retention of 0.18 per cent. instead of an average of 0.25 per cent. shown in No. 1. This agrees with the results of the A. O. A. C. above quoted which show 0.41 per cent. loss on phosphate and potash and only 0.25 loss on ammoniated goods. This same point is proven by the table given under (10).

10. Retention reaches a maximum in stored goods. We have shown above that with 10 cc. water, we get a high retention in one hour but just how long it takes to get the maximum loss under factory conditions we have not determined but believe it requires several days. The following results show that there is no further loss in six months on samples a little over a month old.

Approx. factory guarantee.	Per cent. water-soluble potash		Pot. in insol. Residue (fusion).	Per cent. potash retained.	Average per cent. potash retained.
	5/1/08	10/1/08.			
12-0-4	3.27	3.28	0.36	0.36	Acid potash
10-0-4	3.65	3.65	0.37	0.37	
8-0-4	3.35	3.40	0.34	0.34	0.35
10-0-2	1.66	1.67	0.33	0.33	
8-2-2	2.07	2.06	0.26	0.17	Ammoniates
8-3-3	2.94	3.02	0.28	0.19	
8-4-4	3.73	3.83	0.27	0.18	0.18

In this last table we have attacked the problem in another way. Fusing and determining the potash in the dried water-insoluble residue by the J. Lawrence Smith method and deducting the water-insoluble potash known to be present in the tankage in the case of ammoniated fertilizer we have obtained the potash retained in samples whose exact potash content was not known. The general agreement of results obtained by the two methods is good. Blanks were made on the chemicals used in both cases.

The above results bear out the supposition previously held that the retention of potash is not due in any marked degree to the formation of a chemical compound, but is nothing more nor less than happens to a larger percentage of the potash when it comes in contact with the soil, as shown by the work of Schreiner and Failyer in *Bull. 32, Bureau of Soils*.

The ease with which the retained potash is freed is indicated by the following results:

Approx. factory guarantee.	Potash in insoluble residue (fusion).	Potash in residue soluble in		Potash in residue soluble in water.
		neutral ammonium citrate.	Potash soluble in citric solution.	
12-0-4	0.36	0.21	..	0.07
10-0-4	0.37	0.20	0.23	0.11
8-0-4	0.34	..	0.30	..

We feel safe in concluding from these figures that about 25 per cent. of the retained potash is liberated by the first contact with rain water and about 56 per cent. by the first contact with the soil solution. As a comparison Mr. Cushman's results on feldspars show only 0.025 per cent. of the total weight liberated by one extraction with water. We have therefore in the retained potash not an insoluble valueless form but a form readily available to the plant long before the plant has used the part shown in the water-soluble test, and it is probable that in soils deficient in clay this retained form is of even greater value because it will in a measure resist the wasteful leaching processes until the plant has need of it.

The six states, Alabama, Georgia, Louisiana, Tennessee, North and South Carolina, could, under

their present laws, adopt the plan of reporting all of the available potash as shown by some modified method, and in so doing hasten the time when other states would change their laws.

The laws of the other twenty-seven states mentioned by the 1905 referee are probably modeled, as Mr. Booker has said, after the Massachusetts law "which was framed back in 1873 before we had experiment stations, when the idea was that only water-soluble materials were available."

LABORATORIES,  
SWIFT FERTILIZER WORKS,  
ATLANTA, GA., AND WILMINGTON, N. C.

## ADDRESSES.

### COAL ANALYSIS<sup>1</sup>

By N. W. LORD.

Within the last few years the subject of coal analysis has become of great importance to many lines of industry. The demand for the analysis of coal has come from a great variety of sources and largely from those having little acquaintance with chemical methods and the interpretation of chemical results. The chemists, on the other hand, have been compelled to take such methods as were found at hand, and the result of these conditions has been not altogether satisfactory in many ways.

If we consider somewhat in detail the various determinations made in the laboratory in connection with coal testing, it will be easy to show how much is commercial and how little what might be called scientific. The so-called analysis of a coal is usually a practical test of purity of the material on a small scale, but it also involves determinations which are supposed in some way to indicate the nature of the coal itself.

To illustrate, suppose we consider an ordinary sample of bituminous coal. It may be assumed to consist, first, of an organic constituent composed of vegetable residues more or less altered but retaining traces of its original woody structure and composite character and containing as an integral part certain inorganic components. Like its source, woody fiber, it absorbs moisture in damp weather and gives it up in dry weather. The ultimate chemical composition of this material varies with the extent of the alteration, as shown in the peats, lignites and bituminous and anthracite coals, and also, in all probability, with the nature of the vegetation from which it has been derived. This extremely complex and indefinite material may be called "coal substance" for want of a better term. Intimately mixed with this are inorganic substances, probably mechanically introduced with the original vegetable debris or else precipitated by secondary reactions from circulating waters. These may be in the nature of clays or fine sand and also intimately mixed iron pyrites. I have examined samples of coal under the microscope, in which microscopic crystals of pyrites were scattered through the mass in sufficient amount to give high percentages of sulphur in the total,

yet in which a superficial examination of the coal itself practically showed no pyrites to the unaided eye. Other minerals may be present in the same way, even such unusual constituents as zinc blend, and, as Dr. Hillebrand has shown, considerable percentages of vanadium sulphide. The extremely complex nature of the organic constituents themselves may be inferred from the variable but sometimes very large amounts of sulphur they contain, well shown in the case of certain peats.

Now in addition to this base constituting the principal part of the sample submitted to the chemists for analysis, it has secondly, more or less coarse admixture of slate, clays and other rock-like material occurring in connection with the deposits of coal and not properly separated in mining, bone coal, and also streaks of cannel and other associated materials, coal-like in character, but differing notably even in the organic material they contain from the coal itself. The fact that many of these ingredients on standing or exposure to air rapidly alter by absorption of oxygen, evaporation, etc., makes it appear that the problem is still further complicated.

Now some of the things that the users of coal wish to know and for which they turn to the chemical analysis in the hope of receiving information are the following: the heating power of the coal; the amount of ash or inorganic matter left on burning the coal; the nature of the combustion of the coal, whether flaming, smoking, rapid, or slow; the gas-producing quality of the coal both as to yield and as to the nature of the gas; the nature of the ash yielded by the coal, whether fusible or not; the amount of sulphur the coal contains; the coking quality of the coal and the purity of the coke produced; and the possibilities of improving its quality by coal washing.

In addition to the above are many questions of special character, such as the nature of the coal substance, the relation of its composition to the previous geological history of the deposit, and the relation of total heating power to the heating power actually available for technical operations.

What are the analytical methods at present used in the laboratory to meet this series of questions and to handle this very complex material? Most of the laboratory work is done upon a sample which represents or is intended to represent the average composition of the material and which in no way recognizes the separate constituents of the very complex mineral aggregate of which it purports to be an average. The methods therefore give results only approximately related to the coal substance and difficult of general application.

We have as of generally recognized importance the ultimate analysis as ordinarily made, giving the determination of the hydrogen, the carbon, the nitrogen and the sulphur and the percentage of ash left after burning. This analysis also includes an estimate of the oxygen by difference, which is of course only approximate, and has been frequently pointed out in discussions of the subject. This ultimate analysis is capable of a high degree of accuracy for certain elements, which I think could be safely stated as within 0.05 per cent. in the case of hydrogen and perhaps 0.3 per cent. on carbon, 0.03 per cent. on the nitrogen and 0.05 on the sulphur. I do not mean that closer results are not obtainable, but ordinary work in the laboratory by competent chemists would, I think, run within

<sup>1</sup> Read at the Illinois Fuel Conference, Urbana, Ill., March 13, 1909.

these limits. The value of the ultimate analysis in all technical applications of the coal consists in its giving a reasonably accurate basis for the calculation of products of combustion and for comparisons with the heating power of the coal otherwise determined. The weakest point in the ultimate analysis is the uncertainty of its connections with the actual composition of the organic material as distinct from the impurities. Carbon, hydrogen and sulphur are present occasionally as carbonates, as combined water and as sulphates, respectively, in the slates and other mechanical admixtures, and the ultimate analysis does not distinguish between such occurrence and that in the coal substance. Ingenious efforts to eliminate these uncertainties as affecting the heating power by examination of various samples of the same coal differing widely in percentage of mechanical impurities have been made by several chemists.

In addition to the ultimate analysis, we have the more commonly made "proximate analysis," consisting of the determination of the moisture, ash, fixed carbon and volatile combustible matter in the coal. Much has been written in regard to these determinations.

On the same sample of coal closely agreeing results can be obtained on the ash and fairly close on the moisture. The variations in the volatile combustible is much larger and can only be kept within reasonable limits by very careful adherence to a defined method of procedure. The term moisture simply means the loss in weight under fixed conditions of treatment. It is intended and does bring the material to a condition which can be duplicated closely and represents a fixed basis for comparison, but in no wise stands for all the water in the coal. The volatile combustible, as has been carefully investigated by Professor Parr, is by no means properly named. Only a fraction, and a variable fraction at that, depending largely on the kind of coal, is combustible, and a considerable fraction, consisting of water vapor, carbon dioxide, nitrogen and other diluents is inert or non-combustible. It is well to recollect that the proximate analysis of coal was devised many years ago, and primarily as a means of testing the amount of coke left by coal. The volatile combustible has since been the subject of much discussion and many attempts have been made to correlate it with heating value, geological changes and the various questions arising in coal utilization. Some undoubted connections have been shown, but I feel that possibly too little recognition has been given to the empirical and more or less uncertain nature of the determination.

Of growing importance, particularly in connection with coal washing, and as a means for the study of coal samples, is the application of the separation by gravity or the so-called "float and sink" tests, in which the coal crushed to a moderate degree of fineness is separated on solutions of high specific gravity, chloride of calcium for specific gravities up to 1.35 and chloride of sulphate of zinc for higher specific gravities. Chloride of zinc solution can be made of a specific gravity as high as 2 and by dilution any of the intermediate gravities can be obtained. I have used this method in my laboratory for years to separate heavy mineral materials like slate and pyrites, as preliminary to the study of the composition of coal. The method is excellently adapted to tracing out the variations in composition as the inter-mixed mineral substances are eliminated. It will enable the experimenter to distinguish with considerable accuracy

between the inherent intimately mixed ash and sulphur compounds and the coarser and mechanical contaminations.

In recent years the leading factor in the commercial valuation of coals has become the calorific value or heating power of the coal and to-day the most important demand on the laboratory is the determination of this. The widely extending use of the bomb calorimeter is leading to new problems for the investigation of the chemists. Here again the heating value of the sample is modified more than by mere dilution by the nature of the mineral aggregate. As Mr. Turner and others have shown, the heating value is not entirely proportional in a given kind of coal to the residue left after deducting the ash and the moisture, but that there are factors depending on the influence of the inorganic material. Work of this kind is of great importance in order that the effect of ash, moisture and pyrites on the commercial value of coals may be more accurately known.

Calorimetry demands considerable training and experimental skill and the recently adopted policy of the Bureau of Standards of furnishing materials of known heating value so that the constants and correction of the calorimeter can be determined is greatly to be commended. The possibility of error in calorimetric determinations due to alteration of samples should be borne in mind. A very finely pulverized coal sample will oxidize in many cases very rapidly, and comparative results by different chemists on such a sample are liable to be very unsatisfactory unless all made at approximately the same time on samples that have been sealed in air-tight receptacles. Experiments made by the Fuel Testing Plant afford ample evidence of the extent to which this alteration may take place.

The determination of the water equivalent of the calorimeter experimentally gives rise to many difficulties and hence, except for those having had a great deal of experience in fundamental measurements, it is far better to use the calorimeter as a comparative instrument and depend for its constants upon burning substances of known calorific value such as are furnished by the Bureau of Standards. Commercial chemicals are quite variable and different samples of naphthalene, benzoic acid, etc., from different dealers will differ notably in their heating value. Recently the writer has obtained very successful results by the method of mixtures, adding hot water to the calorimeter from the Dewar flask or thermos bottle in which it is possible to read with great accuracy the temperature of the added water and to add the water to the calorimeter with only a very small correction for radiation loss during the addition. The method has proved successful in the hands of students who have made a number of water equivalent determinations agreeing within a very small limit of error with the calibration of the calorimeter obtained in other ways. Of course, this method has the advantage of being absolute and not relative.

The foregoing outline has dealt with the laboratory side of the question. All the analytical work, calorimetric work and everything else in connection with the testing depends for its economic value on the fundamentally representative nature of the sample of coal tested in the laboratory. Here is the weakest point in the commercial application of the results. Coal sampling is a matter now prominent before the technical world. Now that the extending



recognition of the value of laboratory work is leading to the purchase of coal on chemical specifications the whole question of sampling is under review. Ingredients most affected by sampling are obviously moisture, ash, sulphur, and calorific value. In a recent paper of great interest Mr. E. G. Bailey has presented a large number of results in which he criticizes existing methods and lays down certain general deductions from carefully conducted experiments as to the general principles involved in the securing of correct samples. Mr. Bailey has, in my opinion, done a very valuable piece of work both in calling attention to the importance of the subject and in the experiments that he has brought forward. As having been connected with the government work at St. Louis, I feel called upon to correct certain misapprehensions in regard to that work which I think have unintentionally on his part led him to place in a somewhat false light as to the accuracy with which the sampling was done. As I follow his paper he makes a fundamental assumption that the variations in the portions of coal taken at the plant from the same car shipment and sent to the Boiler, the Gas Producer and Briquetting and Washing Plants were identical in composition with the car load samples and that the variations shown in these different portions were due to variations in sampling of the portions at the various plants, whereas, the facts of the case are that the different portions taken from the car were not supposed to be sampled from the car but simply portions unloaded at different points, and the reason why analyses were made of the separate portions was because it was recognized that the car load was not uniform as far as contents of ash, sulphur, etc., were concerned, and that the car load analysis could not be taken for the different portions without a preliminary thorough mixing of the whole car load, which was not practical. This is clearly stated on page 284 of Professional Paper 48, Part I, from which I quote:

It was intended that the car sample should represent the average of the whole car, while the other samples stood for different portions of it. These would average about 5 tons each. In some cases the car sample was taken on only a part of a car. The large variation in the different samples in a few cases shows the irregularity in the coal in the car.

Experiments were made at St. Louis and published in this same work, giving the analysis of duplicate samples, and while the results were not very satisfactory and some errors were found, they were not of the magnitude given by Mr. Bailey from his comparison of the other samples based on the assumption which I have shown was not warranted and which was contrary to the facts as we stated them at the time. Br. Burrows has discussed the question of mine samples, but the comparison of these with coal shipped from the mines makes no allowance for the extent of cleaning that the coal underwent in shipping and in taking the mine samples. As stated, several duplicate samples on the car loads were run to check the St. Louis sampling and the worst result obtained, I think, was the one given on page 287, in which an extreme variation in ash on a coal averaging 15 per cent. ash was a little over 2 per cent. This coal was selected as the worst obtainable from the standpoint of sampling and the variation of the highest and lowest samples from the average of all the experimental samples on this coal was only a little over one per cent. Notwithstanding this criticism that I felt compelled to make of Mr. Bailey's representation of the St. Louis work, I feel that this general

proposition in regard to the uncertain nature of much coal sampling is well sustained. His conclusion as to the amount of sample necessary in order to obtain a representative sample are of great interest. However, I do not feel that the difficulties are quite as great as his experiments would lead one to conclude.

Two things are important to consider:

In the first place, that in crushing coal a large proportion of fine material is produced so that the average size of particle is but little more than one-half the maximum size and therefore results on the distribution of the maximum size pieces greatly aggregate the difficulties. I recently took four samples of screened coal and had them put through a jaw crusher and screened.

In No. 1, 8.8 per cent. was retained by a  $1/2$ " screen and 56.4 per cent. passed a  $1/4$ " screen. This sample of coal was sampled in duplicate at this state of crushing, portions of coal of about five pounds being taken. The two five-pound portions were each separately pulverized, well mixed and analyzed. The first portion gave 13.86 per cent. ash and the second portion 13.56 per cent. A similar experiment on a second sample of coal gave 16.3 over a  $1/2$  inch screen and 46.65 per cent. through a  $1/4$  inch screen. The ash in the first sample, 14.59; in the second sample, 14.49. A third sample of coal gave 7.3 per cent. over a  $1/2$  inch screen and 48.3 per cent. through a  $1/4$  inch screen. The ash in the first sample was 15.11; in the second sample, 15.10. In two of these samples the percentage of ash in the finer portion was considerably greater than the percentage of ash in the coarser portion.

Of course, these results are too few in number to amount to anything, but they show that the finer material is in sufficient proportion to diminish the irregularity introduced by the bad distribution of the coarser lumps in the sample.

A further point in coal sampling which has to be considered is that in the larger sizes there is a natural mixture in the material of the slate and the coal, so that 4-inch lump coal does not represent a mixture of 4-inch lumps of coal and 4-inch lumps of slate to any appreciable percentage of the ash present. In other words, the inspection element must enter coal sampling, and no man would draw a moderate sized sample of a coal in which he has a large percentage of lumps of slate as large as the lumps of coal, while the occasional presence of even a large lump of slate would have but little influence on the ash percentage of the resulting sample.

Mr. Bailey gives what he names the size weight ratio or the relation between the maximum sized piece of coal in the sample and the weight of coal necessary to take in order that the sample may be certainly representative within an error of one per cent. of ash.

Now his figures lead to very large samples in cases of lump coal, but the foregoing indicates that the size ratio should probably be that of the maximum slate sizes present in the coal lumps, or free, rather than the actual coal lump size. The moderate variations in the ash percentage of the different lumps would have far less influence in disturbing sampling than the presence of equivalent sized lumps of slate.

Obviously, therefore, careful inspection must precede the sampling in the case of lump coal and the presence of large pieces of slate and pyrites in lumps in the coal taken into

consideration in determining the size of sample necessary in order to properly sample the coal.

I have always directed samplers to inspect the coal carefully and break up into small pieces any lumps of slate, bone coal or pyrites found or anything else that did not look like coal before taking or dividing the sample.

Of course, it is well known that no system of sampling which is purely mechanical is satisfactory for materials in which coarse distribution of the components exists, unless the whole of the material is crushed to approximately such limits as are defined by Mr. Bailey. This is the principle involved in the sampling of lead and copper, and gold and silver ores, where the system of sampling involves the crushing of many tons of material. Such a system of sampling is, of course, out of the question with lump coals where the crushed material would be to a certain extent rendered of small value. The system of sampling adopted in this case must be based upon an estimate of the maximum size of slate and pyrites, constituting an important portion of the impurities.

The difficulty of eliminating the personal element in doing such sampling is one of the problems which the Committee on Specifications will have to contend with. Meanwhile, the sampling problem is before us and must be adequately solved before the laboratory analysis of the coal reaches its full application.

The preparation of the laboratory sample from the field sample is a much more simple matter and is easily within the reach of present methods. One of the principal difficulties involved at this point is the avoiding of changes in the composition of the sample due to loss of moisture and to oxidation. I notice in many experiments the coal is ground to 100-mesh or even 200 before analysis. I think this is a step in the wrong direction. The finer the powder the more prone to oxidation and loss of moisture, and I think the effort of the sampler should be to determine a lower limit for Mr. Bailey's "size-weight-ratio" as well as a higher, and not to reduce the sample beyond this point, before weighing out for analysis.

We have considered that a sixty-mesh sample will meet the ordinary requirements where 1 gram is taken for the determination, which is within Mr. Bailey's figures as I understand them.

## REVIEW.

### PHARMACEUTICAL CHEMISTRY DURING 1908.

(Concluded from page 260.)

#### Organo-Therapeutics or Organo Remedials.

The first to call attention to this class of remedials was Brown Séquard, who advanced the hypothesis that "all glands of the body give to the blood useful principles, the absence of which is felt when these glands are extirpated or destroyed by disease." This hypothesis was extended to include various organs and that in a diseased condition of an organ, an extract prepared from the same organ of a healthy animal serves as a remedial agent. The efficacy of extracts of certain organs may be best judged by the success attending the use of such preparations as Iodothyridin (thyroid ext.), suprarenal preparations, testaden, spermin

(testacle ext.), ovaraden (ovaries ext.), manimae (udder ext.), Linadin (spleen ext.), etc. New in this line are:

Manimin, an extract of the manimary glands, useful as hemostatic in uterine hemorrhage.

Paratoxin, a toxin obtained from bile and used in tuberculosis.

Leciferrin, a lecithin iron preparation from egg yolk.

Neuroprin, an extract of the nerve tissues useful in nervous diseases and as an antidote in strychnine poisoning.

Pancrobilin, a nucleo enzyme from the pancreas and gall, useful in constipation.

Orchicithin, an extract of the testes of the ox which is employed in sexual neurasthenia.

Astauxin, a calcium paranucleinate used as antirachitic.

Cellasin, a carbohydrate and fat splitting-ferment claimed to hydrolyze 3000 times its weight of starch or sugar.

#### Alkaloids and Glucosides.

Among the purin derivatives, Theophyllin (Theocin), a 1.3-dimethyl, 2.6-dioxypurin and its alkali double salts, still maintains a front rank among the diuretics. Through interaction between theobromin and monochlorhydrin, a dioxypopyl-theobromin has been prepared (Bayer, D. R. P. 191106). In an analogous manner, a 1.3-dimethyl-7-oxyethylxanthin has been prepared from theophyllin and glycolhydrin. Paraxan, a dimethylamino derivative of 1.7-dimethylxanthin, introduced by Boehringer and Sohn, has been withdrawn because of its irritant gastric action. Schwabe<sup>1</sup> has prepared various alkyl derivatives (ethyl, propyl, benzyl) of theophyllin and through oxidation of ethyl theophyllin, he obtained a dimethylparabehenic acid. These products are still in the experimental stage. A new diuretic is the double salt of theobromin sodium and sodium lactate called Theolactin.<sup>2</sup>

#### Morphine Derivatives.

The hydroxyl groups present in morphine are intimately associated with its toxic action, which, through its narcotic characters, differs from all other opium alkaloids, its action being chiefly upon the nerve centers of the brain. Upon closing these OH groups by substituting one or both of these hydrogens by alkyl or acidyl radicals, the narcotic characters disappear, while on the other hand, a spinal excitant (tetanic action) is developed. Thus, codeine produces, like morphine (but in lesser degree) narcosis, followed by an elevated reflex, which, if the dose be sufficiently large, develops tetanic convulsions. This action upon the spinal cord increases with the number and molecular weight of the alkyl groups introduced; hence codethylene, with its ethyl group, is more intense in action than codeine, which contains but one methyl group. Among all possible derivatives, it is immaterial as to whether an acidyl or alkyl radical, aliphatic or aromatic, is introduced. There is practically no qualitative difference in action so long as the same hydrogen is replaced. During recent years a number of derivatives of the codeine type have been introduced. These substances, while less active for relieving pain, exert a sedative effect on the unstriated muscles of the bronchi, and reduce the disposition to cough; hence are of value in phthisis, bronchitis, asthma, etc. Among these were Dionine, the hydrochlorid of ethyl morphine (HO.C<sub>17</sub>H<sub>17</sub>.NO.O.C<sub>2</sub>H<sub>5</sub>,

<sup>1</sup> *Ber. d. Chem. Ges.*, 40, 1744.

<sup>2</sup> *Chem. Ztg.*, 1908, 367.

HCl), Heroin, the hydrochlorid of diacetic ester of morphine,  $(\text{CH}_3\text{COO})_2\text{C}_{17}\text{H}_{17}\text{ON}, \text{HCl}$ , and Epiosin, an amidazole derivative of morphigenine. Quite recently, the J. D. Riedel Co. has prepared a bromomethyl morphine derivative, morphosan (D. R. P. 166362, 175796, 191088), and the Knoll Co., a triacetyl derivative (D. R. P. 175068), the two hydrogens of the hydroxyls and one of the nucleus being substituted by acetyl groups.

Nascein: This opium alkaloid is employed to a limited extent as well an antispasmin (narcein sodium, sodium salicylate) and narceyl (ethyl narcein hydrochlorid) as sedatives and antispasmodics. Recently, the Knoll Co. have prepared various alkyl derivatives through action of dimethyl and ethyl sulphate on the alkali salts of narcein and homo-narcein (D. R. P. 174,380, 183,589). Esters of these are prepared through treatment with dehydrating agents as acid anhydrids, the carboxyl hydroxyl group with the H of the methylene, separate as water, yielding aponarceine (D. R. P. 187,138). Arecolin, the methyl ester of arecaidin, a myotic alkaloid found in the betel-nut, has been prepared synthetically by Wohl<sup>1</sup> from methylamido- $\beta$ -dipropionic aldehydtetraethylacetal, by action of conc. hydrochloric acid, the resulting *n*-methyl- $\Delta$ -tetrahydropyridin aldehyd is through its oxim converted into methylhexahyronicotinic acid (arecaidin). Gadamer and Ginzl<sup>2</sup> find in columbo root, three alkaloids, analogous to berberin but differing in the number of hydroxyl groups and ester arts. Columbarin,  $(\text{C}_{20}\text{H}_{22}\text{NO}_2)$ , the principal alkaloid, contains 4 methoxy groups. New among the quinine salts are the nucleinate, a combination of 60% of the alkaloid and 40% of nucleinic acid, employed subcutaneously in syphilis and quinine anhydromethylenecitrosalicylate, a compound of this alkaloid and novaspinin. This contains less quinine and more salicylic acid than a salicylate or the acetyl salicylate. Xaxaquin is a quinine acetyl salicylate which combines antirheumatic and analgesic effects. A new method for preparing esters of quinine is embraced in the German patents 178,172 and 178,173, of the Vereinigten Chinin Fabriken zu Frankfurt, utilizing the Grignard's reaction in which anhydrous quinine and alkyl, aryl or aralkyl magnesium halids react in presence of ether. The resulting quinine oxymagnesium halids are then esterified by acid chlorids or their anhydrids. Barger and Carr<sup>3</sup> propose the formula  $\text{C}_{33}\text{H}_{30}\text{O}_5\text{N}_2$  for ergotin, the anhydrid of the amorphous ergototin (m. p. 162-164°), which is more active than the former.

Cannabinol: This active principle of hascheesh is assigned the formula  $\text{C}_{21}\text{H}_{30}\text{O}_2$ , boils at 230° (0.1 mm.), forms a yellow thick mass which oxidizes readily in the air. It contains a phenolhydroxyl and an aldehyd group.<sup>4</sup> Pictet<sup>5</sup> isolated pyrrolidin ( $\text{C}_4\text{H}_9\text{N}$ ) and *N*-methyl pyrrolin ( $\text{C}_5\text{H}_9\text{N}$ ) from tobacco. In poppy leaves, pyrrolidin and the base  $\text{C}_{11}\text{H}_{18}\text{N}_2$  (b. p. 240-250°), called Dauien, similar to nicotin, were also isolated. In the seeds of the poppy, pepper, parsley and cocoa leaves, *c*-methylpyrrolin and other bases of the pyrrol series were isolated. The author considers that these simple bases, whose molecules contain hydrated pyrrol nuclei, are decomposition products of the albuminoid bodies of

plants, from which, through condensation, high molecular complex alkaloids are formed. According to the work of Nierenstein<sup>1</sup> the Decker's formula for tannin, a derivative of phthalic anhydrid, is more probable than the older view of its gallic acid origin.

C. Liebermann<sup>2</sup> finds an oily base (b. p. 132-137° at 11 mm.) in cocaine, which is the ethyl ester of anhydroecgonin. Saxuranin is a glucosid ( $\text{C}_{22}\text{H}_{24}\text{O}_{10}$ ) isolated from *Prunus Pseudocerasus*, m. p. 210-212°. Taxicatin is a glucosid of the *Taxus baccata*, which forms needles fusing at 166-167°. Velledol is the active constituent of *Viscum album* used in arteriosclerosis.

#### Miscellaneous Chemicals.

Phenyl dihydroquinazolin tannate has been introduced under the title of desalgin (A. Voswinkel, Berlin) as an appetizer. Plejopyrin is a condensation-product of benzamid and phenyldimethylpyrazolin (m. p. 75°), used in migrain. Quietol produced by the action of valeric acid on the product of the interaction between dimethylamin, chloroxyisobutyric acid and propyl alcohol,  $(\text{CH}_3)(\text{CH}_2\text{N}(\text{CH}_3)_2):\text{CO.CO.CH}_2.\text{CH}(\text{CH}_3)_2(\text{COOC}_3\text{H}_7)$ , the substance fuses at 118° and is proposed as a sedative. Asiphyl is the mercury salt of *p*-anilinarsenic acid, possesses the combined action of atoxyl and mercury. Torulin, a dry stable yeast proposed in infectious diseases. Meligrin is a condensation product of dimethyloxyquinine and methylphenylacetamid used in migraine.

Thiozin is a linalyl sulphur compound used in all cases where sulphur is indicated for external use. Chromium sulphate has recently been recommended in locomotor ataxia, cirrhosis of the female breast, neurasthenia, functional impotency. Diacellulose is a hemicellulose preparation made from agar-agar through the action of enzymes or hydrolytic agents, used in diabetes.

Medicinal quackery existed in the earliest periods of history, whether practised by the Babylonians in placing their sick in the market places where the general public might prescribe, or as carried on by the Egyptian priests in the form of magic rites or as during the middle ages when it reached its zenith in the magic Theriacs, compounded mixtures of everything medicinal known, for which most extravagant claims were made. Such conditions continued until the complete separation of medicine and pharmacy which was made by legal status in Germany in 1350. During the period following, the apothecary took up manufacturing processes necessary for the preparation of all of his medicinal chemicals. This era was marked by the discovery of benzoic, lactic, hydrocyanic, citric, tartaric, tannic and pyrogallic acids, glycerol, ethyl acetate and nitrite, ether, morphine and the cinchona alkaloids. Most of these, as well as others not mentioned, were discovered by apothecaries. With the establishment of the firms of Schering, Merck, Riedel and others during the early part of the last century, competition and convenience transferred the art of manufacturing gradually from the apothecary to the manufacturing chemist. With the discoveries of chloral, chloroform, phenol, salicylic acid, etc., and the introduction of the patent system, the era of synthetic chemistry became firmly established. The accidental discovery of the anti-

<sup>1</sup> Ber. d. chem. Ges., 40, 4712.

<sup>2</sup> Archiv. d. Phar., 244, 255.

<sup>3</sup> Jour. Chem. Soc., 91, 337.

<sup>4</sup> Czerkis Ph. Post, 49.

<sup>5</sup> Chem. Ztg., 1907, 804.

<sup>1</sup> Ber. d. chem. Ges., 40, 916.

Ph. Jour., 641, 3604.

pyritic properties of acetanilid in 1888 opened to synthetic chemistry an entirely new field, the application of pharmacology to structural organic chemistry. Since this, organic synthesis has achieved triumphs in all departments of *materia medica*, covering the fields of hypnotics, antipyretics, local anesthetics, antiseptics, diuretics, arsenicals, etc. The study of the structure of such natural products as morphine, cocaine, quinine, adrenalin, etc., has enabled the synthetic chemist to supply us with a large number of remedies, cheaper and in many respects superior to nature's originals. Within the last ten years, new conditions have arisen, which through the combined influences of quackery and competition, have not only thrown discredit on the true and legitimate fields, but also through superiority of numbers threatened their very existence. In various parts of our country so-called "Chemical Companies" have been established by certain promoters, whose past history will not bear close scrutiny, the objects of such companies being to flood the market with cheap imitations of well-established synthetics employing for this purpose mixtures in which acetanilid plays the part of the ingredient. Since this chemical possesses antipyretic, analgesic and antiseptic properties, the field of substitution is large. Such practices are not only culpable but criminal, in that they endanger the life of the patient, defeat the purposes of the physician, and place the standard products substituted in discredit. Standard synthetic preparations have also to contend with another evil, and this is the flooding of the market with certain low-grade chemicals of Swiss origin, which are sold under titles that leave no doubt as to the purpose for which they are intended. Such imitations of standard medicinal synthetics which have attained standing in the medical profession are to be had through these channels at prices far below the legitimate cost of production.

Still another class of so-called synthetics have appeared, which practically flood the market and destroy confidence in the legitimate aims of true synthetic chemistry in the interests of pharmacology and medicine. This is the abuse and application of the term "synthetic" as applied to simple mechanical mixtures. Such preparations are given titles either similar in character to our true synthetics or such as would indicate their use; these are then variously described as "condensation" or "reduction-products," produced by secret processes upon a mixture of a number of well-known medicinal chemicals, securing thereby a "shot-gun" combination of them all. The following will illustrate:

**Nephaldol:** According to the manufacturers, this is prepared through the action of citric and salicylic acids on phenetidin in certain proportions, and after the reaction is over the resulting free acids are neutralized by quinine and sodium carbonate. Examination of this preparation has shown it to consist of a mixture of sodium salicylate, phenacetin and quinine.

**Arseniol:** This is given the simple title of sodiumchlorophosphoricarsenate and is sold at \$9.00 a pound. Analysis has demonstrated it to consist of a mixture of sodium arsenate, phosphate and chlorid.

**Nopain,** lauded as a synthetic, consists of a solution of cocaine, phenol, adrenalin and glycerol in alcohol.

Many other citations might be made, but this suffices to illustrate the deception practised upon the medical profes-

sion, who, of course, are unable to distinguish the true from the false. Certain classes of physicians are not blameless for this condition of affairs, as the following notice will show. Recently a journal devoted to the exposure of business frauds, "Der seelle Geschaefstmann" of Cologne, has inserted in a reputable journal the following notice:

"For Physician. Wanted: Licensed physicians who are disposed to furnish favorable reports for advertising purposes of a newly introduced chemical preparation of epoch-making importance (germicide). Fee from 500 to 1000 marks."

As a result, a large number of offers from physicians were received in reply. One among these ran as follows: He was owner of a well-patronized dispensary in a large city and was not forced to earn tainted money. He was, however, prepared to give the desired opinion and thought it best for the manufacturer to furnish him with the report already prepared, as the manufacturer was the best judge of what was needed.

Further comments are unnecessary.

V. COBLENTZ.

## NOTES AND CORRESPONDENCE.

### THE NEW BRADY GAS FILTER.

Owing to the installation of gas engines for blast furnace gas in the largest iron and steel works throughout the country, the chemists of these various plants have been confronted with several problems in gas analysis. One of the most difficult of these to solve satisfactorily was the determination of dust in gas.

Before blast furnace gas can be used in gas engines it must be subjected to a thorough cleansing. This is usually accomplished in three steps: dry cleaners, wet cleaners and final mechanical scrubbers. When ready for the gas engine the gas must contain only about 0.005 of a grain of dust per cu. ft.

The fine physical condition of the dust in the engine gas (gas ready for engine), and the large amount of dust and moisture in the raw gas make the accurate determination of dust per cu. ft., in either case, no easy matter. It was after trying all the forms of apparatus now known for such determination, with little success, that the Brady Gas Filter was devised.

This apparatus consists of four parts as shown, disconnected, in Fig. 1. Part 1 (numbered from left to right) consists of a brass shell provided with an outlet and an inlet. Part 2, the filter, consisting of an ordinary 94 mm. by 33 mm. Soxhlet extraction shell, is supported within Part 1. The brass shell is of such diameter that there is a space of about  $\frac{3}{16}$  of an inch between the paper shell and the inner surface of the brass shell. The method of supporting the filtering shell within Part 1 is by securing the edge of the former between two correspondingly tapering cylindrical faces. One of these faces is within the inlet end of Part 1, and the other is on the outside of a brass cylinder, Part 3. These tapering faces form a wedge which securely holds the paper cartridge in place, acting as its own washer, and protecting a space of about  $\frac{1}{2}$  inch inside the opening of the filter paper from dust, so that it can be handled with safety after the experiment. Part 3 forms the extreme inlet of the apparatus, and is provided with inside threads so that

it can be screwed to a sampling pipe. Its inner surface must be perfectly smooth so that there is no chance for accumulations of dust before the filter is reached. Part 4 is a loose nut which holds Parts 1 and 3 together while in use.

The apparatus may be used in any position but the preferred arrangement is horizontal. When the gas to be filtered contains moisture the filtering device must be heated to about 100° C. by enclosing it in an asbestos-lined box,

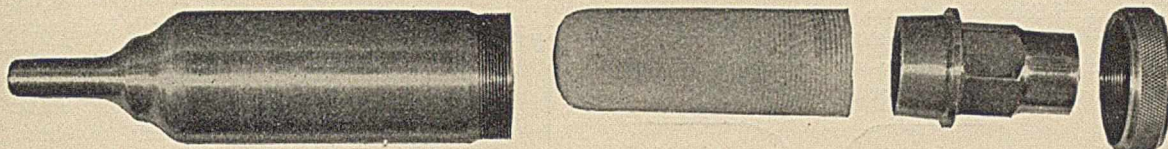


Fig. 1.

heated with an electric light, or by any other available means. The nipple on the exit end of Part 1 is provided with threads so that it can be removed and replaced with aluminium tubes, containing a dehydrating agent, in case it is desired to determine moisture in the gas (see Fig. 2).

The advantages of this apparatus as to simplicity are easily seen. Gravity seems to cause the heavy particles of dust to settle on the bottom of the shell, while the lighter particles form a porous coating on the upper surface. This action prevents the filter paper from becoming clogged as

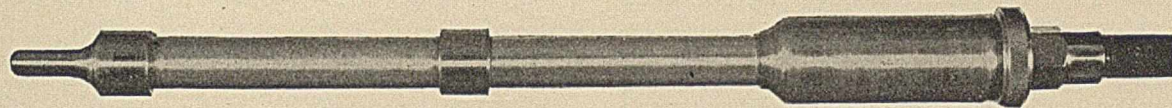


Fig. 2.

long as heat enough is applied to keep the paper dry. About twice as large samples of gas can be passed through this apparatus as through any other we have ever tried. We have also found the number of grains of dust per cu. ft. to be higher when determined by this apparatus than with the others.

Thus far the device has been used for filtering blast furnace gas only, but there is no reason why it cannot be used to filter air or any other gas. The apparatus described is now being made and sold by E. H. Sargent & Co., whom I desire to thank for the loan of that shown in the illustrations.

L. A. TOUZALIN.

LABORATORY OF ILLINOIS STEEL CO.,  
SO. CHICAGO, ILL.

[FROM THE DEPARTMENT OF PLANT AND ANIMAL CHEMISTRY, MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION.]

#### VOLUMETRIC DETERMINATION OF COPPER IN SUGAR ANALYSIS.<sup>1</sup>

The co-operation of the laboratory in the experiments conducted by other departments of the Station has often rendered necessary quantitative determinations of reducing sugar, sucrose, lactose and starch in a variety of products. The final step in every case is the determination of the cuprous oxide precipitated from Allihn's solution by the reducing action of the sugar. After a rather long study of different methods of filtration and the various ways of de-

termining the amount of precipitate as copper, cuprous and cupric oxides, the following method was adopted since it proved the most satisfactory and yielded the best of results if reasonable attention was paid to details. It might be said, further, that as such work often has to be done at odd times it is desirable to maintain a supply of sugar tubes<sup>1</sup> and only to titrate when there are a number of tests on hand. By exercising a little care the same tubes can be used repeatedly without change of felt.

The process consists of heating an aliquot of the sugar solution with the mixed Allihn's solution (30 cc. of "white," 30 cc. of "blue" and 60 cc. of water) and filtering by aid of suction through a sugar tube with an asbestos felt supported by glass wool. The cuprous precipitate is transferred to the tube, washed with hot water until free from alkali and then with alcohol. The copper is dissolved in 5 cc. of concentrated nitric acid, thoroughly washed with hot water, and the filtrate run into an Erlenmeyer flask by means of suction. The solution is evaporated to small

volume or, at least, until nitrous fumes are no longer given off. Too great concentrations should be avoided as it often results in the precipitation of a very insoluble form of copper and the loss of the determination. Twenty cc. of a saturated solution of zinc acetate, 20 cc. of potassium iodide (165 g. to 1000 cc.) and 60 cc. of water are added and the free iodine titrated with N/10 sodium thiosulfate solution (24.83 g. per liter). The thiosulfate is run in gradually, with constant shaking, until the brownish yellow color (iodine) has been largely destroyed, then 2 cc. of starch paste (1 g. to 200 cc.) are added and the titration continued until the blue particles have entirely disappeared. Towards the end of the reaction the flask should be stoppered and shaken thoroughly.

The copper equivalent of the thiosulfate is determined by diluting 25 cc. of a standard copper solution with water, evaporating and titrating exactly as in the test. The standard solution is prepared by dissolving 10 grams of pure dry metallic copper in 200 cc. of concentrated nitric acid and making up to a liter with water at 20° C. The solution should be analyzed gravimetrically and will keep almost indefinitely. From this data the reducing action of the sugar solution can be readily calculated in terms of copper and by conversion tables the corresponding amount of sugar. While the first reading of this method might give the impression that it was rather difficult, in reality after a few trials it is extremely simple, can be carried out rapidly and the titration is very sensitive.

E. B. HOLLAND.

<sup>1</sup>An adaptation of the Low zinc-acetate method.

<sup>1</sup>Eimer and Amend, No. 3263.

### MERCURY SEALS IN FAT EXTRACTION APPARATUS, AND A NEW FORM OF FLASK.

One of the first to mention and describe a mercury seal in connection with chemical apparatus is Karsten<sup>1</sup> who used it in gas analysis apparatus to prevent the gases from coming in contact with corks or rubber stoppers or tubing. Fig. 1 shows his arrangement and needs no further explanation. Michaelis<sup>2</sup> was the next to describe a mercury seal, shown in Fig. 2; it is all glass and was used for making horizontal connection between the parts of the apparatus where cork or rubber would be objectionable. Schwartz<sup>3</sup> describes and illustrates an apparatus to be used for extraction with ether, ligroin, etc., in which he used two mercury seals for

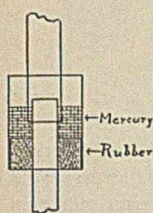


Fig. 1.

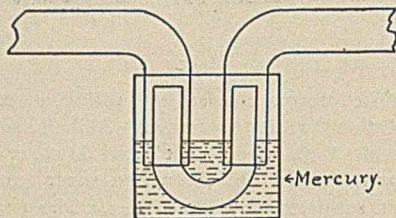


Fig. 2.

connecting the different parts of his apparatus; his method is shown in Fig. 3, the parts being all glass. Until this time nobody had used a mercury seal for connecting a fat extraction flask with a condenser. Knorr<sup>4</sup> was the first to describe such an arrangement; his flask is shown in Fig. 4, while Fig. 5 shows his condenser with a thimble, *A*, fused on at its lower end; *B* is an extraction tube with a perforated platinum disk fused in near the bottom for holding the substance to be extracted. For extracting a finely divided substance some kind of packing not affected by the solvent must be put on this disk. The thimble *A* (Fig. 5) fits over

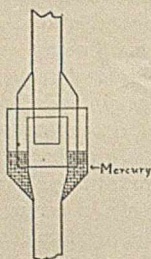


Fig. 3.

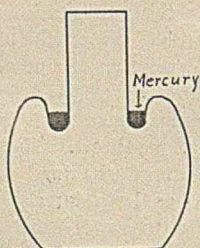


Fig. 4.

the neck of the Knorr flask (Fig. 4) and dips into the mercury contained in a channel around the neck. Near the lower end of the extraction tube there are three short nipples which rest on the neck of the flask, while the tip extends into the flask. In this original form the Knorr apparatus is in use in many laboratories to-day and is listed in all catalogs of chemical apparatus. The flask of this apparatus, however, has a serious disadvantage: on account of its shape it is extremely hard to clean or to transfer anything from it. The first attempt to overcome these difficulties was by Wheeler and Hartwell,<sup>5</sup> who used a flask of the usual

<sup>1</sup> *Zeit. anal. Chem.*, **11**, 213.

<sup>2</sup> *Dingl. Poly. Journ.*, **247**, 36.

<sup>3</sup> *Zeit. anal. Chem.*, **23**, 368.

<sup>4</sup> *Proc. 7th An. Con. Assoc. Off. Agr. Chem.*, 1890 (*Bull.* **28**, Bur. Chem.).

<sup>5</sup> *Journ. Am. Chem. Soc.*, **23**, 338.

shape with a grooved rubber stopper around its neck as shown in Fig. 6. The use of rubber in contact with glass which is heated is, however, never very satisfactory, and especially in this case since the flask must be cleaned for weighing. To make the apparatus more rigid, Robison<sup>1</sup>

used a collar made of maple wood, fitted tightly to the neck of the flask by means of a perforated rubber stopper as shown in Fig. 7, using a flask as shown in Fig. 6. This combination is in use in several large laboratories. The small size of flask in this combination, as well as its shape, makes it somewhat difficult to clean, although a great improvement over the original Knorr shape. An improved form of flask is described by DuBois<sup>2</sup> and is shown in Fig. 7, being of the usual Erlenmeyer shape, which, in connection with a shorter

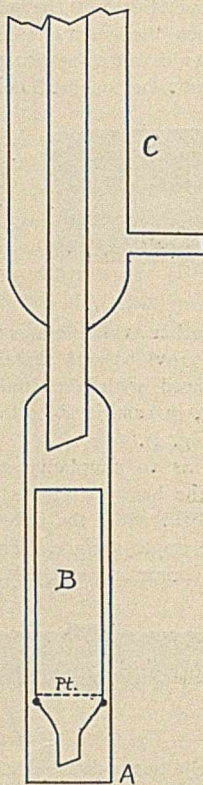


Fig. 5.

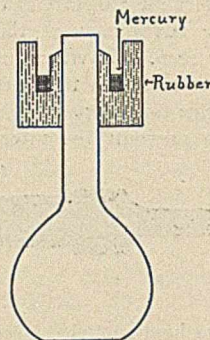


Fig. 6.

and wider neck, is easily cleaned; this flask was used with the wood-collar rubber stopper combination for holding the mercury. After using this latter arrangement for some time one will become convinced that rubber should not be used in contact with heated glass; also that some care is necessary in order to make the joint mercury tight. To overcome the difficulties mentioned in the various forms and arrangements, all of which the writer has used, a flask shown

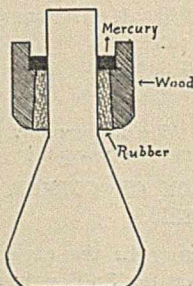


Fig. 7.

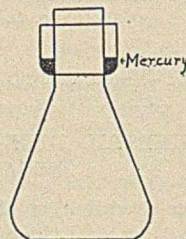


Fig. 8.

in Fig. 8 was made for the writer by a New York firm. It is all glass, Erlenmeyer shape, large neck, can be easily cleaned and substances transferred from it without difficulty; it fits the usual Knorr condenser. It has now been in use

<sup>1</sup> Private communication.

<sup>2</sup> *Journ. Am. Chem. Soc.*, **30**, 797.

for one year and has shown no defects. About the same time when this flask was being made, a flask almost identical in form was imported from Germany; it is, however, a much heavier and taller flask with a smaller neck, but fits the Knorr condenser and is a much more serviceable flask than those in which rubber is used.

ALBERT P. SY.

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#### VARIATION OF MOISTURE CONTENT IN BUTTER AS SHOWN BY DIFFERENT METHODS OF SAMPLING.

The desirability of adhering to fixed methods of analysis is acknowledged by practically all analytical chemists. Of course, it is understood that deviations must be resorted to, to meet conditions which are not identical in different laboratories, but aside from minor changes in methods, it is recognized as unwise, especially in official work, to make a marked change in the fixed and essential details of any method, unless such change has been sanctioned by collaborative work by different analysts.

Even now, it appears that some chemists do not pay sufficient attention to the details of sampling, apparently losing sight of the fact that inaccuracies in sampling at the beginning of an analysis nullify the effects of most careful work later on.

Some time ago the writer had occasion to investigate the effect of different methods of sampling of butter by official inspectors, and the results are so striking that they are given here for publication.

The butter sampled was contained in sixty-pound tubs, and the method followed was an exact duplicate of the method followed by the official inspectors.

*First Experiment.*—Sample No. 1. Taken with butter ladle from the edge of the bottom of the tub, approximately one pound being taken.

Sample No. 2. Taken with ladle from the center of the bottom of the same tub.

Sample No. 3. Regular official method of sampling with butter trier, five plugs drawn diagonally from the whole length of the tub.

Water, No. 1, 12.82–12.80%. Average, 12.81%.

Water, No. 2, 13.35–13.29%. Average, 13.32%.

Water, No. 3, 12.00–12.19%. Average, 12.09%.

*Second Experiment.*—No. 1-a. One-pound sample taken with ladle from center on top of sixty-pound tub.

No. 2-a. One-pound sample taken with ladle from center on bottom of same sixty-pound tub as in 1-a.

No. 3-a. One-pound sample taken with ladle from edge of bottom of same sixty-pound tub as in 1-a.

No. 4-a. Sample taken with butter trier in regular official way, five plugs being withdrawn diagonally from the length of the tub.

Water, No. 1-a, 13.87–13.80%. Average, 13.84%.

Water, No. 2-a, 14.43–14.52%. Average, 14.48%.

Water, No. 3-a, 14.77–14.69%. Average, 14.73%.

Water, No. 4-a, 14.12–14.04%. Average, 14.08%.

*Third Experiment.*—No. 1-b. Sample taken with ladle from edge of bottom of sixty-pound tub.

No. 2-b. Sample taken with ladle from center of top of same sixty-pound tub as 1-b.

No. 3-b. Sample taken with ladle from center of bottom of same sixty-pound tub as 1-b.

No. 4-b. Sample taken with trier from two sections of the tub and split lengthwise with a knife; no regular official sample taken in this case.

Water, No. 1-b, 14.33%.

Water, No. 2-b, 13.62%.

Water, No. 3-b, 15.57%.

Water, No. 4-b, 13.40%.

*Fourth Experiment.*—No. 1-c. Sample taken from sixty-pound tub by inverting tube, removing same, rejecting a layer one and one-half inches thick from the bottom and securing the sample, approximately one pound, from the center of the butter remaining.

No. 2-c. Sample taken in regular official way from the same tub as 1-c, the butter trier being used, securing the sample diagonally from the whole length of the tub.

Water, No. 1-c, 20.5%.

Water, No. 2-c, 17.6%.

From the above it will be seen that different methods of sampling the butter are responsible in these cases for a variation as high as 2.9%. Indeed, there appears no reason why there should not be even greater variation than above when the manner in which water is held in butter is considered. A variation of 2.9% is sufficient to account for a flagrant violation of the 16% water limit of the Internal Revenue Department, and official inspectors and chemists should view with much concern the method of sampling of the product before final judgment is passed.

The exceeding great desirability, therefore, of adhering to the tried methods of sampling is in these experiments decidedly emphasized.

As to effects of prolonged drying on moisture determination in butter, I have found that by the official method four to five hours is the limit beyond which variation in moisture is no greater than the difference between parallel determinations.

FLOYD W. ROBISON.

LABORATORY, MICHIGAN DAIRY  
AND FOOD DEPARTMENT.

#### EXTRACTIVES FROM GAYAULE (PARTHENIUM ARGENTATUM).

This is a record of work done with गयाule, plant and rubber, in January, 1906.

The samples as received comprised a stalk of गयाule about two feet high, about a pound of the comminuted plant resembling coarse sawdust, and a small sample of the rubber produced commercially by mechanical means.

A microscopic section of the stalk was made for me by Dr. Norman Mason, of this city. The making of the section was said by Dr. Mason to be a difficult matter, the wood being about as hard as a cherry stone and the bark soft, and dragging on the knife on account of the rubber, oils and resins contained in the latter.

Iodine green was found to stain the rubber cells. These cells were entirely in the bark. There was none of the root to the sample.

The rasped wood, a factory product, was divided into 15 gm. portions. On one of these the moisture determination was made by keeping in a vacuum over sulphuric acid for 48 hours at room temperature.

This method was adopted as there were other volatile

matters not water present in the sample. The moisture found was 4.5 per cent.

Another portion was burned for ash, and yielded 3.56 per cent. Of the ash 61.0 per cent. was calcium carbonate.

Another 15 gm. portion was extracted with acetone in a Soxhlet extractor. The product, after evaporating the acetone and drying at 105°, amounted to 9.57 per cent. This product was saponified with alcoholic potash. On separating the saponifiable from the unsaponifiable, the fatty and resin acids amounted to 3 per cent. of the weight of the wood. The unsaponifiable was 2.2 per cent. of the wood.

The discrepancy between the 9.57 per cent. taken and the 5.2 per cent. recovered was due in part to the fact that part of the original extract was water-soluble and another part volatile.

No effort was made to separate the various fatty and resin acids.

The 2.2 per cent. of unsaponified matter was somewhat interesting. It had a buttery consistency and when warmed an odor suggesting at once menthol and oil of rose geranium.

On the same portion which had been extracted by acetone and after drying the same, an extraction was made with benzol. From the benzol extract the "rubber" was precipitated with a large quantity of alcohol. After drying, this product weighed 5.04 per cent. This should not be taken as the total rubber in the sample, for unless the cell walls are ruptured it is not to be supposed that the rubber solution can pass out.

On another original portion the boiling water extract dried at 105° weighed 6.1 per cent. This extract was entirely soluble in warm water to a yellow solution. The solution did not precipitate gelatin, gave but a slight precipitate with ferric alum and possessed no dyeing properties. The odor was that of logwood extract.

This ended the work on the wood. A portion of the gayaule rubber as produced by mechanical means was dissolved in benzol and the rubber precipitated by alcohol. The yield was something like 45 per cent.; I have mislaid the figures.

It is undoubtedly the presence of a large quantity of resinous matter associated with the rubber that enables the extractives to collect together as the wood is ground under water. The ground wood floats off and the rubber gradually collects as one mass under the roller.

Is there not a hint in this for the collection of the rubber contents of the milkweed? The rubber from the latter is of far finer quality than the gayaule product, which would hardly be used were it not for the high price of the real rubbers of commerce.

CHAS. E. SWETT.

PROVIDENCE, R. I., April 9, 1909.

*Editor Journal of Industrial and Engineering Chemistry.*

DEAR SIR: In the April number of the *Journal of Industrial and Engineering Chemistry*, page 280, is a report of a judicial decision concerning Adeps Lanae and Wool Grease or "Degras."

While the particular decision is manifestly correct, the report contains a quotation from a previous judicial decision which describes wool grease. This description is radically wrong. Wool grease does not contain "from 15 to 20 per cent. of potash." It contains no potash. Of course

I am now referring to the commercial product and not the wool fat or suint as occurring in the wool.

The writer has seen this decision brought up by the examiners where it was relied on to tax wool grease of somewhat different appearance from the ordinary, under a higher classification.

In the cases mentioned the appraisers were not sustained, but the curious thing is that a description so easily proven wrong should be so frequently quoted.

Yours truly,

CHAS. E. SWETT.

#### MR. BAILEY'S PAPER ON ACCURACY IN SAMPLING COAL.<sup>1</sup>

This paper is the most important contribution to the question of paper sampling that has appeared for years. It is deserving of the highest praise, and though our experience is not in accord with all the conclusions reached by the author, particularly conclusion No. 1 in the summary, in which he states that errors from 3 to 5 per cent. in ash determinations are of ordinary occurrence, and errors of from 15 to 30 per cent. are frequently encountered, still we recognize its great value.

Assuming that every delivery of coal to the plant we have in mind, contains the same percentage of ash, the variations from the average ash of many hundred determinations ranged from 2 per cent. below to 3 per cent. above this average. But as the coal is not entirely uniform in composition, as shown, first, by inspection, and secondly, by the boiler house records where the amount of coal and resultant ash is regularly weighed, and the amount of combustible remaining in the ash determined, and the power developed from the coal recorded in terms of electrical units per pound of coal, we must conclude that the real error is probably much less than the maximum error indicated above.

These figures are obtained from a plant where the coal as unloaded is run through a crusher, and the crushed coal is sampled by taking a scoop at regular intervals, a representative of the coal company being present during the sampling, though the actual work is done without his aid. The sample drawn as indicated above is broken down by hand and quartered in the ordinary way, the sample received at the laboratory filling a Mason's fruit jar of one quart capacity. This sample represents about 400 tons. The general results of this method are entirely satisfactory to the parties concerned, as indicated by the fact that this mode of sampling has been in use for more than ten years at this plant, and there is always active competitive bidding by the coal companies for the business.

The specifications are rather severe, and heavy fines are exacted for failure to meet the requirements, nor is a premium allowed for coal that surpasses the standard set in the contract.

Taking up the more frequent cases where a purchaser receives but one car in each shipment, and the money settlement for this coal is made upon the findings of the chemist, and where the necessities of the case require a sampling of the car before receipt by the purchaser, hence before unloading there are two points which must be considered and

<sup>1</sup> See THIS JOURNAL for March.



duly weighed: first, the amount of money that can be profitably expended in drawing and testing samples, and secondly, the accuracy in sampling that is attainable without prohibitive cost.

The difference in value between good semi-bituminous coal of from 5 to 7 per cent. ash and poor coal with 12 to 15 per cent. ash, in this market is 30 cents per ton, so that the whole possible difference between the buyer and the seller is \$15.00 per car. The cost of sampling by this method outlined below may be put at \$1.50, so that there remains \$13.50 for "over-head" charges, which must include chemists' charges, transportation of samples, profit to consumer or coal merchant. It can thus be seen that the sampling cost must be kept low in order that there be some advantage occurring to the parties concerned. The sampling method which we have used for fifteen years is as follows: Three holes are dug in the coal, one in the middle of the car, the other two at diagonal corners of the car. Large scoops full of coal are taken every 12 to 15 inches on the way down, care being exercised to get a fair proportion of lump and fine coal. This gross sample is broken down by hand, quartered and sampled in the ordinary way. To carry out this sampling requires from three to four hours' time of two properly trained laborers.

Using the method as outlined, our experience is that on successive samplings of the same car, the first being made by ordinary laborers trained for it, and the second, when the samples are drawn under our personal supervision, both yield results upon analysis differing by less than 1 per cent. in ash, which means a difference in price, upon the specifications, commonly in use here, of from \$3.00 to \$4.50 per car. This possible difference of \$4.50 per car, when the total difference involved is only \$15.00, would be an unsurmountable obstacle to the laboratory valuation of single cars of coal, were it not for the fact that in practice the analysis of the single car represents simply one of a number of shipments, and the error is evidently not always in the same direction.

We commend Mr. Bailey's paper for putting in concrete and clear form the errors that must arise from imperfect sampling, and the precautions that must be taken to secure any desired degree of accuracy. He evidently realizes that the most important applications of his work will be to sampling materials other than coal, where the value of the cargo is many times that of coal, and where errors admissible in coal work would mean a large monetary loss to one of the parties concerned. We have had an opportunity to judge the practical accuracy of "car sampling" of coal at a plant where the power developed from the fuel is used to pump water, and the efficiency of the coal is measured in "feet pounds" per pound of fuel. The variations in the composition as shown by the analysis are accompanied by corresponding variations in the work done at the plant. At this plant coal containing over 10 per cent. ash is rejected, so that the variations studied only comprises a total difference of 5 per cent. in ash.

The exposition of the relation between the analytical and the mathematical results in Mr. Bailey's paper is extremely good, and we consider the points he makes in regard to drawing a large gross sample, and the initial reduction of this gross sample to a sufficient degree of fineness, to be distinct and important contributions. We have also

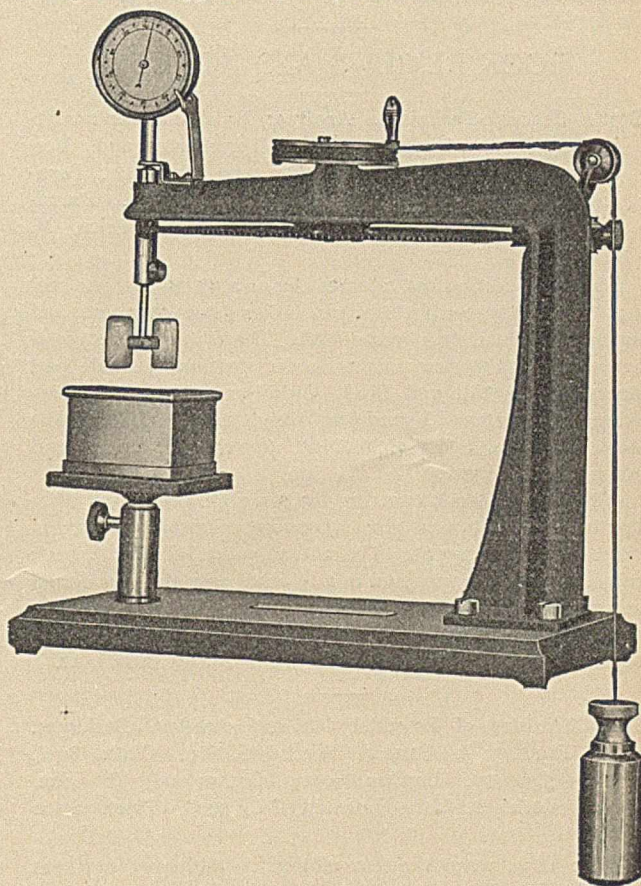
realized the importance of this, but never has it been put before us in such a logical and convincing form.

As we have said before, Mr. Bailey's paper has a greater value for the proper sampling of materials other than coal; and we wish to congratulate the author upon the admirable selection of the substance used to demonstrate his points, as he could hardly have found any material other than coal upon which accurate analytical data could have been so easily obtained. In fact the paper should have a more comprehensive title.

PENNIMAN & BROWN.

#### A NEW VISCOSIMETER.

We are in receipt of the particulars regarding the new Stormer Viscosimeter, designed by Chief Chemist Stormer, of the J. I. Case Threshing Machine Co., and made by the Bausch & Lomb Optical Co., Rochester, N. Y. The instrument is distinctly new in design, and since it comes from a practical chemist who has found it superior to other forms in making a large number of determinations daily, it may be expected to appeal to other practical men.



The principle employed is that of a paddle wheel driven by a constant force. This paddle wheel is equipped with indicator so that the number of revolutions made in a liquid within a given time may be recorded, or the time required to register a given number of revolutions may be used as the basis for determining the comparative viscosities of oils, varnishes, etc. The principal points of advantage which have been gained are:

Only a 50 cc. sample is required for the determination of viscosity and the temperature of this small quantity may be easily controlled.

Only a few seconds are required to make a test and the temperature variation during the test is negligible.

The reading may be repeated and checked with great ease, it being only necessary to wind the indicator back to zero in order to be ready to repeat the determinations.

The force exerted is constant throughout the experiment.

Different oils may be run successively without the loss of time, since a clean cup and a cleaning of the small paddle wheels puts the instrument in order for a new test.

With this viscosimeter there is not such a great variation in viscosities as is shown in some of the outflowing types of instrument.

Only the stop-watch need be kept in mind, since the number of revolutions is automatically recorded and a convenient brake stops the revolutions of the wheel instantly at the desired moment.

Further information, directions for use, and prices may be obtained of the makers.

## BOOK REVIEWS AND NOTICES.

**Post's Chemisch-Technische Analyse: Handbuch der analytischen Untersuchungen.** Dritter Vermehrter und Verbesserter Auflage, Herausgegeben von Prof. Dr. Bernhard Neumann. 8vo., Bd. 1, pp. xxix, 974. Braunschweig: F. Vieweg und Sohn, 1906-'08. Price, M. 23.50.

The third edition has retained the arrangement of the second so far as possible, but much has been rewritten and much new matter has been added. The editor calls especial attention to the new matter under Calcium Carbide and Acetylene, Asphalt and Pitch, Cadmium, Aluminum, Chromium, Tungsten, Vanadium, Molybdenum, Hydrofluoric Acid, Bromine, Sodium Sulphide, Antichlor, Alumina and Aluminum Sulphate.

Like Lunge's book covering the same field, this was written by specialists and must therefore necessarily be somewhat uneven in merit. The actual value of such a book can scarcely be determined in any other way than by actual use and no estimate of it will be attempted. The printing and illustrations are of the high order that we have grown to expect from the firm publishing it. EDWARD HART.

**The Chemistry of Essential Oils and Artificial Perfumes.** By ERNEST J. PERRY. Second edition. Cloth, 8vo., viii + 546 pp. London: Scott, Greenwood & Son. New York: D. Van Nostrand Co., 1908. Price, \$5.00 net.

Since 1899, when the first edition of this most excellent work by Mr. Perry appeared, it has served as a standard guide and reference book to all chemists and others who had to do with the examination of essential oils and artificial perfumes. There were 411 pages in the first edition and these have been increased to 546. Many parts of the book have been rewritten and brought down to date and much new matter has been added. One chapter which appeared in the first edition, namely, that on terpenes oils, has been omitted inasmuch as, in the opinion of the author, this

subject does not appear to be of sufficient importance for detailed treatment. Among the interesting chapters containing new matter are those on rosemary, lavender and spike-lavender, and linaloe oils. In this edition a comprehensive appendix in the form of three large insert sheets has been added, showing at a glance the standards laid down for the principal essential oils in eleven pharmacopoeias of the principal countries. In the second edition Mr. Perry's work will unquestionably continue to be a leading source of information and a standard work of reference to chemists everywhere. The typography and general make-up of the book are beyond criticism. W. D. RICHARDSON.

## NEW BOOKS.

**Die Entwicklung der Leuchtgaszerzeugung seit 1890.** By W. BERTELSMANN. Sammlung chemischer und chemisch-technische Vorträge. XII. Band, 7 und 8 Heft. 90 Ss. mit 38 Abbildungen. Stuttgart: Ferd. Enke, 1908. Preis, M. 2.40.

**Die Lack- und Firnisfabrikation.** In: Monographien über chemisch-technische Fabrikationsmethoden. By PROF. MAX BOTTNER. Verlag Wilhelm Knapp, Halle a/S, 1908. Preis, geh., M. 4.50.

**Mine Sampling and Chemical Analysis of Coals Tested at the United States Fuel-testing Plant, Norfolk, Va., in 1907.** By J. SHOBER BURROWS. Washington, D. C. (Office of the Superintendent of Documents), 1908 (1909). 23 pp., 8° (U. S. Geol. Survey, Bull.).

**Die Analyse des Kautschuks, der Guttapercha, Balata und ihre Zusätze.** By DR. RUDOLPH DITMAR. Verlag von A. Hartleben. Wien und Leipzig, 1908. Mit 42 Textabbildungen und 4 Tafel. Geheftet M. 11.

**Decorative Glass Processes.** By ARTHUR L. DUTHIE. New York: D. Van Nostrand Co., 1908 (1909). 278 pp., ill., 8°. Price, \$2 net.

**The Fractionation of Crude Petroleum by Capillary Diffusion.** By M. P. CRAM and JOS. ELLIOT GILPIN. Under the Supervision of D. T. Day. Wash., D. C., Office Supt. of Documents, 1908 (1909). 33 pp., diags., 8°. (U. S. Geological Survey Bull.).

**Die Untersuchung von Eisengallustinten.** By F. W. HINRICHSEN. Stuttgart: Verlag Ferd. Enke, 1909. Preis, M. 4.40.

**Kalzium cyanamid (Stickstoffkalk oder Kalstickstoff) als Düngemittel.** By E. KEMPSKI und H. IMMENDORFF. Stuttgart: Eugen Ulmer. 124 Ss. Preis, geh., M. 3.50.

**Alloys and Their Industrial Applications.** By E. F. LAW. Philadelphia: Lippincott, 1909. 16 + 269 pp., ill., cl. Price, \$4 net.

**The Dyeing and Cleaning of Textile Fabrics.** By F. A. OWEN. A Handbook for the Amateur and Professional. Based partly on notes of H. C. Standage. New York: John Wiley & Sons; London: Chapman and Hall, Ltd., 1909. 12° vi + 253 pp., cl. Price, \$2.00 (8/6 net).

**An Introduction to the Science of Radioactivity.** C. W. RAFFERTY. New York: Longmans, Green & Co., 1909. 14 + 62 pp., cl. Price, 75 cents net.

Die Grundzüge der allgemeinen Chemie und die Technik der Untersuchung der Rohmaterialien und der Betriebskontrolle in der Seifenindustrie. By DR. C. STIEPEL. Verlag für chemische Industrie, H. Ziolkowsky Aushurg.

## SCIENTIFIC AND INDUSTRIAL SOCIETIES.

## AMERICAN CHEMICAL SOCIETY.

## Indianapolis Joint Meeting.

A very successful joint meeting of the Middle West Sections of the American Chemical Society was held on Friday and Saturday, March 26th and 27th, under the auspices of the Indiana Section at Indianapolis. The participating Sections were the Chicago, St. Louis, Cincinnati, Louisville, University of Illinois, Columbus and Indiana. The program was as follows:

FRIDAY, MARCH 26, 1909.

7.00 P.M.—Dinner at the German House, corner Michigan and New Jersey Streets. After dinner was served there were addresses as follows:

The American Chemical Society..... W. R. WHITNEY  
Camphor..... W. A. NOYES  
Address..... JOHN URI LLOYD  
Address..... C. F. MABERY

SATURDAY, MARCH 27, 1909.

The Sections met in Shortridge High School, 3rd floor, north side, corner North and Pennsylvania Streets, at 9 o'clock. The following papers were presented:

A Method for Use in Volumetric Analysis (10 min.)... W. R. SMITH  
Some Analytical Methods Connected with the Examination of Boiler Water (15 min.)... S. W. PARR  
Urinary Nitrogen of Men in Health (20 min., Lantern)... H. S. GRINDLEY  
The Destruction of Platinum Crucibles through the Ignition of Magnesium Ammonium Phosphate (10 min.)... R. E. LYONS  
Research Work Being Carried on in the Ohio State University (20 min.).....  
Fermentation with Respect to Fusel Oil Content (15 min.)..... A. M. BRECKLER  
The Preparation of Hydroxamic Acid from Hydroxylamine Salts of Organic Acids (15 min.)... R. OESPER  
On the 3',3'-Diketonic Acids (15 min.)... J. B. GARNER  
Electro-Deposition of Metals from Perchlorate Baths (10 min.)..... F. C. MATHERS

The members of the Society were the guests of Pitman-Myers Co., pharmaceutical chemists, at an informal noon luncheon at their laboratory, 111-117 N. Capitol Avenue.

The afternoon was given to visits to Eli Lilly & Co., pharmaceutical chemists, 210-214 East McCarty St., and to Kingan & Co's packing house, Union Stock Yards.

## INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Minutes of meeting called by the temporary committee to discuss advisability of holding the Eighth International Congress of Applied Chemistry in New York City, held at the Chemists' Club, on April 3, 1909.

W. H. Nichols in the chair.

After a few introductory remarks, in which he explained

the proceedings up to date, the chairman, Dr. W. R. Nichols, opened the meeting.

The minutes of the previous meeting were read by the Secretary, and duly approved.

A great many letters were read, in which great interest in the movement to secure the meeting of the Eighth International Congress of Applied Chemistry in New York was expressed, and it was noted that not a single disapproval of the plan was received.

The report of the committee appointed to obtain congressional action was read, duly approved, and made a part of these minutes.

Votes of thanks were extended to the Hon. Burton Harrison, Congressman of New York, and to Dr. H. W. Wiley, on motion of Prof. Bogert, seconded by Prof. Baskerville, and the committee was discharged on motion of Dr. Charles A. Doremus, seconded by Dr. T. J. Parker.

Dr. Wiley, addressing the meeting, stated what progress had been made in preparing for the next (seventh) Congress of Applied Chemistry in London.

Mr. Toch moved that the invitation to the Eighth International Congress of Applied Chemistry to meet in New York, which is to be issued by the Government, should be supported by invitations from American universities, educational institutions, scientific associations and individual firms; that a circular should be sent by the Secretary requesting the issuance of these invitations and addressed to the Honorable General Secretary of the Seventh International Congress of Applied Chemistry, Mr. William Macnab, 10 Cromwell Crescent, London, S. W., England; that these invitations should be sent in care of the secretary of this committee prior to May 15th, so that all the invitations together can be handed to the congress authorities in London. This motion was seconded by Dr. Baekeland, and unanimously carried.

It was decided to leave the discussion of the financial side of the congress until after the invitation had been finally accepted.

It was also decided to continue the work with the temporary committee and leave the permanent organization until the invitation has been accepted.

The following universities, educational institutions, scientific organizations and industrial establishments were represented at the meeting:

Harvard University, by Clifford Richardson.  
Columbia University, by M. T. Bogert.  
Cornell University, by W. D. Bancroft.  
University of Pennsylvania, by Walter T. Taggart.  
University of Pittsburg, by W. A. Harmon.  
Massachusetts Institute of Technology, by Henry Howard.  
College of the City of New York, by Charles Baskerville.  
Syracuse University, by E. N. Pattee.  
Lafayette College, by Edward Hart.  
New Hampshire College, by Charles L. Parsons.  
Rutgers College, by R. G. Wright.  
Polytechnic Institute of Brooklyn, by Irving W. Fay.  
Massachusetts Agricultural College, by Chas. Wellington.  
Chemists' Club of New York, by I. F. Stone.  
Franklin Institute of Philadelphia, by S. P. Sadtler.  
American Chemical Society, by C. L. Parsons, M. T. Bogert,  
T. J. Parker, Wm. McMurtrie, L. M. Dennis and A. P. Hallock.

American Electrochemical Society, by C. A. Doremus, E. F. Roeber and A. von Isakovics.

Society of Chemical Industry, by William H. Nichols.

American Institute of Chemical Engineers, by S. P. Sadtler.

Verein Deutscher Chemiker, by A. P. Hallock.

N. Y. Section American Chemical Society, by L. H. Baeckeland.

N. Y. Section Society of Chemical Industry, by M. Toch.

N. Y. Section American Electrochemical Society, by E. F. Roeber and G. A. Sperry.

N. Y. Section Verein Deutscher Chemiker, by E. G. Love.

New England Sec. Society of Chem. Industry, by Henry Howard, A. A. Claffin and L. Loring.

Lehigh Valley Section American Chemical Society, by E. Hart.

Philadelphia Sec. American Chemical Soc., by W. T. Taggart, W. C. Cornell and C. E. Vanderkleed.

North Eastern Sec. American Chemical Soc., by Henry Howard and A. A. Claffin.

Manufacturing Chemists' Assn. of the U. S., by Henry Howard, chairman Executive Com.

General Chemical Co., by W. H. Nichols and T. J. Parker.

Grasselli Chemical Co., by Harry C. Grant.

Roessler & Hasslacher Chemical Co., by J. Hasslacher.

Arnold Print Works, by Roscoe L. Chase.

Cochrane Chemical Co., by L. Loring, Vice-Pres.

Niagara Electrochemical Co., by J. Hasslacher.

Merrimac Chemical Co., by H. Howard, Vice-Pres.

Carl H. Schultz (Inc.), by A. P. Hallock.

Schoelkopf, Hartford & Hanna Co., by I. F. Stone.

Toch Bros., by Maximilian Toch.

Nichols Copper Co., by W. H. Nichols.

Perth Amboy Chemical Works, by J. Hasslacher.

Badische Co., by Adolf Kuttroff.

Farbenfabriken of Elberfeld Co., by H. Schweitzer.

H. A. Metz & Co., by E. A. Widmann.

National Aniline & Chemical Co., by I. F. Stone.

Hudson River Aniline Color Works, by L. I. Waldman.

Institute of Fermentology, by M. Wallerstein.

Eimer & Amend, by F. Klein.

National Gum & Mica Co., by J. Alexander.

Charles Eneu Johnson & Co., by Chas. H. Spayd.

Charles Lenning & Co., Inc., by W. C. Cornell.

H. K. Mulford Co., by E. E. Vanderkleed.

Naval Smokeless Powder Works, by Geo. W. Patterson.

Adjourned.

H. SCHWEITZER,  
*Secretary.*

NEW YORK, April 7, 1909.

DEAR SIR:

At the last meeting, held April 3rd, representatives of many American universities, educational institutions, scientific organizations and industrial establishments were present, all evincing the greatest interest in the plan of inviting the Eighth Congress of Applied Chemistry to meet in New York in the year 1912. A large number of letters were also received in which the movement was heartily endorsed, without a single expression of disapproval.

The meeting was informed that a joint resolution, "authorizing the President of the United States to invite the International Congress of Applied Chemistry to hold its eighth

meeting in the United States of America, in the year Nineteen Hundred and Twelve," had been passed by the 60th Congress.

To supplement this official invitation on the part of our Government, it was decided to call upon American universities, educational institutions, scientific organizations and industrial establishments to request the Seventh Congress, which will be held in London during the week of May 27th to June 2nd, to accept this invitation. It was concluded that this would be best accomplished by special letters, promising every assistance to make the Eighth Congress an extraordinary success in this country.

You are, therefore, respectfully asked to address such a letter to the Honorary General Secretary, Mr. William Macnab, 10 Cromwell Crescent, London, S. W., England, and to send it prior to May 15th, in care of the undersigned secretary, who will take charge of such communications and deliver them as a whole to the authorities of the Seventh Congress.

Trusting that you will comply with this request, which will not place you under any financial obligation whatsoever, I am,

Yours very respectfully,

H. SCHWEITZER,

*Hon. Secretary N. Y. Section, Society of Chemical Industry,  
117 Hudson Street, New York City.*

#### AMERICAN SOCIETY FOR TESTING MATERIALS.

##### Coal Specifications Committee.

The American Society for Testing Materials has appointed a large and representative Committee on Coal Specifications. The work of the committee will be to determine upon suitable specifications for the purchase of coal for different purposes, which will be satisfactory alike both to producers and consumers of coal. The organization of the committee embraces the appointment of various sub-committees to consider the various subdivisions of the subject. The work in the first instance will be done mainly by correspondence, the suggestions received from the different members being assembled by the sub-committees and then transmitted to the members of the sub-committees for further recommendations and advice. It is not anticipated that many meetings will be necessary. It is hoped that this most important work will be carried through at an early date to a successful and satisfactory conclusion.

#### PERSONAL NOTES.

Mr. G. M. MacNider was appointed, on Jan. 1st, Feed Chemist and Microscopist of the North Carolina Dept. of Agriculture. Mr. MacNider was formerly Assistant Chemist of Soils in the same Department.

Dr. W. A. Syme, Assistant Chemist to the N. C. Experiment Station, and Assistant Professor of Chemistry at the Agricultural and Mechanical College of the State, has been appointed State Oil Chemist.

Mr. Philip McG. Shuey, formerly chemist for the Savannah Guano Co., has opened a laboratory for fertilizer and fertilizing materials in Savannah, Ga.

The Fuel Testing Company, 220 Devonshire St., Boston,

has been organized for the purpose of assisting the consumer in the selection of fuel and the most economical operation of boiler plants and other heat generating systems, with Mr. E. G. Bailey as mechanical engineer and Mr. W. B. Calkins as chemist.

## OFFICIAL REGULATIONS AND RULINGS.

### FOOD INSPECTION DECISION 106.

*Amendment to Food Inspection Decision 77* (A definition of the terms "Batch" and "Mixtures" as used therein).—The definition of the term "batch" as given on page 4, lines 12 to 14 of Food Inspection Decision 77, is hereby extended to include also the contents of any one package, cask, or other container holding 500 pounds or less of dye, even though the contents of such package, cask, or container has not undergone the same treatment at the same time and the same place as a unit.

The word "mixtures" as used on page 3, line 15 from the bottom, and following, of Food Inspection Decision 77, is hereby declared to mean not only such mixtures as consist wholly of certified coal tar dyes but also those which contain one or more certified coal tar dyes (and no other coal tar dyes or dye) in combination with other components, constituents, or ingredients not coal tar dyes, which other components, constituents or ingredients are in and of themselves or in the combination used harmless and not detrimental to health or are not prohibited for use in food products; the exact formula of such mixtures, including all of the components, constituents, or ingredients, or other parts of the mixture, together with a statement of the total weight of mixture so made, must be deposited with the Secretary of Agriculture and a one (1) pound sample thereof must be sent to the Secretary of Agriculture, but such formula need not appear on the label; in lieu of which may appear the legend "Made from certified lots Number ——— and Number ———, etc.," and no mention need be made of any constituent or constituents other than those of the certified coal tar dyes employed.

H. W. WILEY,  
F. L. DUNLAP,  
GEO. P. McCABE,

*Board of Food and Drug Inspection.*

Approved:

JAMES WILSON,  
*Secretary of Agriculture.*

WASHINGTON, D. C., March 19, 1909.

### JUDGMENTS, FOOD AND DRUGS ACT.

No. 38, February 17, Misbranding of Canned Corn (Underweight).

No. 43, March 13, Misbranding of Canned Peas (as to weight).

No. 44, March 13, Misbranding of Meal (as to milling process).

No. 45, March 13, Adulteration and Misbranding of Whiskey (as to color, age and source).

No. 46, March 13, Adulteration of Eggs (Filthy, decomposed animal substance).

No. 47, March 13, Misbranding of Maple Sirup (as to presence of maple sirup).

No. 48, March 17, Adulterated and Misbranded Vanilla Extract (a colored imitation).

No. 49, March 17, Misbranding of Coffee (as to geographical source).

(T. D. 29627—G. A. 6887). March 16, 1909. *Casein or Lactarene*.—The article commercially known as casein or lactarene held to be free of duty as lactarene, under paragraph 594, tariff act of 1897, and not at 20 per cent. *ad valorem* as a nonenumerated manufactured article under section 6 of said act.—United States *v.* Brownell (T. D. 29374) followed.

(T. D. 1446.)

*Denatured Alcohol.*

Authorizing Formula No. 1 for use in the manufacture of textile cleaning soaps and wall-paper removers.

TREASURY DEPARTMENT,

OFFICE OF COMMISSIONER OF INTERNAL REVENUE,

Washington, D. C., December 28, 1908.

SIR: You are hereby informed that Formula No. 1 (to 100 gallons of alcohol add 5 gallons of approved wood alcohol) is hereby authorized for use in the manufacture of textile cleansing soaps. You will please inform the ——— of this authorization, in compliance with their application forwarded in your letter of the 15th instant.

You are also informed that the same formula, No. 1, is hereby authorized for use in the manufacture of wall-paper removers. You will please inform the ——— of this authorization, in compliance with their application of the 8th instant.

Respectfully,

JOHN G. CAPERS, *Commissioner.*

MR. CHAS. W. ANDERSON, *Collector, Second District, New York.*

United States Circuit Court of Appeals, Sixth Circuit.  
No. 1809.

Hartman and Hartman *v.* United States.

Error to the circuit court of the United States for the northern district of Ohio.

(Decided February 2, 1909).

Before LURTON and SEVERENS, Circuit Judges, and KNAPPEN, District Judge.

LURTON, *Circuit Judge*, delivered the opinion of the court:

The plaintiffs in error were jointly indicted and convicted for violation of the act of August 2, 1886, as amended by the act of May 9, 1902, known as the oleomargarine act. The indictment contained eighteen counts. Count 1 charges a violation of Section 3 of the act by carrying on the business of manufacturers of oleomargarine without having paid the special tax required by law. Counts 2, 3, 4, and 5 charge violations of Section 13 of the act by failing to destroy stamps on emptied oleomargarine packages. Counts 6 to 14, inclusive, charge a violation of the thirteenth section of the act by refilling stamped packages which had contained tax-paid oleomargarine. Counts 15, 16, and 17 charge violations of Section 5 of the act by failing to keep books, give the required bond, and put up sign. Count 18 charges a violation of Section 17 by defrauding or attempting to defraud the United States of the tax on colored oleomargarine produced.

The defendant Henry Hartman was found guilty on all the counts. The defendant Frank Hartman was found guilty upon counts 6 to 14, inclusive, and not guilty upon the other counts. Each of the defendants was adjudged to pay a fine of \$1,000 and to be imprisoned in the Cleveland workhouse for a period of six months.

A motion that the Government be compelled to elect upon which count it would proceed or demand a conviction was overruled. There was no reversible error in this. The offenses joined were merely statutory misdemeanors of the same class, and the fact that various penalties were attached by which imprisonment in a penitentiary was possible under some of the counts did not prevent a joinder of counts under Revised Statutes, 1024. *Morris v. United States*, 161 Fed. Rep., 672. Both defendants were found guilty upon counts 6 to 14, inclusive. Those counts rest upon section 13 of the oleomargarine act, and charge the offense of packing oleomargarine in old stamp-paid packages which had been emptied and upon which the stamps had not been destroyed. The judgment awarded was one which might have been imposed under the general verdict upon these counts irrespective of any other. When there are a number of counts in an indictment and the verdict is a general one, a judgment which might have been awarded under any one of the counts will be applied, upon a writ of error, to any count good in law upon which there was evidence to go to the jury. The question was given full consideration in a similar case in which the opinion of this court has just been filed. *Hardesty et al. v. United States*. It follows, therefore, that we need consider only those counts upon which both defendants were convicted, namely, those from 6 to 14, inclusive.

Those counts were for refilling empty stamp-paid oleomargarine tubs or packages, the old stamps upon which not having been destroyed, contrary to the provision of the 13th section of the act which reads as follows:

"That whenever any stamped package containing oleomargarine is emptied, it shall be the duty of the person in whose hands the same is to destroy utterly the stamps thereon; and any person who wilfully neglects or refuses so to do shall for each such offense be fined not exceeding fifty dollars, and imprisoned not less than ten days nor more than six months. And any person who fraudulently gives away or accepts from another, or who sells, buys, or uses for packing oleomargarine, any such stamped package, shall for each such offense be fined not exceeding one hundred dollars, and be imprisoned not more than one year. Any revenue officer may destroy any emptied oleomargarine package upon which the stamp-paid tax is found."

There was evidence tending to show that the plaintiffs in error were engaged in the business of manufacturing oleomargarine by mixing with the white, tax-paid oleomargarine a coloring material which gave the product the yellow shade of butter for the purpose of selling, vending, or disposing of the same to persons other than those of their own family tables and that they had packed this colored produce so made by them in tubs, baskets, or packages which had contained tax-paid colored oleomargarine and had been emptied and that they had done this fraudulently, knowing that the stamps upon the said emptied packages had not been destroyed as required by law when the packages were emptied.

By far the most important of the evidence resulted from a search of the premises occupied by the plaintiffs in error and in which they carried on their business. The evidence thus disclosed was objected to as incompetent upon the theory that the search warrant under which it had been procured was irregular and illegal. We need not stop to determine the regularity of the search warrant, for, conceding it to have been illegally issued or illegally executed, the evidence which was thereby discovered was not incompetent under the direct authority of *Adams v. New York* (192 U. S., 585) and *Hardesty et al. v. United States*, decided by this court (164 Fed. Rep., 420).

Aside from the errors assigned upon admissibility of evidence already briefly noticed, the assignments go the charge of the court. It is difficult to know the precise objection upon which counsel rely. We have given attention to the parts excepted to and to the charge as a whole. We find no error of which plaintiffs in error can complain. Judgment affirmed.

(T. D. 29636). *Drawback on Alloy*.

TREASURY DEPARTMENT, March 20, 1909.

SIR: The Department's regulations of April 16, 1901 (T. D. 22963), providing for the allowance of drawback on Babbitt metal manufactured by Merchant & Co. (Incorporated), of Philadelphia, Pa., with the use of imported lead and antimony, are hereby extended, so far as applicable, to cover the exportation of alloy manufactured by the Leddell-Bigelow Company, of New York City, in part from imported lead, antimony, and antimonial lead, in accordance with the sworn statement, dated February 20, 1909, transmitted herewith for filing in your office.

In liquidation, the quantities of imported lead and antimony and antimonial lead which may be taken as the bases for the allowance of drawback may equal the quantities declared in the drawback entry, after official verification of exported quantities, provided they shall not exceed 87-1/2 pounds of lead and 12-1/2 pounds of antimony for each 100 pounds of alloy exported, with an allowance for waste not to exceed 1 per cent. of such quantities.

Respectfully,

JAMES B. REYNOLDS,  
Assistant Secretary.

(63422.)

COLLECTOR OF CUSTOMS, NEW YORK.

(T. D. 29651). *Carnauba-wax Substitute*.

UNITED STATES *v.* MORNINGSTAR.

U. S. Circuit Court of Appeals, Second Circuit. March 16, 1909. No. 185 (suit 4964).

1. MINERAL WAX—POPULAR MEANING.

There being no mineral waxes in a chemical sense, the provision for "wax \* \* \* mineral" in paragraph 695, tariff act of 1897, must have been used according to the popular meaning of those words.

2. CARNAUBA-WAX SUBSTITUTE.

Carnauba-wax substitute, which is compounded of carnauba wax (a vegetable wax) and paraffin (a mineral wax) and is to all appearances a waxy substance used for the same purpose as other waxes, is free of duty under paragraph 695, tariff act of 1897, relating to "wax, vegetable or mineral."

3. CONSTRUCTION—SYNTHETIC CLASSIFICATION—ARTICLE COMPOUNDED OF TWO ENUMERATED SUBSTANCES.

An article compounded of two enumerated substances may be classified under a provision separately enumerating those substances; as carnauba-wax substitute, which, being composed of a vegetable and mineral wax, is classifiable under a provision for "wax, vegetable or mineral."

APPEAL from the Circuit Court of the United States for the Southern District of New York.

[Decision adverse to the Government.]

The decision below (T. D. 29121) affirmed a decision by the Board of United States General Appraisers, G. A. 6609 (T. D. 28220), which had reversed the decision by the collector of customs at the port of New York on merchandise imported by Charles Morningstar & Co.

J. Osgood Nichols, assistant United States attorney, for the United States.

Everit Brown, for the importers.

Before LACOMBE, COXE, and NOYES, Circuit Judges.

This cause comes here upon appeal from a decision of the Circuit Court, Southern District of New York, affirming a decision of the Board of General Appraisers, which reversed a decision of the collector, classifying the merchandise in suit as a nonenumerated manufacture under the provisions of the tariff act of 1897.

Per CURIAM: The relevant paragraphs are both on the free list and read as follows:

PAR. 695. Wax, vegetable or mineral.

PAR. 633. Paraffin.

The importation is known as "carnauba-wax substitute," carnauba wax being a vegetable wax. The Government's chemist admits that, although the so-called mineral waxes are not regarded as waxes in the chemical sense, paraffin belongs to that group. Evidently Congress used the words "mineral wax" in their popular sense, otherwise they would cover nothing. The article in question is compounded of carnauba wax and paraffin, and when completed is to all appearances a waxy substance used for the same purpose as are other waxes and containing no animal wax. We concur with the Board and the Circuit Court.

The decision is affirmed.

(T. D. 1472). *Oleomargarine*.—The placing of bottles or other containers of coloring matter in original packages of oleomargarine by manufacturers is not warranted by the law and regulations, and goods found on the market in such condition will be subject to seizure.

TREASURY DEPARTMENT,

OFFICE OF COMMISSIONER OF INTERNAL REVENUE,

WASHINGTON, D. C., March 23, 1909.

To Collectors, Revenue Agents, and Others Concerned:

Recent investigations of violations of the oleomargarine law, through the addition of coloring matter to the uncolored product by keepers of hotels, restaurants, and boarding-houses, developed the fact that some manufacturers were sending out original packages of oleomargarine with bottles or capsules of coloring matter placed therein, and this practice leads the purchasers to believe that it is sanctioned by the Government and they have a right to thus manipulate the goods.

Section 6, act of August 2, 1886, as amended, prescribes the manner of packing oleomargarine by manufacturers

and retail dealers, it being specifically provided that the goods shall be packed by the manufacturers in firkins, tubs, or other wooden packages, marked, stamped, and branded as the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, shall prescribe, and no authority is given in this section for the placing of extraneous matter in these packages.

Section 20 of this act provides:

That the Commissioner of Internal Revenue, with the approval of the Secretary of the Treasury, may make all needful regulations for the carrying into effect of this Act.

Under this section the Commissioner is empowered to make "all needful regulations" for the execution of this law, and in view of the violations growing out of the practice on the part of manufacturers of shipping original packages with bottles, tins, capsules, or other containers having therein coloring matter, packed within such original packages, it is clearly within the power conferred upon the Commissioner by Section 20 to prohibit by regulations this practice, especially as there is no provision in the law to warrant it.

It is held, therefore, that the placing by manufacturers in original packages of oleomargarine bottles or any other form of containers of coloring matter is not warranted by the law and regulations, and must be discontinued. Officers of this Bureau are instructed to warn manufacturers against this practice and to inform them that the continuance of the same after receipt of this notification will subject the goods found on the market to seizure.

JOHN G. CAPERS,  
Commissioner.

## INDUSTRIAL AND TRADE NOTES.

### Phosphate Imports of Germany.

Supplementing the report of one year ago by the Berlin consulate-general on the sale of phosphates for fertilizers in Germany, Consul-General Robert P. Skinner now sends additional information from Hamburg:

The use of superphosphates by German farmers is practically universal. There is also a great and growing demand for a crushed furnace-slag fertilizer consisting of 14 to 18 per cent. phosphoric acid and 40 per cent. of lime,<sup>1</sup> concerning which I may make future communication, as it is a material of great utility in softening soils, and one which the United States could produce, probably, in unlimited quantities. The German phosphate-rock importers desire 77-degree rock, with a tolerance of 1 degree, but they have been getting American shipments of as low degree as 73 degrees. All prices are quoted per degree and per ton. The present price is about 8.5 d. (\$0.17) per degree.

The world's total production of phosphate rock increased in 1907 to the amount of approximately 250,000 tons. The United States produced about 135,000 tons less than in the previous year, Algeria and Tunis about 320,000 tons more, and the South Sea Archipelago about 43,000 tons more. The progressive production of phosphate in northern Africa is to a great extent a consequence of the increasing demand on the part of European agriculture, which has almost absorbed the entire quantity produced.

<sup>1</sup>Thomas slag.—Ed.

In the course of 1907 the first shipments of phosphate from Nauru, German Polynesia, appeared on the local market. The quality is good, and this product is considered a valuable addition to the several kinds of phosphates imported from the Polynesian Islands. Owing to the improvements made on the island of Nauru, both in respect to mining and shipping facilities, it is expected that larger quantities of Nauru phosphate will be imported.

Phosphate, which is free of duty when imported into Germany, is ground and converted into superphosphate, by treatment with sulphuric acid, in numerous factories in this country. It requires about \$30,000 to erect a factory to produce 3,000 tons of such acid.

The demand for phosphate, generally, is growing, but this is not the case as respects Tennessee rock. As the following statistics show, the exports of Tennessee phosphate have decreased. Hamburg and the adjoining city of Harburg import chiefly Florida rock phosphate and the Algerian product. Considerable quantities are also received from Tunis.

Of the shipments of phosphate arriving in Hamburg very small quantities are re-exported, the chief consumers being the German farmers. It would not be remunerative for the German superphosphate factories to seek a market for their article outside of Germany, in northern Europe, or elsewhere, as well-organized competing factories may be found wherever there is any considerable demand for this fertilizer.

While the freight rate per ton of phosphate from Algerian ports is 7 s. (\$1.70) per ton, and from Tunisian ports 7 s. 6 d. (\$1.82), shipments from American ports are generally subject to a freight rate approximating 10 s. (\$2.43). Of late almost no ships have arrived here from ports in the United States carrying whole cargoes of phosphate. This article now usually arrives in lots of 1,500 to 2,000 tons, on tramp steamers loaded with other bulk goods, such as cotton, cotton seed, cereals, etc.

The statistical situation of phosphate rock is as follows:

*Exports from American Ports.*

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	474,053	490,366	572,311	561,040	591,719
Florida pebble.	315,612	364,446	404,985	482,912	564,702
Peace River, Fla.....	62,910	81,650	91,155	41,742	36,729
Tennessee.....	113,948	121,965	94,301	101,466	92,112
So. Carolina...	67,445	90,000	78,802	.....	.....
Total.....	1,033,968	1,148,427	1,241,554	1,187,160	1,285,262

*American Exports to Europe.*

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	469,597	483,559	546,944	550,521	584,799
Florida pebble.	141,251	219,166	218,838	209,617	296,371
Tennessee.....	113,948	121,965	80,298	88,105	92,172
Total.....	724,796	824,690	846,080	848,243	973,342

*German Imports from United States.*

	1903.	1904.	1905.	1906.	1907.
Florida rock..	304,935	284,780	261,407	314,820	278,226
Florida pebble.	20,250	71,700	30,582	24,770	50,189
Total.....	325,185	356,480	291,989	339,590	328,415

*Exports from Algeria and Tunis.*

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Algeria.....	301,112	344,969	347,747	302,262	343,087
Tunis.....	360,621	457,133	529,645	757,993	1,040,300
Total.....	661,733	802,102	877,392	1,060,255	1,383,387

*Imports at Hamburg and Harburg.*

	1903. Tons.	1904. Tons.	1905. Tons.	1906. Tons.	1907. Tons.
Florida rock..	120,669	105,493	138,795	146,676	140,504
Florida pebble.	.....	.....	.....	.....	19,632
Algeria.....	21,326	29,125	40,415	40,430	36,675
Gafsa.....	22,330	8,525	6,250	10,600	11,091
Senam.....	.....	.....	.....	3,000	1,500
Ocean Island..	2,700	4,800	5,450	7,300	.....
Christmas Is- land.....	3,772	5,950	2,788	3,000	2,950
Aruba.....	750	3,150	1,227	2,808	.....
Total.....	171,547	157,043	194,925	215,814	212,352

The total production of all countries was as follows:

	1906. Tons.	1907. Tons.
United States.....	2,052,000	1,917,000
Tunis.....	758,000	1,040,300
Algeria.....	302,300	343,000
South Sea Islands.....	247,000	290,000
France.....	469,400	476,700
Belgium.....	163,600	180,000
Other countries.....	100,000	100,000
Total.....	4,092,300	4,347,000

The quotations at end of December, 1907, in Hamburg, per degree per 1,000 kilos (2,204.6 pounds), were:

	Per cent.	Cents.
Florida hard rock.....	76 to 80	17.1 to 18.6
Florida pebble.....	68 to 73	13.6 to 14.0
Tennessee.....	78 to 80	15.7 to 16.2
Algeria.....	63 to 70	14.3 to 14.8
Algeria (Tunis).....	57 to 63	13.6 to 14.0
Tunis-Gafsa.....	57 to 63	14.0
Christmas Island.....	80 to 85	20.7
Ocean Island and Nauru..	83 to 87	20.7

*U. S. Consular Report, March 30, 1909.*

**Formosa Camphor Exports.**

The following review of the Formosa camphor trade is by Consul Carl F. Deichman, of Tamsui:

The total amount of camphor exported in 1908 shows a decrease of over 1,000,000 pounds from the previous year, and is attributed to the increased activity in the camphor districts of China and Japan, and especially to the extensive use of synthetic camphor in various arts and manufactures in which formerly the natural camphor was used. This decrease was steady, notwithstanding the fact that the price of the natural product fell considerably.

The demand has slightly increased with the present year, 1909, but it is not likely that the amount exported will total the amounts exported in previous years from this island. The following table shows the export of camphor from Formosa during the year 1908, with the countries to which exported and the quantity and value to each in pounds and United States gold:



Countries.	Pounds.	Value.
United States.....	1,365,910	\$ 524,100
England.....	458,850	166,681
France.....	277,970	100,460
Germany.....	53,200	19,522
Hongkong.....	560,196	241,936
British India.....	3,990	1,419
Japan.....	535,591	250,102
Total.....	3,255,507	\$1,304,220

#### More Patents Revoked in United Kingdom.

Consul-General Robert J. Wynne, of London, reports that, on the ground that the articles are not sufficiently manufactured in the United Kingdom, the following patents have been revoked:

The British-Westinghouse Electric and Manufacturing Company (Limited) have a patent for an arc lamp, but grant a license to a German company to export the lamps to Britain. The British comptroller-general held that there was no evidence to prove that the German company could not manufacture this article in the United Kingdom and sell at a profit at present prices.

Another revocation was of a patent to United States patentees, for fastening strips used in box-making.

#### Essential Oils in Sicily.

In answer to inquiries, Consul William Henry Bishop, of Palermo, furnishes the following information concerning essential oils in his district and the effects of the earthquake on the industry in Sicily:

No bergamots are grown in Sicily, and no bergamot oil is produced in this consular district. The whole supply has been coming from a small section of southern Calabria, opposite Messina, one of the regions most afflicted by the disastrous earthquake of December 28 last. The great production of essential oils, including orange oil, has been at Messina and vicinity, and 75 per cent. of the total production for Italy was customarily exported from that place. Our late consul at Messina, Dr. Arthur S. Cheney, had made a report on the subject, which no doubt covered the conditions, practically for all of Sicily, up to that time. (Published in Consular Trade Reports for January 23, 1909.)

The average annual production of orange oil in the Province of Palermo has been about 1,100 pounds. None is manufactured in the provinces of Trapani, Girgenti, and Caltanissetta, constituting the remainder of the consular district. Even the output of this vicinity was usually sent to Messina for export. The season of manufacture begins with September and ends with December, or in the more elevated region may be prolonged through January. There was seen in 1908 the phenomenon of low prices with a small output, while prices in 1907 were high with a very large output. This was due to the fact that, owing to the profitable rates then realized, there had been a great rush to produce, resulting in large stocks being left over.

The result of the earthquake has been to double or triple prices of essential oils. This large advance is true of all derivatives of the citrus fruit, such as citrate of lime, citric acid, etc. It is believed, however, that the panic of alarm

from the disaster is being used to some extent as an element of speculation. A considerable stock was really found in the warehouses unharmed by the general destruction of Messina; factories remain in the small towns near there, such as Ali and Barcellona, and, as the time demanded for manufacture is not long, fruit which would under ordinary circumstances have been exported, will be rapidly made up into essences, etc., to meet the demand. Prices may therefore be soon expected to drop much nearer to a normal level.

It was one of the signs of awakening life at Messina that two manufactories of citrate of lime were opened at Gazzi, a suburb of that city, before January 20th. Some ten thousand families in the province of Messina and Catania, engaged in the industries following the harvesting of the citrus fruits, were thrown out of employment by the earthquake.—*U. S. Consular Report*, March 20, 1909.

#### Artificial Silk Manufacture.

The following report concerning the manufacture of artificial silk in France, and its relative merit as compared with silk manufactured from the so-called "natural fiber," is furnished by Consul John C. Covert, of Lyons:

The following information on the subject of artificial silk is a translation of a communication received from a prominent French manufacturer in answer to a number of interrogatories which I had submitted to him:

There are three varieties of artificial silk, to wit: Chardonnet, or nitrocellulose; Givet, or cuproammoniacal; and Xanthate cellulose, or viscose. There are five great mills and a number of smaller ones in France in which these three methods are employed. The smaller mills have not succeeded on account of the heavy expenses compared to the small product. The large mills are the Chardonnet, at Besançon, which produces from 1,763 to 2,204 pounds per day; the Givet process, at Givet, in the Vosges, which produces 1,763 pounds per day—this company has a smaller factory at Izieux, Loire, which turns out about 440 pounds per day of silk hair (crin)—and the Viscose Company, at Arques-la-Bataille (Seine-Inferieure), which produces 1,763 pounds per day, and which is expected in two months to have a capacity of 2,645 pounds—this company has another Viscose mill at Vals, which produces 440 pounds per day and will soon turn out 771 pounds per day.

There is no important manufacture of artificial silk in the United States, although that country consumes about 882,000 pounds per year. Machinery enters very largely into the cost of the production of viscose, and as machinery is brought to a high state of perfection in the United States I cannot see why the high rates of wages should prevent the successful manufacture of viscose in that country.

The Givet is an improvement on the Chardonnet process and the Viscose is an improvement on the Givet. It may be roughly stated, considering the quantity of production, consumption, freight, and wear and tear of machinery, that the cost of production is \$2.70 to \$2.90 per kilo (2.2 pounds) for the Chardonnet, \$2.30 to \$2.50 for the Givet, and under \$2 for Viscose.

The Viscose method embodies as far as appearance, qual-

ity, touch, and cheapness are concerned, all the finest and best qualities. Instead of employing the expensive raw material, such as cotton, at 20 cents per 2.2 pounds, ordinary wood pulp is used at 5 cents per 2.2 pounds. Instead of using expensive dissolvents, such as alcohol or ether, ordinary water is sufficient.

You ask if we have succeeded in making an article which is not damaged by dampness or water. This talk about damages by water is a prejudice, for there is no tissue made where artificial material solely is employed, if we expect the tresses and gallons, elastic tissues which are especially made at St. Chamond and Barmen, but these are combined with natural silk, cotton, or schappe. It is used more especially in the woof, and if a drop of water falls upon the thread in the skein it may diminish its tenacity or resistance, but this same water cannot act upon the woven material.

The mixture of a number of textiles, as in Arnure, thus makes a sort of a protected material and renders it physically impossible that the water should spread through to injure the material, since only a small part of it is exposed to contact with water, the rain, or the moisture of the atmosphere. Moreover, experience has demonstrated that this is a question of no importance, and it may be said that this is simply a prejudice. However, there is room for improvement here, and our chemists are perseveringly studying this question. They have already achieved some important results, and it is altogether probable that this prejudice concerning the effect of water will be removed in a few months.

This artificial silk is employed usually in the woof in goods manufactured for the Orient, where brilliant coloring is admired; it is also used for lining for scarfs, skirts, mixed cottons, and for upholstery. It has even been employed in taffetas and in umbrella covers, which is a positive answer to the objection that it will not stand water. At present there is a demand in the United States for a sort of heavy tulle made of ovale of 500 deniers of artificial silk coming from France. This material will be fashionable next season, being used on dresses as a trimming over a foundation of satin or taffetas.

The actual daily production of artificial silk amounts to about 44,000 pounds. About 30,000 hands are employed in the works manufacturing this material. It is exported chiefly to the United States and Germany, and it is reported that some is sent to Japan. This refers to the exportation of the thread and not the manufactured article.

I calculate that the total annual American consumption purchased from France, Germany, and Italy is about 882,000 pounds, but it may be half again as large, for this silk is employed in many kinds of textiles.

It must be borne in mind that in the present condition of science and industry we cannot expect to have cheaper raw material than this wood paste.

I base my opinion of the future consumption on the fact that to-day the minimum consumption is from 39,700 to 44,100 pounds per day, and this at an average price of \$3.28 to \$4.25 per kilo (2.2 pounds), according to the quality. The result is that when producers are satisfied with a reasonable profit, or when the demand will not be far ahead of the production, the price will fall to \$2.30 or \$2.90. Artificial silk can be used in mixed goods in all the great markets for cotton in general and in all the textile markets. On the other hand, I do not think that, consid-

ering the present cost of living, there is any reason to expect a decline in the cost of silk. In short, it must be admitted that some of the adverse criticisms uttered concerning artificial silk are absurd when we remember that it is the same process that the natural silk goes through, as carried on in our laboratories, where natural silk is charged with metal, frequently 80 per cent., and even 200 per cent.

Other silk men of Lyon have expressed the opinion that the high wages ruling in the United States should not be an obstacle to the successful prosecution of the artificial silk industry in that country. This industry is comparatively new and developments may be expected in the work at any moment, as a number of chemists are engaged in trying to perfect the process.—*U. S. Consular Report*, March 17, 1909.

#### The Bleaching Process.

In compliance with instructions from the Bureau of Manufacturers, Special Agent Davis made inquiries in regard to the process of bleaching flour in Europe, and reports as follows:

I am now in position to state that there is no law in France, Germany, or Great Britain prohibiting or regulating the bleaching of flour by chemical or electrical process. As in the United States, some millers in all the countries named oppose bleaching, or find no need for it, while others employ it.

Recently the Alsop Company (electrical process) was sued by the Andrews Company (chemical process) before the Lille (France) tribunal. The case went to the court of appeals, which has rendered its decision incidentally affirming that the bleaching of flour was an improvement, and that it was not injurious to public health.

#### Mining and Minerals, Canada.

Consul-General William Harrison Bradley, of Montreal, forwards the following report on mineral production in Canada:

In the following statement are given the quantities and values of mineral products of Canada for 1908, as reported by the Minister of the Department of Mines before a meeting of mining engineers in the city of Montreal:

Metallic Products.		
Classification.	Quantity.	Value.
Copper, pounds.....	64,361,636	\$ 8,500,885
Gold.....	.....	9,559,274
Pig iron from Canadian ore,		
tons.....	99,420	1,664,302
Lead, pounds.....	45,725,886	1,920,487
Nickel, pounds.....	19,143,111	8,231,538
Cobalt, pounds.....	1,853,286	112,253
Silver, ounces.....	22,070,212	11,667,197
Total.....	.....	\$41,655,936

(To be continued).

#### CORRECTION.

On page 223, March number, in the abstract "Modern Electric Pyrometry," 8th line, read "The accuracy even at 1200 C. is within 2 to 5 degrees" instead of "2 to 5 per cent." as printed.

For title of third article under *Notes*, April No., p. 260, read "A Simple Rapid Process Vinegar Generator for 'Experimental' Use instead of 'Generator'."

Remove the word "not" from the fifth line from bottom, second column, page 260, April No.