THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

VOL. II. JUNE, 1910. No. 6

BIBLIOTEKA POLITECHNIKI LWOWSKIEJ

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

PUBLISHED BY

THE AMERICAN CHEMICAL SOCIETY.

BOARD OF EDITORS.

Editor:

W. D. Richardson.

Associate Editors.

Geo. P. Adamson, E. G. Bailey, G. E. Barton, Wm. Brady, Wm. Campbell, F. B. Carpenter, Virgil Coblentz, Francis I. Dupont, W. C. Ebaugh, Wm. C. Geer, W. F. Hillebrand, W. D. Horne, L. P. Kinnicutt, A. E. Leach, Karl Langenbeck, A. D. Little, P. C. McIlhiney, E. B. McCready, Wm. McMurtrie, J. Merritt Matthews, T. J. Parker, J. D. Pennock, Geo. C. Stone, F. W. Traphagen, Ernst Twitchell, Robt. Wahl, Wm. H. Walker, M. C. Whitaker, W. R. Whitney.

Published monthly. Subscription price to non-members of the American Chemical Society $6.00 yearly.

Vol. II. JUNE, 1910. No. 6

EDITORIALS.

USES FOR RARE ELEMENTS AND SPECIAL COMPOUNDS.

It frequently happens that investigators have put aside and regarded as impracticable, the suggested use of many of the more difficultly obtained chemical elements and compounds, in consequence of the fact that some of these are at present regarded as unavailable—whether such unavailability is the result of either a very limited present supply, or a cost which is prohibitive for the purpose for which the material is desired.

Manufacturers are throwing away many materials which are, at present, looked upon as waste products, and would gladly welcome any suggested use for the same. Through the coöperation of the investigator and the manufacturer, mutual difficulties might be overcome. With a more intimate coöperation, the requirements of the investigator might be supplied by utilizing the waste products of the manufacturer.

The fundamental step towards obtaining this coöperation must be the securing of information concerning the availability of the materials needed and the uses which may be made of them.

When we consider the marvelous improvements recently brought about by the application of electricity to chemical industry, and the accomplishment thereby of results hitherto unobtained, we must be prepared to revise some of our information concerning materials previously regarded only as "museum specimens," and place many of these in the category of substances practical for industrial purposes.

Twenty-five years ago aluminum was not commercially available; to-day, millions of pounds are used in the industries. Only a few years ago, the element silicon was regarded as a curiosity; to-day it may be purchased by the ton—uses having been found for it and convenient methods devised for its preparation. The same might be true of many other elements and compounds, which, at the present time, have but little application.

The Division of Industrial Chemists and Chemical Engineers now has a committee which is endeavoring to deal with this problem. This committee will probably act in the capacity of a clearing-house between the manufacturer and consumers. The committee is composed of former President W. R. Whitney, of Schenectady, N. Y., M. C. Whittaker, of Gloucester, N. J., and Gellert Alleman, *Chairman*, of Swarthmore, Pa. The members of this society are asked for suggestions regarding the scope of the investigations to be undertaken, and we hope that all will aid in this important work.

The committee proposes to publish as complete a list of the prices and availableness of the chemical elements as it can obtain, and would be glad to get information to add to this list. It will later probably take up relatively novel or newly available compounds. Such new compounds as come to the notice of members will receive attention by the committee if they are informed of them. GELLERT ALLEMAN.

ORIGINAL PAPERS.

A COMPARISON OF THE METHODS FOR DEPOSITING IRON ELECTROLYTICALLY.

By S. A. TUCKER AND E. SCHRAMM.

Received April 1, 1910.

The experiments herein described include the sulphate and chloride baths as these have been used by most investigators. Other electrolytes have been tried without much success, such as ferrous fluorsilicate, but it was considered best to restrict the experiments to the more promising methods and, by comparing them under certain conditions, to decide which would be the most practical for the deposition of metallic iron.

The first solution tried was made by dissolving 200 grams of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in one liter. This gives about 29 grams of iron per liter, or a concentration of 2.9 per cent. of iron. This is the solution as used by Amberg,[1] and probably by Burgess[2] and Hambuechen. The cathodes were clean sheet iron and the anodes consisted of wrought iron bars. The experiments were carried on at room temperature and the results are given in Table I:

TABLE I.—IRON.

Volts.	Amp.	Amp.[]$^{dcm.}$	Amps.[]'.	Lbs. kw. hr.
0.50	0.2	0.176	1.63	4.4
0.56	0.25	0.22	2.02	3.94
0.58	0.30	0.264	2.45	3.76
0.64	0.35	0.308	2.96	3.44
0.68	0.40	0.352	3.27	3.21
0.70	0.45	0.396	3.68	3.12
0.74	0.50	0.44	4.09	2.95
0.90	0.75	0.66	6.04	2.42
1.10	1.00	0.88	8.26	1.98

The current efficiency was determined by inserting a copper coulombmeter in series and gave an efficiency of 95.5 per cent.

The last column in this table shows the effect of increased current density on the energy efficiency. The current was changed temporarily to obtain these figures. In computing the figures for lbs. per kw. hr., the current efficiency was assumed to be the same throughout.

The deposit obtained was silvery white and of a fine crystalline structure. After a while it became badly pitted. The electrolyte kept in condition for a long time; the basic precipitate which formed by oxidation of the air was allowed to collect in the bottom of the vessel. The electrodes were 1 1/2" apart and the current density at the anode was about double that at the cathodes.

Another run was made with the solution and all conditions kept the same as the above except the current density, which was raised to 1 amp. per sq. dcm. The deposit was crystalline and silvery white like that obtained at lower current densities, but showed a greater tendency to form nodules. The current efficiency was nearly 100 per cent., but the voltage drop was 1.2, giving 1.705 lbs. per kw. hour.

A third run was made with ferrous ammonium sulphate solution, with the addition of a small quantity of glycerine. The deposit in this case was smoother and more solid.

Ryss,[3] in his investigations, used a solution containing 200 grams ferrous ammonium sulphate, 50 grams $MgSO_4$, and 4 grams $NaHCO_3$ per liter. Ryss claimed that such a solution gave a smoother and thicker deposit of iron than could be obtained with ordinary ferrous ammonium sulphate.

[1] *Zeit. Elektrochem.*, **14**, 326 (1908).

[2] *Trans. Am. Electrochem. Soc.*, **5**, 201 (1904). *Electrochem. and Met. Ind.*, **2**, 183 (1904).

[3] Ryss, *Zeit. Elektrochem.*, **12**, 697 (1906).

A trial failed to show any improvement in the character of the deposits using such additions, but it did show that the bath had a much greater tendency to form basic precipitate and the time in which it could be maintained in good condition was less than that possible with the simple bath.

The next solution tried was one containing 30 grams $FeSO_4.7H_2O$, 21 grams $Na_2SO_4.10H_2O$ per 100 cc. as described by Kern.[1]

A current density of 1 amp. per sq. dcm. was used. The deposit was dark gray and formed large nodules. At the end of 15 hours the electrolyte was in bad condition owing to the formation of a heavy precipitate.

The net results of the experiments with different sulphate solutions were the conclusion that a solution containing 200 grams per liter of Mohr's salt was the best as regards character of deposit, permanent good condition of electrolyte, and energy efficiency. Attention was next turned to the electrolysis of chloride solutions. The first solution used contained 100 grams $FeCl_2.4H_2O$ and 50 grams NH_4Cl per liter. The cathodes, as before, being of clean sheet iron and the anodes, wrought iron bar. The electrodes were 1 1/2" apart and the bath maintained at room temperature. The current efficiency as determined by a copper coulombometer was found to be 96.5 per cent. and the following data was obtained:

Time of run 21 1/2 hours.

Average current during run = 0.237.

Average voltage during run = 0.42.

Weight of iron actually deposited, 5.14 grams.

Weight of iron theoretically deposited, 5.32 grams.

Current density during run = 0.304 amp. []$^{dcm.}$

No. watt hours = 0.237 × 21 1/2 × 42 = 2.14.

1 watt hour = 2.4 grams i on.

1 kw. hour = 5.28 lbs.

The current was varied temporarily to obtain the following readings:

Volt.	Amp.	Amps. []$^{dcm.}$	Amps. []$^{ft.}$	Lbs. kw. hr.
0.40	0.2	0.260	2.42	5.55
0.44	0.25	0.321	2.98	5.05
0.46	0.3	0.385	3.58	4.83
0.54	0.36	0.450	4.18	4.10
0.57	0.40	0.513	4.76	3.89
0.60	0.45	0.577	5.36	3.70
0.60	0.5	0.642	5.97	3.70
0.72	0.75	0.962	8.94	3.08
1.00	1.00	1.280	11.90	2.22

In the next run a solution of double the strength was used, *i. e.*, 200 grams $FeCl_2.4H_2O$ and 100 grams NH_4Cl per liter. The other conditions were kept much the same as before, excepting that the length of time of the run was increased:

Time of run, 141 hours.

Average current during run, 0.323 amp.

Average voltage during run, 0.67.

Weight of iron actually deposited, 47.145 grams.

[1] Kern, *Trans. Am. Electrochem. Soc.*, **13**, 103 (1908).

Weight of iron theoretically deposited, 47.6 grams.
Current efficiency = 99 per cent.
Current density = 0.56 amp. $[]^{dcm.}$ = 5.2 amps.$[]'$.
No. watt hours = $0.323 \times 141 \times 0.67 = 30.5$.
1 watt hour = 1.55 grams iron.
1 kw. hour = 3.4 lbs.
The following readings were taken:

Volt.	Amp.	Amps.$[]^{dcm.}$	Amps.$[]'$.	Lbs. kw. hr.
0.42	0.2	0.345	3.2	5.42
0.50	0.25	0.432	4.01	4.55
0.64	0.3	0.517	4.08	3.66
0.70	0.35	0.604	5.64	3.26
0.72	0.4	0.69	6.4	3.16
0.82	0.45	0.726	6.75	2.78
0.84	0.5	0.862	8.0	2.71
0.90	0.75	1.29	12.0	2.53
0.98	1.00	1.725	16.0	2.32

A comparison of the two runs given above with the run on ferrous ammonium sulphate solution shows that while the current efficiency is practically the same in both cases, the energy efficiency at any given current density is much higher for the chloride solutions. Comparing the two chloride solutions, we see that the more concentrated solution gives a higher energy efficiency at any given current density.

The physical character of the deposit from the chloride solution was somewhat different from that deposited from the sulphate solutions, being more crystalline than the latter excepting that to which glycerine had been added.

The next electrolyte tried was the ferrous sodium chloride solutions described by E. F. Kern.[1] This was made by dissolving 285 grams $FeCl_2.4H_2O$ and 102 grams NaCl per liter, giving 8 per cent. Fe and 4 per cent. Na. The solution may also be made by dissolving iron in the equivalent weight of HCl. The cathode used was thin sheet iron plate 3 3/4″ × 3 1/2″. The anodes were bars of wrought iron 3″ × 2″ × 1/2″. The electrolysis was carried on in a beaker placed on an asbestos pad with a hole cut in it, and heated by placing an incandescent lamp underneath. This kept the temperature between 50° and 70° C.

Previous runs having all shown a high current efficiency of over 95 per cent., it was not considered necessary to use a copper coulombmeter in this run. The object of the run was to:

(1) Compare the voltage required by this process with the others described.

(2) To find the effect of heating the electrolyte on the energy required.

(3) To find the effect of heating on the physical character of the deposit.

(4) To secure a thick deposit in a short time.

The cathode area was 13.15 square inches.

The electrolyte was kept in condition by adding a little HCl to the bath every day to dissolve the basic precipitate which formed. Water was fed to the bath automatically to make up for evaporation.

[1] *Trans. Am. Electrochem. Soc.*, **13**, 103 (1908).

The following readings were taken:

Volt.	Amps.	Temp.	Current density. Amps.$[]^{ft.}$	
0.42	1.4	60° C.	15	Taken at start.
0.46	1.4	50°	15	
0.54	1.4	40°	15	
0.64	1.4	30°	15	
0.36	1.8	60°	19.3	9 days after start.
0.34	1.6	60°	11.15	
0.32	1.4	60°	15.0	
0.30	1.2	60°	12.85	
0.28	1.0	60°	10.72	
0.26	0.8	60°	8.57	
0.24	0.6	60°	6.43	
0.22	0.4	60°	42.9	
0.20	0.2	60°	2.14	

The above tables show: that the voltage decreases with increased temperature; and that the voltage decreases as the run proceeds.

Comparison of this process with the others tried shows the best energy efficiency for the ferrous sodium chloride electrolyte working at 50°–70° C.

This bath also gave the best and thickest deposits, the iron being gray and non-crystalline.

ELECTROCHEMICAL LABORATORY,
COLUMBIA UNIVERSITY.

STUDIES IN ASPHALT, I.

By C. J. FRANKFORTER.

Received March 23, 1910.

While engaged in testing asphalt for the City Engineer of Lincoln, Nebraska, it was observed that the temperature of the asphaltic mixture, as brought to the street, varied as much as 100° C. maximum to minimum. It was also noticed that the per cent. of bitumen was by no means constant. This seemed a little unusual, and the author decided to experiment and determine if possible the effect of such variations on the paving material.

Literature was consulted, but nothing bearing on the work in mind was found. Paving specifications from Chicago, Brooklyn, New Orleans, and several other large cities, were obtained and consulted. Without exception, these specifications condemned the overheating of an asphaltic cement. Just how hot such material might be heated without injury, or what the harmful effects of overheating really were, was not stated. In all cases the per cent. of bitumen was to be reasonably constant, usually about 10 per cent. of the surface mixture was called for.

Samples of Trinidad, Texas, Cuban Rock, Obispo and Sarco asphalts were collected. Results on two samples only, Obispo and Trinidad, will be presented, since the data on the other brands are as yet insufficient to warrant definite conclusions.

In this paper the author wishes to be distinctly understood as neither recommending nor condemning the asphalts mentioned.

Obispo refined asphalt was a hard substance resembling coal tar in general appearance, but it did not have the "tarry" odor nor was it "sticky" at

ordinary temperatures. The physical properties of this material varied with the temperature as recorded below:

At 0° C.	Very brittle, broke like glass	No odor.
From 5–10° C.	Slightly less brittle	No odor.
From 20–25° C.	Less brittle, enough tenacity to prevent crumbling	No odor.
From 55–60° C.	Softer, very tough	Faint oily odor.
From 90–96° C.	Began to melt	Stronger odor.
From 115–120° C.	Consistency of molasses	Same odor.
From 135–140° C.	More mobile, luster diminished	Stronger odor.
From 155–160° C.	Very mobile	Very strong odor.
From 180–190° C.	Apparently no change	Strong rancid odor.
At 222–224° C.	Flashed	
At 235–238° C.	Burned	

The Obispo flux was a very viscous greenish-black oil having an odor similar to crude petroleum. Its specific gravity was 0.9894. It flashed at 135–137° C. and burned at 161–162° C.

An asphaltic cement is the material which, when mixed with approximately 90 per cent. by weight of sand, constitutes the wearing surface of an asphaltic pavement. In the case of a natural asphalt containing incorporated native mineral matter a larger proportion would have to be used in order that the mixture might still contain the required 10 per cent. of bitumen.

Asphaltic cement is prepared by fluxing a refined asphalt with some oil, either natural or the petroleum residues from oil refineries. The fluxing is carried on until the asphaltic cement reaches the desired consistency, which is determined by testing its ductility and penetration. After consulting the various paving specifications, a penetration of 40 to 45 at 25° C. was decided on as a standard.

In all these experiments a standard Dow penetration machine was used for the penetration tests. For determining ductility, the author constructed a device with which the material was tested under water at any desired temperature. This apparatus consisted of a zinc-lined water-tight trough, 2 meters long, 13 centimeters wide, and 7 centimeters deep. The inside was given a heavy coating of white enamel paint. This white background enabled the operator to determine the exact moment of rupture of the asphalt. In one end of this trough a small hook was fastened, in the other a small pulley. A reel, manipulated by an ordinary crank handle and carrying a light strong cable, was set up over the trough on a framework near the pulley. This cable ran over the pulley and reached to the opposite end. A standard Dow mold was used in this machine, one end hooked to the end of the box, the other to the cable. When the cable was wound up on the reel the mold was pulled apart. On the bottom of this trough two strips, 1 centimeter high, were fastened just far enough apart to permit the mold to slide between them. They were graduated in millimeters and served as a means of guiding the moving end of the mold, thereby ensuring a straight-away pull. They also permitted the result of a test to be read off directly. When a test was to be made, the trough was nearly filled with water of the desired temperature, 0°, 25° or 46° C. The mold containing the asphalt was placed in position and allowed to remain twenty or thirty minutes. The water was stirred constantly in order to maintain a uniform temperature in all parts of the trough and to bring the asphalt to the temperature of the water. The reel was then turned until the asphalt pulled apart and the distance it stretched read off directly.

Penetration is recorded in degrees Dow, equivalent to hundredths of a centimeter. Ductility is recorded in centimeters. Both ductility and penetration were determined according to Dow's directions.

Heating the asphalt to a high temperature causes a loss of volatile matter which is accompanied by a decrease in ductility and penetration, though in no definite ratio.

The three temperatures at which these tests are made are supposed to represent approximately the different temperatures a pavement would be obliged to withstand.

When the Obispo refined asphalt was heated for 15 hours at a temperature of 163–165° C. in an air bath, as prescribed by the paving specifications, it lost 2.12 per cent. in weight. The samples weighed 20.0526 and 20.0812 grams, respectively. There was no moisture in this asphalt.

Table I gives the ductility and penetration figures on Obispo refined asphalt, showing the per cent. of loss due to the heating which caused the above-mentioned loss of weight:

TABLE I.—OBISPO REFINED ASPHALT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Before heating	0.2	5.2	20.0	2.0	9.0	33.0
After heating	0.0	0.2	4.2	0.0	0.5	5.0
Loss.....	100.0%	96.15%	79.0%	100.0%	94.44%	84.84%

By fluxing 102 grams of Obispo refined asphalt with 42 grams of Obispo flux, an asphaltic cement was obtained which had a penetration of 45 at 25° C. The ductility could not be accurately determined, as the material persistently adhered to the amalgamated brass plate upon which the mold was poured.

For heating the asphaltic cement an open-air bath arrangement was used. It was constructed in a way which allowed the asphalt container to rest on a false bottom, and this served to keep it out of direct contact with the flame of the burner. It was possible to stir the mixture at all times. Since a thermometer was used for this purpose, it was easy to keep a very close watch on the temperature.

Table II shows the variation of ductility and penetration of the Obispo asphaltic cement after being heated to different temperatures:

TABLE II.—OBISPO ASPHALTIC CEMENT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Heated to 130° C...	0.9	33.5	64.6	7.0	39.0	106.0
Heated to 150° C...	0.7	27.2	47.8	6.0	29.0	102.0
Heated to 175° C...	0.4	19.0	43.0	5.0	25.0	73.0
Heated to 200° C...	0.1	15.0	40.0	4.0	21.0	68.0

The ductility here recorded on Obispo is relatively very high. Trinidad and Bermudez, the so-called best asphalts, did not show such high figures. There was this difference. In the case of the two latter asphalts the "body" of the mold stretched and seemed to be "rubbery." With Obispo the material pulled out to a fine thread, and this thread stretched out until it was so fine it could scarcely be seen even against the white background. The "body" in this case showed no tenacity or ductility.

Trinidad refined asphalt was a fairly hard grayish black material with no luster and an odor like freshly plowed earth. At different temperatures it behaved as follows:

At 0° C.	Brittle, crumbled rather easily	No odor.
From 5–10° C.	Slightly brittle, not "crumbly"	Faint earthy odor.
From 20–25° C.	Less brittle, not "crumbly"	Stronger odor.
From 45–50° C.	No apparent change	Same odor.
From 65–70° C.	Began to soften	Same odor.
From 102–108° C.	Entirely melted	Disagreeable odor.
From 120–125° C.	Consistency of molasses, showed stringy or fibrous when stirred	Same odor.
From 150–155° C.	Slightly mobile, odor similar to a mercaptan; (Later qualitative test showed the presence of both nitrogen and sulphur.)	
From 170–175° C.	Very mobile (It is very probable that the incorporated mineral matter prevented this asphalt from showing the same degree of mobility as the Obispo, at approximately the same temperature.)	Very strong odor.
At 208–210° C.	Flashed	
At 233–235° C.	Burned	

For fluxing this refined asphalt a heavy petroleum residue was used. It was a viscous greenish black oil having an odor much like cylinder oil. Its specific gravity was 0.9782.

Table III shows the results obtained by treating the Trinidad refined asphalt in the same manner as the Obispo refined asphalt. The samples weighed 20.2276 and 20.1102 grams, respectively. There was no moisture in this asphalt:

TABLE III.—TRINIDAD REFINED ASPHALT.

	Ductility.			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Before heating.....	0.1	1.8	8.0	0.75	1.5	11.0
After heating	0.0	0.2	0.75	0.0	0.2	1.0
Loss.....	100.0%	88.88%	90.63%	100.0%	86.66%	90.9%

The low penetration figures here recorded are accounted for, in part at least, by the presence of mineral matter in the asphalt. This would prevent the needle of the machine from sinking into the material as far as it would otherwise.

Mixing 135 grams of Trinidad refined asphalt with 19 grams of the fluxing oil, produced an asphaltic cement with a penetration of 40 and a ductility of 24 at 25° C. It was necessary to heat this asphaltic cement to 130° C. in order to get a thorough mixture.

Table IV shows the results on this asphalt, when heated to various temperatures:

TABLE IV.—TRINIDAD ASPHALTIC CEMENT.

	Ductility			Penetration.		
	At 0° C.	At 25° C.	At 46° C.	At 0° C.	At 25° C.	At 46° C.
Heated to 130° C.	1.3	24.0	29.3	4.0	40.0	165.0
Heated to 150° C...	0.2	20.8	29.0	4.0	24.0	104.0
Heated to 175° C...	0.1	15.6	28.8	3.0	20.0	85.0
Heated to 200° C...	0.1	10.6	23.0	2.0	14.0	62.0

Ductility and penetration are the necessary characteristic properties of an asphalt which make it valuable as a paving material. It is these properties which prevent a good asphalt pavement from cracking up in the winter or from becoming so soft in the summer that traffic tends to wear it off the crown of the street into the gutters. So, if these properties are decreased, the efficiency of the asphalt as a paving material would be seriously impaired.

There are certain streets in Lincoln, Nebraska, where the asphalt pavement has deteriorated much more rapidly than it should. At the time these streets were paved the writer was testing the asphalt for the city engineer. The mixing tanks were known to have been heated to a temperature which caused the asphaltic cement to flash and burn. At other times the mixture of asphaltic cement and sand, even after it was dumped into the street from the wagons, showed a temperature above 200° C. The hottest load was 220° C., or 428° F. The exact location of these overheated portions were noted and they are now the worst spots in the street. So in this case the results obtained in the laboratory were confirmed by actual outside observation.

TABLE V.—SOLUBILITY OF OBISPO AND TRINIDAD ASPHALTS.

	Per cent. asphalt soluble.		Mineral matter in asphalt.		Per cent. organic matter soluble.	
Solvent used.	Obispo.	Trinidad.	Obispo.	Trinidad.	Obispo.	Trinidad.
Acetone.....	45.83	14.14	0.43	34.93	46.02	21.73
Benzol.....	99.45	65.01	0.43	34.93	99.87	99.9
Carbon bisulphide..	99.53	65.05	0.43	34.93	99.95	99.96
Chloroform.....	99.55	60.77	0.43	34.93	99.97	93.39
Ether (ethyl).....	not det.	44.87	0.43	34.93	not det.	68.95
Ligroin (0.710)....	68.88	40.4	0.43	34.93	69.17	62.08

The testing of the solubility of asphalts in various organic solvents was taken up as a preliminary to an attempt to determine the constitution of the so-called "Asphaltene" and "Petrolene." Comparing the lest two columns on the right, it would seem that there is a great difference in the constitution of the organic matter of there two asphalts. The per cent. of mineral matter here recorded as constant is the average obtained by various methods both direct and indi-

rect with and without oxidizing agents on many samples of each asphalt.

All the common methods of extracting the soluble portions of an asphalt were tried and set aside. Some were accurate, but too slow; others were fairly rapid but finally divided mineral matter would get away. The following extraction apparatus was found to work better than any of the others, considering both time and accuracy.

Glass tubes 6 centimeters long and 2 centimeters in diameter were obtained. At one end of each of these tubes was a slight constriction which produced a rim (see illustration). Over this rimmed end a C. S. & S. filter paper, No. 589 "Blue Ribbon," was placed. Over this, a C. S. & S. filter paper, No. 575, was laid. The two papers were then firmly and carefully pressed down over the end of the tube and securely fastened with platinum wire. (Copper wire was later found to be just as satisfactory.) The superfluous paper was then clipped off close and the capsule thus formed extracted with the solvent which was to be used on the asphalt. Three or four of these capsules could be prepared at a time and the extraction allowed to proceed while the attention was directed elsewhere.

The tube with its weighed sample was then placed in a Soxhlet extractor having ground glass joints. In the lower part of the Soxhlet a piece of sealed and weighted glass tubing was placed. This tube served a double purpose. It supported the capsule so that about half of it was above the top of the curve of the siphon tube of the extractor, and it displaced a large volume of the solvent thereby causing the apparatus to siphon over more often. The small amount of solvent needed enabled the operator to control easily the volatilization and re-condensation on the sample.

In these tests small samples, never more than 1 gram, were used, as it was found the best results were obtained with samples of such weight and less time was required for extraction. The samples were not pulverized, those powdered showing a tendency to "cake" and clog the filter. This made it more difficult to dissolve out the incorporated organic matter.

With this apparatus very accurate duplicate results were obtained. The amount of mineral matter recovered by evaporating the solution and igniting the residue was not sufficient to cause any appreciable change in the percentage figures.

The writer is indebted to the city engineer for the samples of asphalt and for the paving specifications; also to the Globe Asphalt Company, of Pittsburg, for samples of their products.

The author wishes to take this opportunity of expressing his most sincere and hearty thanks to Chancellor Samuel Avery, of the University of Nebraska, for his kind advice which was offered at the most opportune moments and which proved of so much value.

REFERENCES.

Jour. Amer. Chem. Soc., **16**, 809; **17**, 55, 275; **27**, 293; **28**, 648.

THIS JOURNAL, **1**, 751.

A. W. Dow, "Directions for Using Dow Penetration Machine." Published by Dow and Smith, of New York.

A. W. Dow, "The Testing of Bitumens for Paving Purposes." From *Proceedings Amer. Soc. for Testing Materials*, Vol. III, 1903.

Byrne, "Inspection of Materials and Workmanship Employed in Construction."

Byrne, "Highway Construction."

Richardson, "Modern Asphalt Pavements."

Stillman, "Engineering Chemistry."

Ulzer and Fraenkel, "Chemical Technical Analysis."

Thorpe, "Outlines of Industrial Chemistry."

Brannt, "Petroleum and Its Products."

Sadtler, "Industrial Organic Chemistry."

Allen, Vol. II, Pt, 2: "Commercial Organic Analysis."

UNIVERSITY OF NEBRASKA,
CHEMICAL LABORATORY.

ON THE FORMATION OF CARBENES.

By D. BASIL W. ALEXANDER.

Received March 2, 1910.

Since the appearance of the note on a constant-level reservoir,[1] the writer has received sundry inquiries regarding the last paragraph; it seems therefore advisable to give the investigations that produced that statement. This article is not to be considered exhaustive by any means, but only gives results and hints in the hope that other workers may take up the problem, and give us results that may help to a better understanding of this subject.

As early as May, 1905, it was noticed by the writer that although carbenes in an asphalt are represented by the difference between the amounts soluble in CS_2 and CCl_4, nevertheless when the carbenes are separated and dried, only a portion is then soluble in CS_2, showing that a change takes place which renders them insoluble in CS_2, and only slightly more so in $CHCl_3$; this change being brought about either by drying, or some other unconsidered cause, such as the free action of daylight. It is stated by A. S. Cooper, formerly State Mineralogist for California,[2] that by the action of daylight asphalt undergoes polymerization, and certain portions are rendered less easily dissolved than before the action of light. Some work was done along these lines, but was temporarily abandoned on account of other and more pressing business, so it was not until early in 1909 that it was taken up again. At this time it was noticed that certain other laboratories with which the writer had been able to compare results had not agreed with his own results when determining carbenes by Clifford Richardson's carbon tetrachloride method, while other laboratories established and controlled by the writer were in fair agreement. This led to investigation, and it was

[1] *J. Am. Chem. Soc.*, **31**, 1052.

[2] *Bull.* **16**, Cal. State Mining Bureau, p. 18.

found that the chemist consistently finding a larger amount of carbenes than he, was in the habit of standing his solutions of bitumen in CCl_4 in beakers, on a glass shelf, placed half-way up a window having a northern exposure.

The following experiments were then made: A kettleful of Durango when melted, was thoroughly stirred and portions taken from the top, middle and bottom, and dissolved in CS_2 and CCl_4, then filtered:

	Top. Per cent.	Middle. Per cent.	Bottom. Per cent.
Bitumen by CS_2.....	99.1	99.3	99.6
Bitumen by CCl_4.....	94.8	94.4	94.3

Another and larger portion was taken from the same kettle, and from this samples were submitted to several chemists, with the following results:

	Per cent.
Associated results:	
Soluble in carbon tetrachloride.....	94.8
Soluble in carbon tetrachloride.....	95.1
Outside results:	
Insoluble in carbon tetrachloride.....	10.8
Insoluble in carbon tetrachloride.....	11.2
Insoluble in carbon tetrachloride.....	11.9
Insoluble in carbon tetrachloride.....	13.6

From our own sample (which gave 98.9 per cent. soluble in CS_2), two portions, of about a gram each, were covered with 100 cc. of CCl_4 in an Erlenmeyer flask, one being set on a window ledge and the other in a cupboard in the photographic dark room. These were filtered next day, and amounts soluble obtained:

(*a*) Exposed in window, 85.3 per cent., or 13.6 per cent. carbenes.

(*b*) Stood in cupboard, 94.9 per cent., or 4.0 per cent. carbenes.

Showing an increase of 9.6 per cent. carbenes due to the light.

It was considered possible that temperature might have had some effect, so two more fresh portions were covered with 100 cc. of CCl_4 and both stood together on the window ledge, but one was fitted with a close-fitting sheath of black paper. The results next day were:

(*c*) Unsheathed flask, 83.7 per cent., or 15.2 per cent. carbenes.

(*d*) Sheathed flask, 93.8 per cent., or 5.1 per cent. carbenes.

Here we have a difference of 10.1 per cent. carbenes due to light.

The filtrates from these two samples were allowed to stand, both unsheathed, on the regular CCl_4 shelf in the analysis room in subdued light for a day, and then filtered:

(*e*) Filtrate from (*c*) gave additional carbenes, 0.5 per cent. of original amount taken.

(*f*) Filtrate from (*d*) gave additional carbenes, 3.3 per cent. of original amount taken.

This seems to show that the carbenes were contained in the sheathed sample and only needed the light to bring them into evidence.

The filtration was done without any precautions against light, and the filtrates were allowed to stand for three days in the dark and again filtered:

(*g*) Filtrate from (*e*) gave additional carbenes, 0.6 per cent. of original amount taken.

(*h*) Filtrate from (*f*) gave additional carbenes, 1.6 per cent. of original amount taken.

These carbenes might have been produced during filtration, and probably were, so the filtrates from (*g*) and (*h*) were stood in full sunlight for three hours, and on filtering:

(*i*) Filtrate from (*g*) gave 2.3 per cent. additional carbenes.

(*j*) Filtrate from (*h*) gave 7.9 per cent. additional carbenes.

Thus it may be seen that the total amount of carbenes obtained from the two original samples, (*c*) and (*d*), differ to the amount of only 0.7 per cent.

To further investigate the possible effect of temperature the mode of procedure was slightly changed; three samples were taken from the original can of supply, covered with 100 cc. of CCl_4 in three Erlenmeyer flasks; the flask sheathed in black paper was further covered with white paper, another with white paper only, and the third left uncovered. All three flasks were placed on a board and set in full sunlight for 6 hours, and filtered:

(*k*) Unsheathed flask, soluble in CCl_4, 76.2 per cent, or 22.7 per cent. carbenes.

(*l*) White paper only, soluble in CCl_4, 84.4 per cent., or 14.5 per cent. carbenes.

(*m*) White and black paper, soluble in CCl_4, 93.5 per cent., or 5.4 per cent. carbenes.

Only the filtrate from (*m*) was saved, and that was set in the dark for two months, and on filtering gave:

(*n*) Additional carbenes 2.5 per cent. of amount taken for (*m*).

A further standing for two months, in the dark, of the filtrate from (*n*) gave:

(*o*) Additional carbenes 0.4 per cent.; but on allowing the filtrate from (*o*) to stand in full sunlight for only two hours we obtained:

Additional carbenes 10.4 per cent.

Even at this the total amount of carbenes did not come up to the amount obtained in one setting in the sun, as in (*k*).

It was considered possible that the effect might not be due entirely to the CCl_4, and so a fresh sample of the material was spread as thinly as possible on a piece of glass and exposed to full sunlight for $7^1/_2$ hours. About a gram of this was weighed out, and also the same amount of the fresh material, and subjected to the regular operations:

Regular method, soluble in CCl_4, 93.4 per cent., or 5.5 per cent. carbenes.

Exposed asphalt, soluble in CCl_4, 93.7 per cent., or 5.2 per cent. carbenes.

It is evident the CCl_4 is partly, at least, responsible for carbenes.

A further examination by fusing some of the carbenes obtained with a fusing mixture showed the presence of chlorine in them, a blank determination with the same chemicals showing none.

Having reached this point, we desired to know the reliability of results formerly obtained, so we used two samples that had been reported thus:

Test No.	Per cent. 10790.	Per cent. 10792.
Bitumen by carbon bisulphide	99.5	99.5
Bitumen by carbon tetrachloride	99.7	99.5
Penetrometer at 77° F.	34°	54°

Weighed portions of these two samples were dissolved in 100 cc. of CCl_4 and allowed to stand for 6 hours in full sunlight and then filtered:

10790 bitumen by CCl_4, 89.4 per cent., or 10.1 per cent. carbenes.

10792 bitumen by CCl_4, 93.7 per cent., or 5.8 per cent. carbenes.

It was here that the effect of penetration was noticed, as the above results show that the harder asphalt contained the larger amount of carbenes, the other conditions being identical, or nearly so.

Carbenes are generally supposed to be produced by overheating asphaltic oils during their condensation into asphalt, and experiments were conducted along these lines. For this purpose three samples of an asphaltic oil were heated at 400° F. until they came to asphalt:

	Penetrometer.	Sol. in CCl_4. Per cent.
Sample No. 1	51	99.8
Sample No. 2	25	99.4
Sample No. 3	21	99.5

Fresh portions of these three samples were dissolved in CCl_4 and exposed to direct sunlight for 6 hours and filtered:

	Per cent.
Sample No. 1	98.9
Sample No. 2	98.2
Sample No. 3	98.9

The filtrates were treated the same way, and gave:

	Per cent.
Sample No. 1	97.0
Sample No. 2	94.8
Sample No. 3	94.1

It is apparent that asphalt made by evaporation at a comparatively low temperature does not suffer the decomposition that produces carbenes, and tends to confirm the theory that they are the result of "cracking" in the stills; but the action of light will still produce them, especially when it is run down to a low penetration.

Three samples of Durango that had been dissolved in CS_2, decanted, and the bitumen recovered from solution and heated to 300° F., were examined for their solubility in CCl_4, with the following results:

		Before treatment. Per cent.	After treatment. Per cent.
Test No. 10615.	Soluble in CCl_4	99.2	99.4
Test No. 10615.	Soluble in CCl_4	99.2	99.4
Test No. 10706.	Soluble in CCl_4	92.3	92.8

It will be noticed that the second sample is a duplicate of the first.

It does not appear that the solubility of an asphalt in CCl_4 is affected by dissolving it in CS_2, and subsequently recovering the bitumen.

Satisfactory results were not obtained from refined Trinidad asphalt, on account of the extremely fine mineral matter, so a sample of the Trinidad asphalt was dissolved in CS_2, filtered, and the filtrate swung in a centrifuge, the solvent evaporated, and the residue heated to 300° F., this being the same treatment given to the above samples. Test Nos. 10615 and 10706.

The following results were obtained:

Bitumen by carbon bisulphide, 99.7 per cent.

(*a*) Soluble in CCl_4 after exposure to sunlight for $15^1/_2$ hours, 73.9 per cent., or 25.8 per cent. carbenes.

(*b*) Same as (*a*) except flask sheathed in white over black paper, 99.3 per cent., or 0.4 per cent. carbenes.

(*c*) Filtrate from (*a*) after 6 months in subdued light, carbenes, 2.5 per cent.

(*d*) Filtrate from (*b*) after 6 months in cupboard, carbenes, 0.5 per cent.

Filtrate from (*c*) after sunlight for $7^1/_2$ hours, carbenes, 4.0 per cent.

Filtrate from (*d*) after sunlight for $7^1/_2$ hours, carbenes, 17.0 per cent.

These results appear to subvert the "formation by cracking" theory, and narrow the question down to one of penetration and actinic light. To verify the latter, two fresh portions of the bitumen extracted from Trinidad refined asphalt were dissolved as usual in 100 cc. of CCl_4, and the flasks put in two tin boxes, made for the purpose, having one side, respectively, of red and blue glass; these were exposed to full sunlight for $15^1/_2$ hours and watched so that the sun's rays fell on the solutions through the glass at all times; filtered:

(*a*) Exposed to red rays gave carbenes, 0.8 per cent.

(*b*) Exposed to blue rays gave carbenes, 16.6 per cent.

In the case of (*b*) the flask, after exposure, was stained by the solution on the side next to the light to a dull brown, but hardly stained on the opposite side at all; it was nearly all removed by CCl_4 with a feather; the flask (*a*) was not stained, and washed clean. The filtration of these samples was done in the dark room under red light, and there the filtrates were allowed to stand in their respective colored boxes for six months nearly, when they were again filtered in the dark room:

(*c*) Filtrate from (*a*), additional carbenes, 0.8 per cent. of original amount taken.

(*d*) Filtrate from (*b*), additional carbenes, 3.2 per cent. of original amount taken.

The filtrates were exposed to sunlight for 7 hours and filtered:

(*e*) Filtrate from (*c*), additional carbenes, 15.9 per cent. of original amount taken.

(*f*) Filtrate from (*d*), additional carbenes, 6.7 per cent. of original amount taken.

The filtrates were again exposed to sunlight for 7 hours, but the sun was obscured nearly all the time; filtered:

Filtrate from (*e*), additional carbenes, 2.4 per cent. of original amount taken.

Filtrate from (*f*), additional carbenes, 2.0 per cent. of original amount taken.

These results cannot be called satisfactory, inasmuch as the total amount of carbenes in each case are not the same, as one would logically expect them to be. However, more work will be done on these lines.

It has been noted above that a sample of asphalt showing no carbenes by our regular method, would display them is exposed to light; and it was wondered if the reverse would be true, so a sample that showed 82.2 per cent. soluble in CCl_4, though the penetration was 81° Penr., was dissolved in 100 cc. of CCl_4 and allowed to stand for the regular time of 18 hours, all operations, after weighing, being conducted in the dark room. After filtering in the dark we obtained:

Soluble in CCl_4, 92.8 per cent.

So even light cannot produce carbenes unless the conditions are favorable. Investigation along these lines were discontinued for the present, but continuing the subject of penetration, experiments were conducted on Gilsonite, using 100 cc. of CS_2 and CCl_4, and exposing to full sunlight for 7 hours:

	Sol. in CS_2.	Sol. in CCl_4.
(*a*) Screened from light.....	99.9	99.6
(*b*) Unscreened from light.....	99.9	48.0

The filtrates from the CS_2 solutions were further exposed under the same conditions for 20 hours, but there was no change, except that the flask *above* the solution was stained brown. The filtrate from CCl_4 solution (*a*) was exposed to full sunlight for 7 hours and filtered:

	Per cent.
Soluble in CCl_4.....	76.7

The carbenes in these cases appear gelatinous, and apparently quite different from the carbenes from Durango grade of asphalt; this quality makes them very hard to filter. During the process of investigation of this material, carbenes of a brown color were obtained, but these results are not yet ready for publication.

Some observations relating to the CCl_4 used may be of interest, and lead to results throwing more light on this subject. During the distillation of solutions of bitumen in CCl_4, to recover the solvent, it has been noticed that HCl is evolved if water is present, the residue in the flask becomes quite brittle when the solvent is evaporated, and the sides of the flask used for distillation show the characteristic "carbene ring." The evolution of HCl is more marked when a copper still is used. A piece of blue litmus paper suspended over a solution of bitumen in CCl_4, especially when in the sunlight, is quickly reddened; again, if a sample of the CCl_4 itself is exposed for a length of time in a stoppered bottle to sunlight, it will separate into two layers, the upper one about 1 per cent., yellowish, watery, and acid; and blue litmus paper is reddened. This layer, however, is not HCl, as it gives a buff, flocculent, not curdy, precipitate with silver nitrate.

SUMMARY AND CONCLUSIONS.

It cannot be affirmed that carbenes are altogether formed during the production of asphalt from petroleum in a still, but that they are due:

(1) To a concentration, or hardness, produced under circumstances about which we can only theorize until we acquire greater knowledge; and,

(2) To a condition effected in the asphalt which when a suitable agent (in this case chlorine) is introduced, renders by combination a portion insoluble and brittle; the action is probably analogous to the formation of "acid sludge" in the refining of distillates by sulphuric acid; and,

(3) To the action of actinic light on solutions of bitumen in carbon tetrachloride, or on the tetrachloride itself, when chlorine is liberated, and is taken up by the unsaturated hydrocarbons forming an insoluble combination.

LATER NOTE.

We are glad to see from Mr. Mackenzie's excellent article in the April number of THIS JOURNAL that he has been able to verify in a great measure our own results, and hope that this publicity may lead to some method of knowing and determining accurately these vexatious carbenes.

We would like to further state that following a suggestion of Mr. Ralph Martin it is now our practice to filter our re-distilled CCl_4 through a layer of $CaCl_2$, which seems to sweeten it considerably.

Another hint we have recently received from Mr. E. O. Heinrich, City Chemist of Tacoma, Wash., is that the formation of HCl is possibly due to the presence of $CHCl_3$ in the CCl_4, derived during manufacture,[1] a reaction being set up under the influence of sunlight, in accordance with the equation:

$$CCl_4 \text{ and } CHCl_3 — HCl \text{ and } C_2Cl_6.$$

1000 DATE ST., LOS ANGELES, CAL.
Feb. 24, 1910.

[1] Richter's Org. Chem., Vol. 1, p. 386.

THE HYGIENE OF THE SMALL CHEMICAL LABORATORY.

By Edward Keller.

Received February 23, 1910.

In perusing the literature on factory-practice of recent years, one is struck by the widespread tendency, expressed therein, to improve the environment of the working people in all fields of industry. Yet, it is too well known that this problem had been neglected for generations. The chemical laboratories have retained, on the whole and in contrast with the modern industrial plants, much of their mediaeval aspect; they generally are full of dense fumes and noisome odors. Consequently, it may be asserted that the chemist may be made a better paying individual by establishing for him favorable and agreeable surroundings where these do not pre-exist; even though one making such an assertion be suspected of humanitarian motives, for the reasons that he himself spends a large part of his life in the chemical laboratory.

I. Ventilation.—It is not the purpose of this paper to deal with the latest improved ventilating and tempering machinery installed in some of our giant plants and buildings. Any one interested therein may be referred to an article on that subject by P. R. Morse.[1] The discussion will be confined to ventilation by natural forces which, when properly conducted, will be shown to be more efficient than the often defectively installed mechanical means in small establishments.

At first sight this subject-matter might appear almost too trivial for a treatise, were it not for the fact that complaints of the working chemists are universally to the effect, that under certain conditions of wind or weather the hoods return the fumes into the working room. These facts at once lead to the conclusion of faulty arrangements in the system of ventilation, incidental to the neglect of applying some of the elementary laws of physics by our architects.

Before analyzing the forces which we must utilize or eliminate in the most economic application of natural ventilation, we must recall to mind the dis-

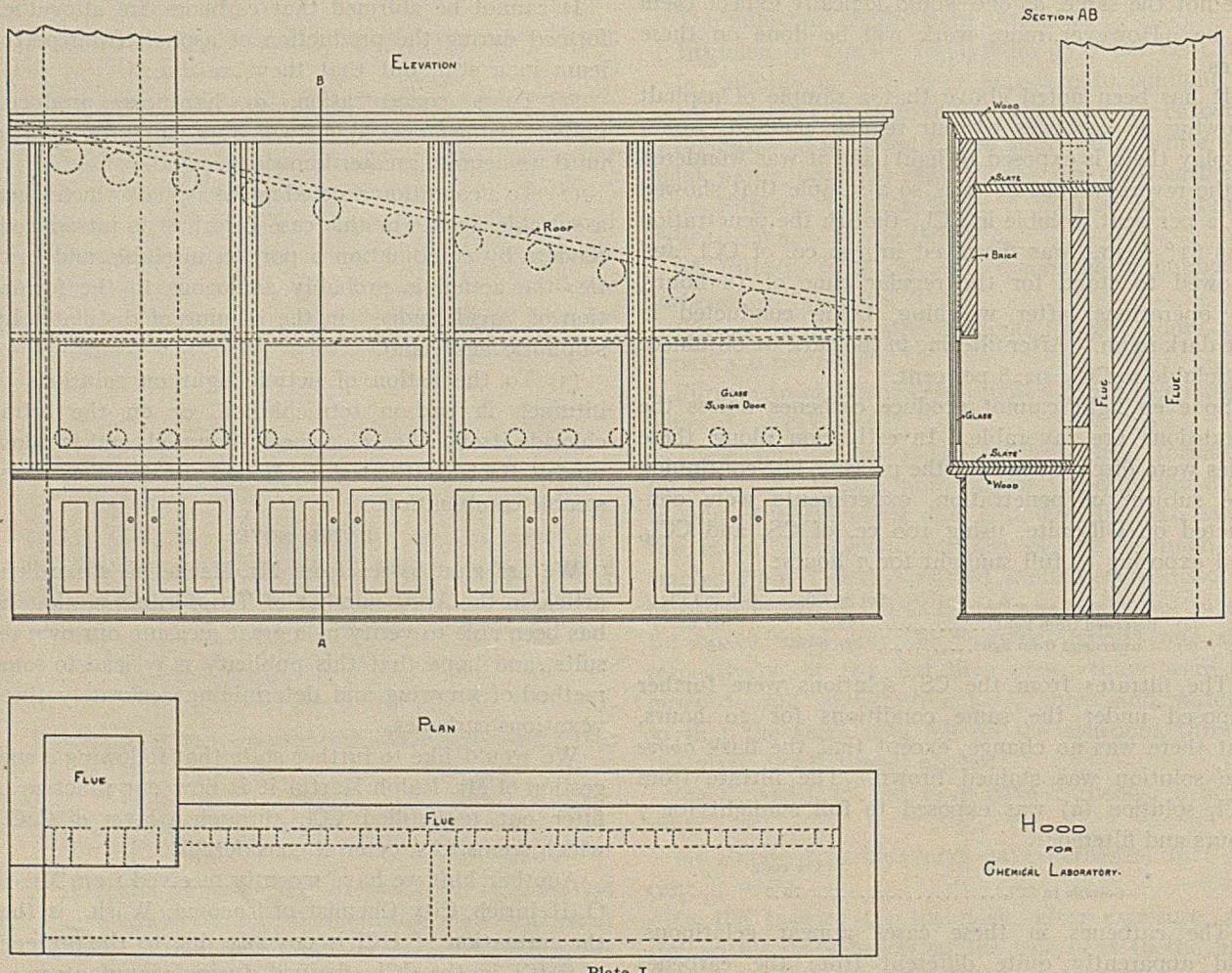


Plate I.

advantage of a laboratory ventilating stack, as regards draught, as compared to the stack of a heating plant, due to the former's small difference of temperature within and without. It is for this reason that

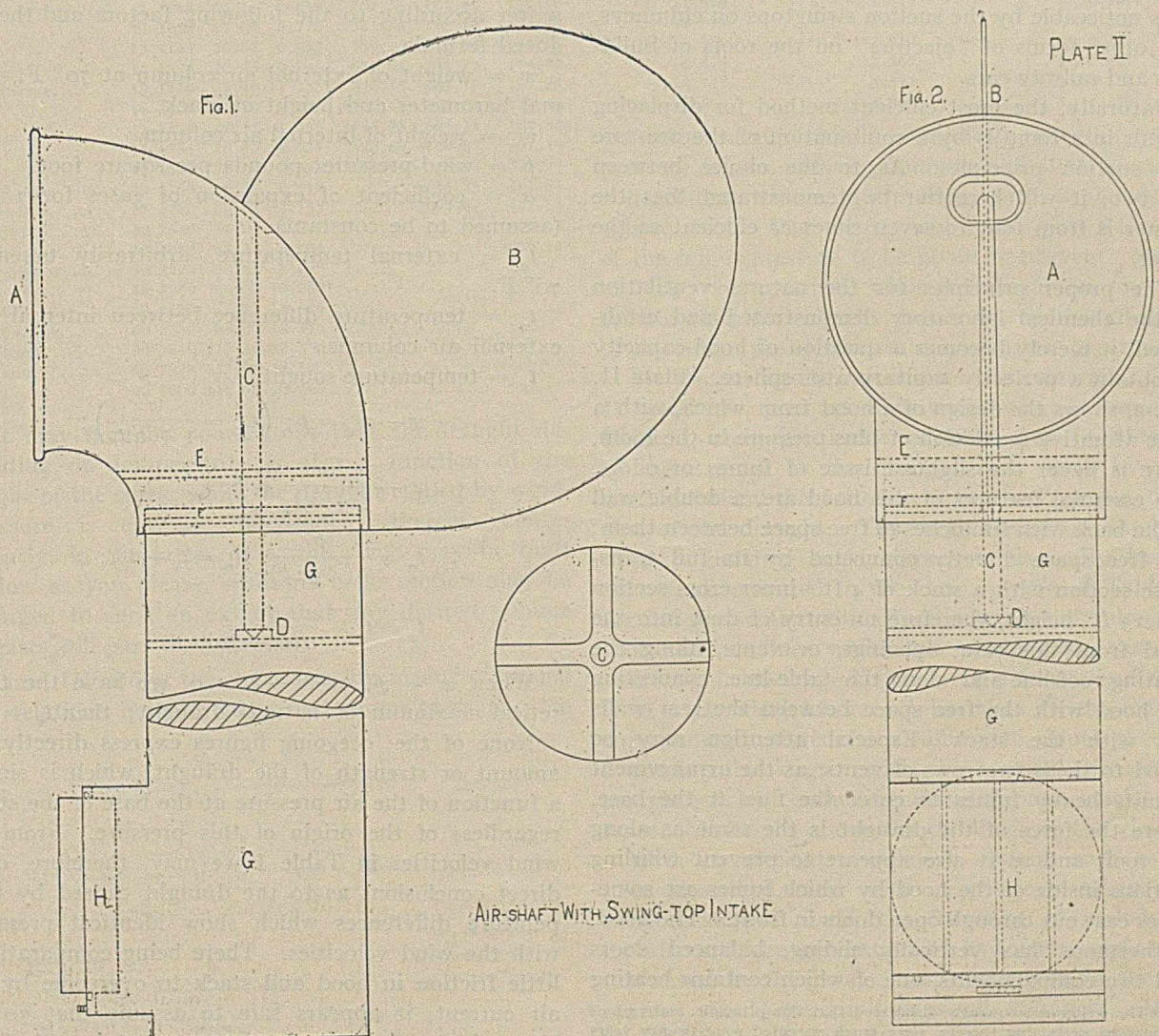
[1] *Engineering Magazine*, February, 1908.

wind and weather play such an important part in its operation. If a certain wind blows down through the stack and drives the fumes from the hood into the laboratory it is not because either east, west, north, or south wind has the tendency to turn at right angles downward. The wind, like any other body in motion, will pursue a straight course, unless deflected by some other force. It has the peculiarity, by blowing over an opening of an enclosed space, to exercise suction or to create within that enclosed space a partial vacuum, while by its velocity-impact it creates a pressure which increases with approximately the square of the wind-velocity. It now becomes self-evident that where the described troubles exist, the stack is offering to the wind a course of least resistance, which again can be due only to a lower atmospheric pressure inside than out, *i. e.*, a partial vacuum existing in the stack and the adjoining room, caused by the suction of the wind in blowing over an open door or window of the respective room. For brevity's sake, the impact-pressure of the wind may be called the plus-pressure while the vacuum pressure must accordingly be termed minus-pressure.

It so happens that very few laboratories, or for that matter any rooms, are exposed to the winds in all directions of the compass. Therefore, when the wind blows from the direction of the sheltered or protected side and there are open doors or windows on the opposite side, there naturally results minus-pressure in the room, with consequent backdraught in hood and stack. It thus becomes clear that in order to obtain reliable ventilation, with constant plus-pressure in a room, we must permanently engage the force of the winds by arranging our ventilators in such a manner that at all times there will be an air receiver in the wind direction, or to have what is known as an injector.

In the writer's laboratory building, skylights have been placed in the four main directions of the compass, two of which open directly into the laboratory, while the other two are connected over the ceiling of other rooms. They can handily be raised and lowered from the laboratory and they have the ad-

PLATE II



AIR-SHAFT WITH SWING-TOP INTAKE

vantage over the ordinary windows in that the draught from them is less perceptible by delicate people and that it less disturbs the gas flames on the working tables.

Where windows or skylights on all sides of a room are impossible, the difficulty of introducing the plus-pressure, at all times and automatically, may be overcome by a device as shown in Plate II, Fig. 1 an "injector."[1] According to the size of the room, one or more airshafts or pipes, *S*, may lead from the roof or through the side-walls into it. These shafts or pipes are capped with swingtops, having a funnel-shaped mouth, *A*, and a vane, *B*, which keeps the mouth turned towards the wind. The ingress of the air into the room may be regulated by one or more registers *H*.

This principle of ventilating by the wind-pressure is generally carried out on all kinds of maritime vessels, although not by automatic injector swingtops, and it is surprising that architects should not have made more general use of it in buildings where perfect sanitation is a prime requisite. The principle of suction by the wind is found more frequently applied, as is noticeable by the suction swingtops on chimneys, and other forms of "ejectors" on the roofs of buildings and railway cars.

Naturally, the most efficient method for displacing the air in a room is by a combination of the pressure and suction principles. As to the choice between the two, it will hereafter be demonstrated that the former is from four to seven times as efficient as the latter.

The proper principles for the natural ventilation of the chemical laboratory demonstrated and established, it merely becomes a question of hood-capacity to obtain a perfectly sanitary atmosphere. Plate II, Fig. 2, shows the design of a hood from which, with a little attentive regulation of plus-pressure in the room, there is never the slightest issue of fumes or odors. The essential features of this hood are, a double wall in the back with six inches of free space between them; the free space directly connected by its full transverse section with a stack of 4 ft.^{2} inner cross section and 25 ft. height, therefore no entry of dust into the hood from this side; openings, or vents, along the slanting roof-line and along the table-line, connecting the hood with the free space between the rear walls and with the stack. Especial attention may be called to these two rows of vents, as the arrangement permits heavy fumes to enter the flue at the base, where the force of the draught is the same as along the roof, and as it also appears to prevent whirling motions inside of the hood by which fumes are sometimes cast out through open doors in front. The hood, furthermore, has vertically sliding, balanced doors and two compartments, one of which contains heating plates, and the other the hydrogen sulphide generator and sufficient space for filtrations or other special work.

Any heating apparatus in the hood will aid the draught in the stack. In some laboratories one finds, for that reason, a gas flame placed in the latter.

In order to prove the superior efficiency of wind-pressure over such small heating appliances, as just mentioned, for the creation of draught, Table I has been compiled. It shows a comparison of pressures by wind-velocity and the same pressures caused by internal and external temperature differences in stacks of various heights. The left-hand portion of the table, showing definitions of winds, their velocities and corresponding pressures, is taken from "Compressed Air and Its Applications," by Gardner D. Hiscox, New York, 1901. The right-hand portion of the table, having in common the pressure column with the left, shows the temperatures which are necessary, in stacks of 25, 50 and 100 feet heights, to produce pressures equal to those produced by the winds. These temperatures have been calculated by the writer according to the following factors and the deduced formula:

w = weight of external air column at 70° F., normal barometer and height of stack.

w_n = weight of internal air column.

p = wind-pressure; pounds per square foot.

α = coefficient of expansion of gases for 1° F., (assumed to be constant).

t_a = external temperature, arbitrarily taken at 70° F.

t_n = temperature difference between internal and external air columns.

t_x = temperature sought.

$$w - w_n = p; \left(w_n = \frac{w}{1 + \alpha.t_n}\right);$$

$$w - \frac{w}{1 + \alpha.t_n} = p;$$

$$t_n = \frac{p}{\alpha(w - p)}; (t_n = t_x - t_a);$$

$$t_x = t_a + \frac{p}{\alpha(w - p)}.$$

When $w = p$, or $w - p = 0$, we have the theoretical maximum of natural draught; then $t_x = \infty$.

None of the oregoing figures express directly the amount or strength of the draught, which is simply a function of the air pressure at the base of the stack, regardless of the origin of this pressure. From the wind velocities in Table I we may, therefore, draw direct conclusions as to the draught caused by temperature differences which show identical pressures with the wind velocities. There being comparatively little friction in hood and stack to overcome by the air current, it appears safe to assume that 50 per cent. of the wind-velocity is converted into draught,

[1] The writer subsequently discovered that this principle, and various mechanisms pertaining thereto, were much patented some twenty years ago.

and taking as an example, from our Table I, the case of a strong breeze with 880 ft. velocity per minute, the draught in the stack would be 440 ft. per minute, or the volume of air passing through our stack during the working day of 10 hours would be 1,056,000 ft.[3] To obtain the same draught by heating the air in our 25 ft. stack, an increase of temperature of (251.56–70) 181.56° F. would need be maintained in the stack.

TABLE I.—COMPARISON OF WIND-PRESSURES WITH CORRESPONDING PRESSURES CAUSED BY DIFFERENCE OF TEMPERATURE IN STACKS OF VARIOUS HEIGHTS.

Observed character of the wind.	Velocity. Miles per hour.	Feet per minutes.	Feet per seconds.	Pressure per square foot. Pounds.	Temperature and height of air-column. Degrees Fahrenheit. 25 ft.	50 ft.	100 ft.
Barely observed...	1	88	1.47	0.005	71.32	70.66	70.33
Just perceptible...	2	176	2.93	0.020	75.31	72.64	71.32
Very light.....	3	264	4.40	0.045	82.11	75.98	72.97
Light breeze.....	4	352	5.87	0.081	92.23	80.87	75.38
Fair breeze.....	5	440	7.33	0.126	105.48	87.12	78.41
Very fair breeze...	6	528	8.80	0.181	122.62	94.97	82.18
	7	616	10.27	0.247	144.72	104.72	86.77
Fresh breeze.....	8	704	11.73	0.323	172.49	116.41	92.16
	9	792	13.20	0.408	206.97	130.12	98.33
Strong breeze.....	10	880	14.67	0.505	251.56	146.64	105.55
	11	968	16.13	0.610	307.53	165.67	113.60
	12	1056	17.60	0.726	381.28	188.24	122.78
	13	1144	19.07	0.852	480.36	214.80	133.11
	14	1296	20.53	0.988	618.95	246.20	144.72
Stiff breeze.....	15	1320	22.00	1.135	826.15	283.79	157.82
	16	1408	23.48	1.291	1160.43	328.62	172.40
	17	1496	24.93	1.458	1796.45	383.38	188.84
	18	1584	26.40	1.634	3426.68	450.47	207.19
	19	1672	27.86	1.821	17134.94	535.18	227.93
	20	1760	29.33	2.018	.....	644.24	251.31
Very brisk.....	25	2200	36.67	3.155	.....	2692.07	427.75
High wind.....	30	2640	44.00	4.547	.....	.....	829.12
	35	3080	51.33	6.194	.....	.....	2414.17
Very high wind...	40	3520	58.67	8.099	.....	.....	.....
Gale.....	45	3960	66.00	10.260	.....	.....	.....
Storm.....	50	4400	77.33	12.684	.....	.....	.....
Great storm.....	60	5280	88.00	18.310	.....	.....	.....
Hurricane.....	80	7040	117.30	32.800	.....	.....	.....
Tornado.....	90	7920	132.00	40.500	.....	.....	(1000 ft.)
	100	8800	146.60	50.000	.....	.....	987.16

It may here be pointed out that the draught depending on temperature is also a function of the height of the stack, while the draught caused by wind-pressure is entirely independent thereof. Consequently, in the latter case, the stack may be built as low as you please, while its cross section may be enlarged to such an extent that any desired volume of gases will pass through it.

Plate III shows the apparatus by means of which the relations between plus- and minus-pressure were determined.[1] For equal pressures at *c*, the corresponding plus-pressure at *a* and the minus-pressure at *b* could be read at the gauges. The latter, used for pressures below one inch of water-column, were of the differential type, capable of convenient reading to one-hundredth of an inch. For higher pressures the ordinary siphon gauge was employed. The results of the measurements are given in Table II. In

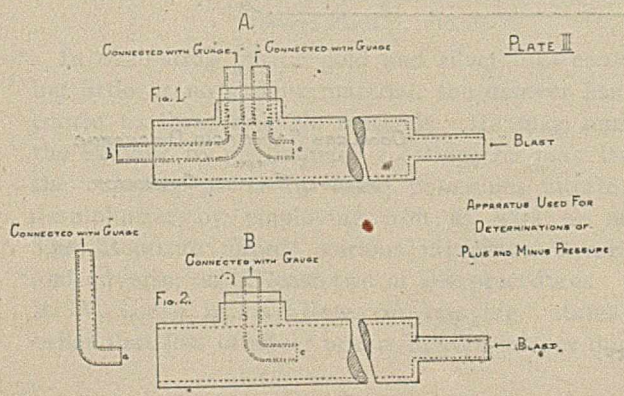


TABLE II.—COMPARISON OF PLUS- AND MINUS-PRESSURE CAUSED BY WIND OR BLAST OF EQUAL VELOCITY.

Plus or velocity-pressure. Pounds per squart foot.	Minus or vacuum-pressure. Pounds per square foot.	Ratio of pressure. Plus to minus.
0.286	0.052	1 : 0.182
0.551	0.078	1 : 0.141
0.806	0.130	1 : 0.161
1.066	0.166	1 : 0.156
1.301	0.239	1 : 0.184
1.545	0.312	1 : 0.202
1.758	0.364	1 : 0.207
2.039	0.437	1 : 0.214
2.341	0.489	1 : 0.209
2.669	0.650	1 : 0.244
4.333	0.962	1 : 0.224
5.894	1.274	1 : 0.216
7.975	1.623	1 : 0.204
9.712	1.956	1 : 0.201
11.616	2.330	1 : 0.201
13.177	2.658	1 : 0.202
14.914	2.939	1 : 0.197
16.646	3.340	1 : 0.201
18.727	3.527	1 : 0.188
19.508	3.886	1 : 0.199

the ratio column it will be noticed that the minus-pressure begins with a minimum and that it reaches a maximum with a plus-pressure of 2.6 pounds per square foot. The figures show the low efficiency of the minus-pressure to be about one-seventh of that of the plus-pressure, while the high one is one-fourth, thus showing the degree of superior efficiency of injectors over ejectors in displacing air in a room.

By comparing the minus-pressure column of Table II with the pressure and temperature columns of Table I, an approximate estimate may be obtained of the damage to the draught in a stack by wind suction, when the latter acts in the opposite direction of the draught. The suction effect of the wind upon a building must, however, naturally be less than that indicated in the ratio column of Table II, for the reason that this effect is active only along the roof- and side-lines, while it is *nil* along the base-line.

II. Deodorization.—To render the fumes and odors from a chemical laboratory harmless to the exterior surroundings, it generally suffices to dilute them to a considerable degree with the atmospheric air, accomplished by conducting them through stacks to a reasonable height above the dwellings of the vicinity.

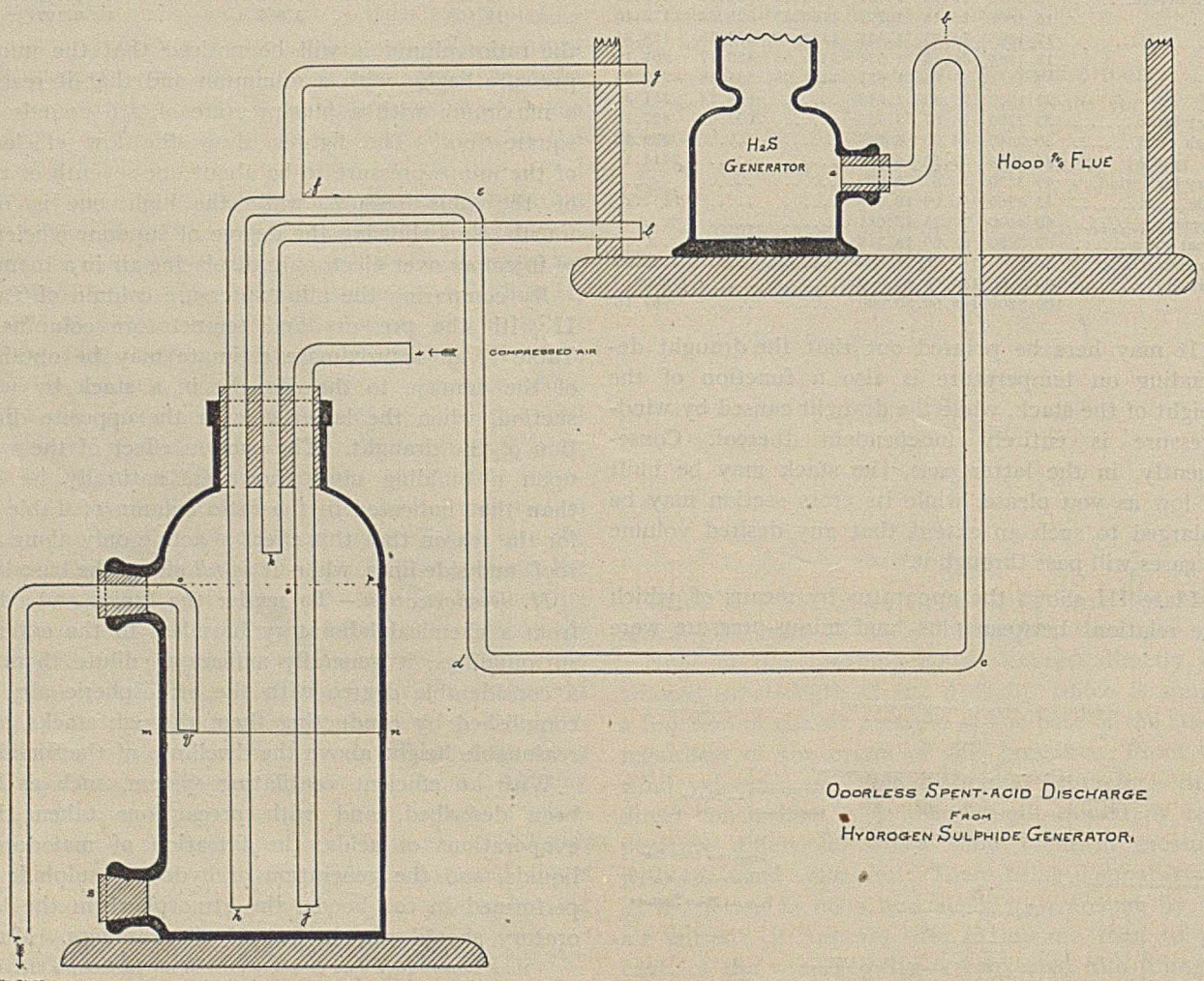
With an efficient ventilating system, such as has been described, and with precautions taken that evaporations of acids, the filtration of malodorous liquids, and the generation of hydrogen sulphide be performed in the hoods, the atmosphere in the laboratory should remain free of all nuisances. Much,

[1] More authoritative data probably exist in the engineering literature. In books available to the writer, they could not be found. For the sake of illustration, merely, actual determinations appeared more simple than the consultation of distant libraries.

of course, depends in the maintenance of discipline by those in charge, and that would appear to be most efficaciously introduced by demonstrating, to the working force's conviction, the utility and efficiency of the contrivances, rather than by adorning the walls with vigorous printed rules.

Odorless Hydrogen Sulphide Generator Drain.—There is, however, another difficulty to overcome in connection with the operation of the hydrogen sulphide generator; it is the discharge and disposal of the spent acid. The latter, upon its release from the generator, is surcharged with the gas which it profusely emits, and when left to flow into drains, which have openings into the laboratory, the gas will enter and may not only become a source of annoyance to the men, but may affect the accuracy of certain chemical work and wreak injury to some of the structural materials; or if after leaving the laboratory, this liquor enters open gutters or partially covered sewers, it will vitiate the atmosphere of the neighborhood.

In the device shown in Plate IV, the writer has found a perfect method for eliminating these troubles, it having been in successful operation in his laboratory for about five years. The form of the hydrogen sulphide generator is immaterial and therefore only its lower portion, with the drain-tube, is indicated in the figure. It is, of course, placed in a hood. The drain system has a trap, *a*, *c*, *d*, *e*, and a vent at *f*, connected with the hood at *g*. The trap is necessary to prevent the gas from escaping through this duct from the generator, and the vent is required to keep the trap filled with the liquor which, otherwise, would be siphoned out by that part of the drain-tube designated by *e*, *h*. The liquor thus flows continuously into the reservoir, *R*, at *h*, filling it to the level *o*, *p*. At this point the discharge tube, *q*, *r*, is filled and through it the liquor is siphoned off until its level in the reservoir reaches *m*, *n*, which operation repeats itself automatically. There always remains a stock of liquor in the reservoir whose surface fluctuates rhythmically between the levels *m*, *n*, and *o*, *p*. Air is injected into the liquor through *i*, *j*, and escapes into the hood through *k*, *l*. At *s* any sediment, or precipitate formed, may be drawn from the reservoir. In addition to the tubes shown in the figure and running through the stopper into the reservoir, a long-tubed funnel may be added, so that filtrates containing hydrogen sulphide may be discarded



Odorless Spent-acid Discharge
from
Hydrogen Sulphide Generator.

Plate IV.

through this drain and made odorless, instead of being poured into the sink with the well-known effects.

The chemical process in the apparatus is as follows: "The liquor is an aqueous solution of ferrous chloride, surcharged with hydrogen sulphide gas. The injected air oxidizes the ferrous to the ferric salt, which is partially precipitated in a basic form. The ferric chloride in solution, by the intimate contact with the inflowing, dissolved hydrogen sulphide, immediately causes the latter's oxidation and decomposition. In the reaction the ferric salt is again reduced to the ferrous state, while hydrogen chloride is formed, and sulphur liberated: $Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S$."

Owing to the permanent stock of ferric chloride solution in the reservoir the discharge at *r* is always odorless; so is also the air issuing at *l*; the only place of odor emission from the drain-system being at *g*, therefore, its connection with the hood is essential.

For common laboratory use the reservoir need not be of the given design. An ordinary five- or ten-pound, wide-necked bottle will serve the purpose just as well. In this case the siphon-tube *g*, *r*, is taken through the sealed stopper with the other tubes, and the bottle freed of the sediment, whenever necessary, by disconnecting the stopper and emptying the whole contents.

This device, when constructed of other acid-proof materials on a larger scale, may readily be applied in industrial plants in which hydrogen sulphide is used.

In conclusion, it may not be amiss to call attention to the facts that the extra cost of installation of the improvements is trifling and the operating expenses practically *nil*, while they greatly contribute to the increase of the "joys" of the laboratory.

Acknowledgment is due my assistants, Messrs. Ferrel and McComas, for the preparation of the drawings from which the cuts in this paper were made.

PERTH AMBOY, N. J.,
Feb. 24, 1909.

THE CRUCIBLE ASSAY OF PYRITIC CONCENTRATES FOR SILVER AND GOLD.

By GEORGE BORROWMAN.

Received March 22, 1910.

In evaluating pyritic gold and silver ores containing little or no gangue material, the assayer has recourse to three crucible methods. He may remove the sulphur by preliminary roasting; he may lessen the reducing power by using potassium nitrate, or desulphurize by employing iron as wire or nails. The literature affords various criticisms, favorable and adverse, on at least two of the procedures. Mr. R. W. Lodge, in his "Notes on Assaying," states the belief that loss of silver occurs in certain ores due to the use of niter. He adduces, however, the results of but two fusions. Messrs. Ricketts and Miller, in their text-book on "Assaying," express lack of confidence in the iron method on ore containing much sulphur. No further comment is made. Mr. H. van F. Furman, in his "Manual of Practical Assaying," says the iron method is preferred by most assayers. Again some authorities recommend a charge for the iron method that yields a basic slag, notwithstanding the well-known fact that such slag is likely to carry values. Others, evidently in recognition of this, prefer a charge containing considerably more acid fluxes and some potassium nitrate. Experimental evidence, however, to substantiate the various opinions, is very meagre and on some points entirely lacking. These circumstances lead the writer to make some investigations, in the hope of obtaining definite data as to the relative efficiency of the various treatments.

In all of the work 0.5 A. T. ton of ore, passed through 100-mesh sieve, was taken for each charge. The fusions were made in a gas muffle, excepting those of a few slags, which were carried on in a crucible furnace. The fusions were started at low heat and gradually raised to about 1200° C., the charges being in the furnace about forty-five minutes. Morganite cupels were used. The fluxes, time of fusion, size of buttons, in short all conditions were kept as nearly uniform as possible. The litharge used contained silver, for which corrections were made.

For the first work a Leadville, Colorado, pyrite was selected. It was almost pure iron sulphide, carrying a little copper. The reducing power was 9.1. Three series of four charges were made up. Series No. 1 consisted of assays for the potassium nitrate method, the following charges being used:

Ore.	0.5 A. T. Grams.
$NaHCO_3$	15.0
PbO	175.0
SiO_2	15.0
Borax glass	10.0
KNO_3	28.5
Salt cover	...

Series No. 2 was first dead roasted and then fluxed as follows:

Ore.	0.5 A. T. Grams.
$NaHCO_3$	15.0
PbO	110.0
SiO_2	5.0
Borax glass	10.0
Argols (R. P. = 10)	2.5
Salt cover	...

Series No. 3 was made up according to the general type of charge usually recommended for the iron method:

Ore.	0.5 A. T Grams.
$NaHCO_3$	30.0
PbO	23.0
Borax glass	10.0
4 Iron nails (20-penny)	....
Salt cover	....

The slags in all cases were liquid and poured well. All were glassy excepting those of No. 3, which were basic. No matte formed in any case. Cupellation gave the following results:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
9.01	8.87	7.88
8.90	8.91	7.23
8.95	8.59	8.29
8.95	9.10	8.29
Av. 8.95	8.86	8.05

It will be seen that Nos. 1 and 2 check closely, while No. 3 is uniformly low. The slags of No. 3 being basic were assayed and found to carry on the average 0.91 mg. With this correction, No. 3 checks the others closely.

The same ore was then assayed with the following charge, recommended by Furman:

Ore.	0.5 A. T. Grams.
$NaHCO_3$	35
PbO	20
SiO_2	15
KNO_3	5
3 Nails (20-penny)	..
Borax glass cover	..

Two fusions were made; the slags were glassy and no matte formed.

Two more charges were run, omitting the nitrate, considerable matte forming in both cases. The two matte-free buttons yielded the following:

	Au + Ag. Mgs.
No. 1	9.17
No. 2	9.04
Average	9.10

These results, it will be noted, are a trifle higher than obtained by any method previously. Furman's charge was further tested by comparing results obtained from it with those from a charge similar to the one used in the first iron fusions. It was taken from one of the recent text-books and consisted of the following:

Ore.	0.5 A. T. Grams.
$NaHCO_3$	30
PbO	20
SiO_2	3
4 Nails (20-penny)	..
Borax glass cover	..

Four charges of each were fused. The slags from the latter mixture were basic, the others as before, glassy. The results of cupellation follow, No. 1 being from the nail-niter treatment:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.
13.61	13.04
13.64	13.27
13.54	13.17
13.74	13.36
Av. 13.63	13.21

These results confirm the preceding. The ore used in the last fusions was taken from a different part of the same lot from which the first assays were made, accounting for the different silver value.

The gold in this ore was merely a trace, too small amount to show any detectable variations. The experiments were concluded by repeating the above iron method tests on a higher grade ore containing more gold. This was also practically pure pyrite carrying values in the form of auriferous argentite. Four assays were made each with of the two iron methods described above. As a check, four more were run by the niter process. The following average results were secured: Series No. 1 is from the iron-niter fusions; No. 2 from the non-niter iron method; and No. 3 from the straight niter assay:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
Av. 78.28	76.54	79.08

Two slags from each were assayed and the following amounts recovered:

No. 1. Au + Ag. Mgs.	No. 2. Au + Ag. Mgs.	No. 3. Au + Ag. Mgs.
3.00	3.62	0.93
2.67	3.50	0.93
Av. 2.83	3.56	0.93

Not more than traces of gold were recovered from the slags.

CONCLUSIONS.

From the foregoing data it seems that with pyrite ores, at least, the maximum amount of niter can be used with impunity, that in fact results are, if anything, a little higher by this method. Iron does not thoroughly decompose highly sulphuretted ores though only silver appears to be carried into the slag. The use of considerable silica apparently assists in breaking up the sulphide, the tendency to matte formation being overcome by a little potassium nitrate. The losses, however, even with basic slags are not very large, but it is evident that when greater accuracy is desired, the more troublesome niter method should be used in preference to the convenient "nail" fusion.

As might be expected, the comparisons show the results of the roasting method to be satisfactory, though higher grade ores might suffer a considerable mechanical loss. In fu ing roasted ores which had contained argentite, the writer found that considerable silver was carried into the slag, probably due to incomplete breaking up of silver sulphate in the roasting.

UNIVERSITY OF NEBRASKA,
LINCOLN, NEB.

THE MILLING OF CANE IN SUGAR MANUFACTURE CONTROL APPARATUS.

By G. L. SPENCER.

Received April 1, 1910.

With very few exceptions, cane sugar factories use heavy mills in the extraction of the juice. In very modern plants the milling equipment consists of a crusher and four mills arranged in tandem. Each mill has three rolls so arranged that the cane receives a double crushing in passing through it. The crusher has two corrugated rolls which break the hard stalks and extract a cons derable part of the juice from them, preparatory to the milling. The pressure upon the rolls is usually controlled by hydraulic devices, that upon the top roll of a mill seven feet long often exceeding 500 tons. The woody residue or bagasse is usually sprayed with water after leaving each mill, except the last of the series, from which it is conveyed directly to the boiler furnaces. The water dilutes the residual juice in the bagasse and facilitates its removal in the subsequent milling.

The quantity of juice that may be extracted varies with the setting of the mills, the quality of the cane, care in eeding the cane to the mills, and the quantity o water sprayed upon the bagasse. A careful laboratory control is necessary to keep a milling plant operating at its highest efficiency.

The control includes the calculation of extraction numbers based upon the weight and analysis of the cane and juice; the calculation of the percentage of saturation or maceration water, *i. e.*, the water sprayed upon the partly extracted bagasse; the calculation of the dilution number, *i. e.*, the percentage of water required to reduce the density of the undiluted or so-called normal juice to the density of the mixed juices. An efficient control requires special apparatus, some very efficient types of which are described below.

Juice Sampler.—The most efficient sampler in the writer's experience is one designed by an engineer of the Calumet Plantation, Louisiana. This instrument (Fig. 1) samples in proportion to the quantity of cane ground. It rarely clogs or fails to operate. The Calumet sampler is shown in section in the illustration. It consists essentially of a plunger with a perforation near one end and so arranged that this perforation is alternately plunged into the stream of juice and withdrawn with a sample. The reciprocating motion is imparted by a crank or eccentric driven by a belt off one of the mill-roll shafts. Fig. 1 is from a working drawing of a sampler arranged to draw juice from the inclined canal or chute from a crusher. The projecting lip, inside the canal, insures the filling of the hole in the plunger. The sample is discharged from the bottom of the plunger into a gutter leading to a storage vessel containing a preservative.

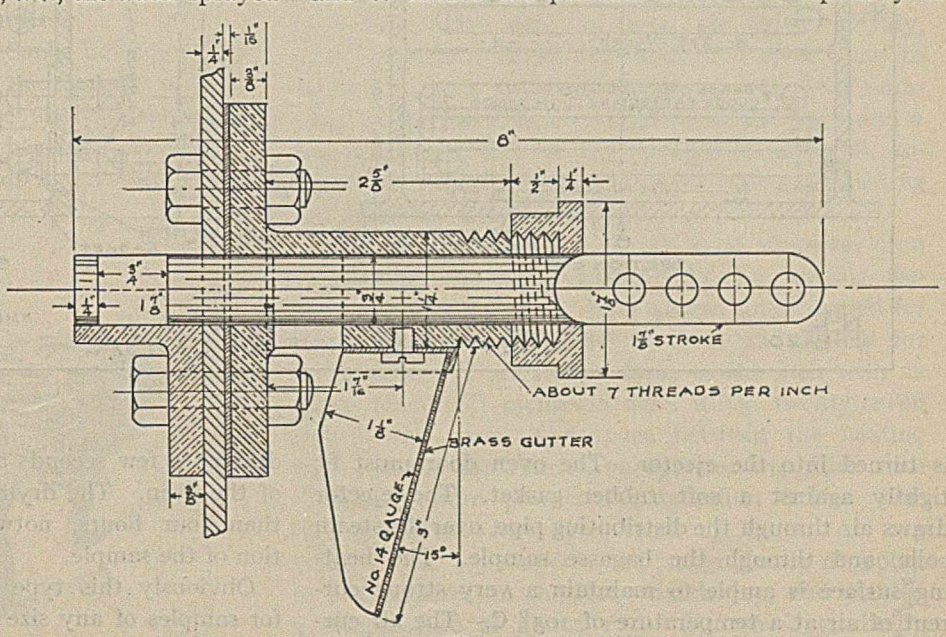


Fig. 1.

Various modifications of this sampler permit its use in sampling from canals and pipes.

Juice Scales.—Automatic scales have been used, usually with indifferent success, in weighing the mill juice. The "hammering" of the heavy charges requires very substantial and expensive construction in an automatic scale and almost constant skilled attention. The hopper- or tank-scale with type registering beam, is inexpensive and efficient. The tanks should be provided with a hot water spraying device to keep them clean.

Apparatus for Bagasse Analysis.—Bagasse is necessarily sampled by hand, owing to milling conditions and the nature of the material. It is usually prepared for analysis by cutting with a butcher knife, a knife mounted similarly to the old-fashioned feed cutters, or by chopping devices. An efficient machine is made in Delft, Holland, especially for preparing bagasse for analysis.

The customary quantitative tests are moisture, fiber (marc) and sucrose. The writer has devised the apparatus described below to minimize labor and to reduce the personal errors and especially to enable chemists to promptly obtain the desired data.

The oven shown in Fig. 2,[1] in section, from a working drawing, will dry 200-gram samples in about 90 minutes. Efficient vacuum ovens require from 4 to

[1] Suggested by the Soxhlet oven.

6 hours and in order to obtain results promptly with the usual types of ovens, the portion dried must be very small, large samples requiring 24 hours drying.

The oven is best described in an outline of the method of using it: 100–200 grams of bagasse are placed in a tared brass tube. The tube has a perforated bottom, 625 round holes per square inch, or is of 100-mesh gauze, also a perforated cover. The cover is held in place by bayonette catches. It should enter the tube and have a narrow flange to make a good joint with the edge of tube "A" of the oven. The sample tube is inserted into tube "A" and steam is turned into the ejector. The oven door must fit tightly against a soft rubber gasket. The ejector draws air through the distributing pipe, over the steam coils, and through the bagasse sample. The heating surface is ample to maintain a very strong current of air at a temperature of 105° C. The air current should be as strong as the coils will heat sufficiently; this is usually as much as the ejector will draw.

The air should be strained through fine gauze before admitting it to the oven. Moisture-free air would doubtless reduce the time required for drying, but for sugar-factory purposes this is unnecessary. Tubes "A" and "B" should be closed with tight covers when not in use.

In the fiber (marc) determination sample tubes similar to those for moisture are used. These hold from 50 to 100 grams of bagasse. The tube and contents are placed in a stream of boiling-hot water, after a preliminary digestion in cold water; or a syphon apparatus similar to the Soxhlet extractor, without the condenser, into which boiling water is passed, may be used. After the extraction of the water-soluble content of the bagasse, the sample is drained a few seconds and these placed in tube "B" of the oven. The drying is usually completed in less than four hours, notwithstanding saturated condition of the sample.

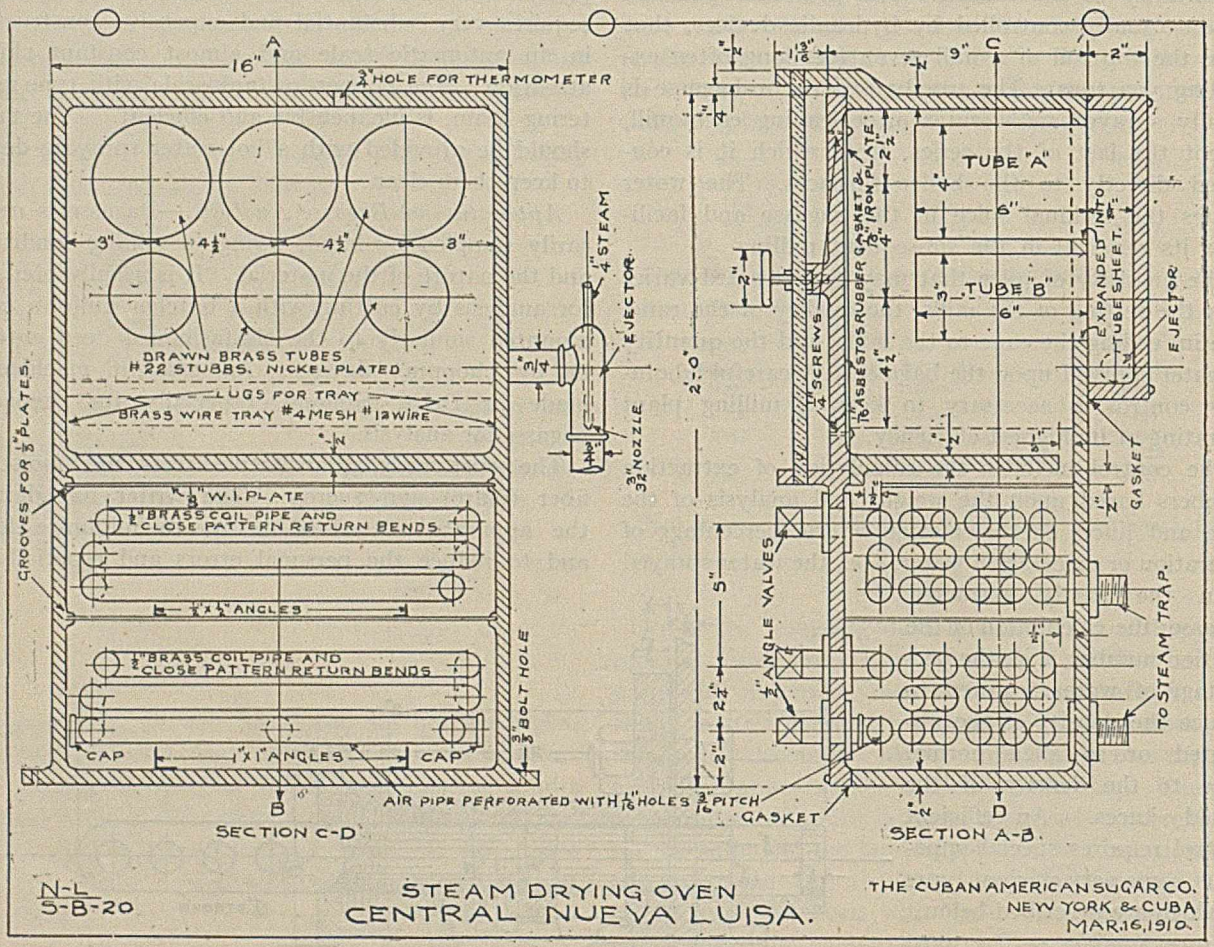


Fig. 2.

Obviously this type of oven may be constructed for samples of any size and could be readily adopted for certain classes of work in agricultural laboratories.

The wire tray is for use in drying samples of molasses and other materials that are not disturbed by a strong current of air.

The writer's experimental oven was built of 2-inch

planks, but he has since equipped the laboratories with ovens of cast iron, as per Fig. 2. The oven should be insulated with magnesia covering. It is very essential that all joints be well made and that air enter the oven only at the distributing pipe. The nozzle of the ejector is designed for steam of about 70 lbs. pressure, and for low pressures the opening may be larger than indicated. Failure to obtain the desired temperature, given a good steam pressure, is usually due to leakage of air at the joints or to drawing too little air over the coils.

In the usual method of estimating the sucrose in the bagasse, 50 grams of the material are digested in a flask, at boiling temperature, with 500 grams of water containing 5 cc. of a 5 per cent. solution of carbonate of sodium. The flask is fitted with a reflux condenser. The time consumed in introducing the bagasse into the flask and the errors involved, the large item of breakage and occasional loss of tests, led the writer to prepare special copper apparatus. This apparatus is a copper beaker 4 inches in diameter by 6 inches deep and provided with a flange and ground joint brass cover. The cover should be heavy and have a hole in it to receive a cork and tube condenser. A straight tube about four feet long forms a suitable condenser. A thin metal tube fixed permanently to the cover may be used but glass is more convenient in controlling the temperature. Clamps are only necessary for holding the cover, when the apparatus is placed in an inclined position in a water bath. An electric hot-plate is the most convenient heating device.

It is probable that the new Sachs-LeDocte digesters, but of large size, used in the analysis of sugar beets, would answer in bagasse analysis, especially where a water bath is used in heating. In this apparatus a brass ring cover is used. A thin rubber

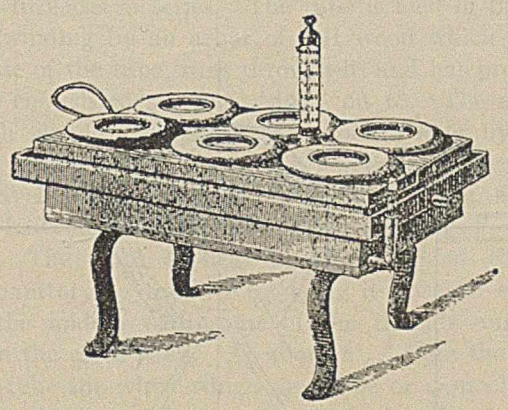


Fig. 3.

cap is slipped over the ring. In placing the cover in position on the beaker, the rubber is bulged downwards by pressure of the thumbs and on releasing it a partial vacuum is formed in the vessel. This vacuum is sufficient to hold the cover in position, providing the contents of the beaker are not heated to boiling. The Sachs-LeDocte apparatus as arranged for use in beet analysis is shown in Fig. 3.

A plain copper beaker with a rubber cap slipped over its edges would answer the purpose in bagasse analysis, though the life of the rubber would probably be short.

CUBAN-AMERICAN SUGAR COMPANY,
NEW YORK AND CUBA.

AN ELECTRIC COMBUSTION FURNACE, LABORATORY TREATING FURNACE AND RHEOSTAT.

By GEORGE M. BERRY.

Received February 17, 1910.

On account of the increased demands upon an already well loaded gasolene gas generator with the attendant impoverishing of the air in the room, where among about one hundred burners six combustion furnaces were kept going constantly during the day, the cost involved owing to the use of high grade gasolene, and on account of the lack of an assuredly sufficient heat to yield complete combustion, without especial preparation of samples, at times when the gasolene in generator was getting "thin" the writer determined to use some form of furnace heated electrically. Knowing something of the workings, but nothing of the construction of the furnaces used by Mr. C. M. Johnson,[1] and something of the platinum wound furnace described at the May 1908 Meeting of the Iron and Steel Institute, but not feeling satisfied with either of these, the writer, in July, 1908, set about some experiments with a view to making a more satisfactory furnace. A brief summary of the more important steps of the work and a detailed description of the furnace as adopted, together with some salient points concerning the making and materials, are here given.

The first furnace had a 10″ x 3″ diameter iron cylinder as the outer casing. As the heating element it had a 24″ x $^3/_4$″ bore quartz tube covered for the middle 11″ with asbestos cloth and wound for the middle $7^3/_4$″ at twelve turns to the inch with 22 gauge (B. & S.) nichrome wire, using twenty-seven feet of the wire. The space between the heating wire and the three-inch iron cylinder was filled with chemically pure powdered magnesium oxide. This furnace lasted forty-five ten-hour days. At 115 volts it took 3.5 amperes at first, gradually dropping to 2.4 amperes on the forty-fourth day, and yielded a temperature of about 1750° F., which gradually dropped to about 1450°.

Furnace No. 2 had a 12″ x 6″ diameter iron cylinder as outer casing. As the heating element a 24″ x $^3/_4$″ bore quartz tube covered for the middle 13″ with asbestos cloth and wound for the middle $7^3/_4$″ with

[1] *J. Am. Chem. Soc.*, **30**, 773.

22-gauge chrome nickel resistance wire from another manufacturer, using twenty-seven feet of the wire. The space between the heating wire and the 6″ iron cylinder was filled with "light" calcined magnesium oxide, commercial. This lasted fifteen ten-hour days. At 115 volts it took 3.5 amperes, gradually dropping to 2.8 amperes and yielded a temperature of about 1850° F., dropping to 1800° F.

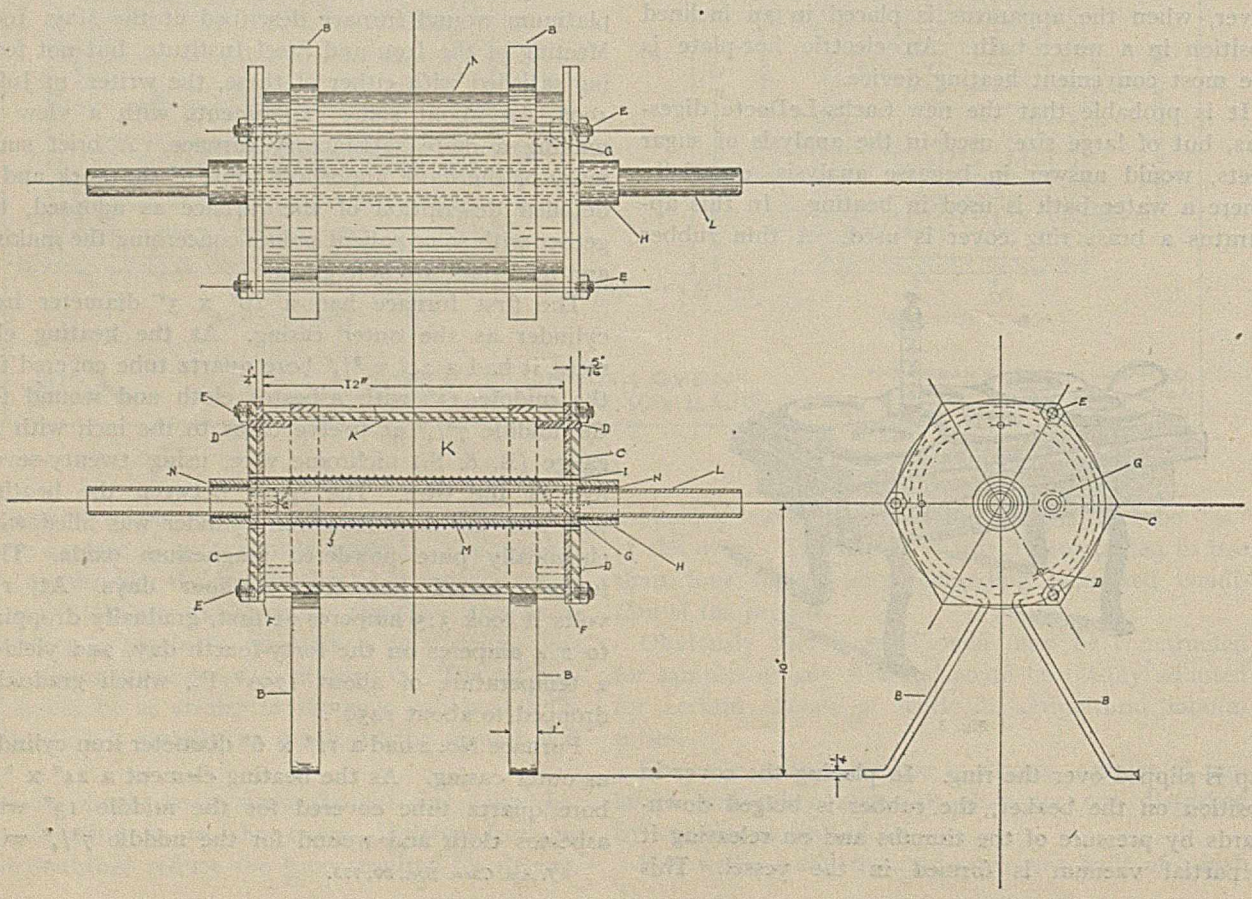
Furnace 2A was made the same as Furnace 2 and with same kind of wire, but with chemically pure MgO as heat insulator. The results were about the same, except for a slightly increased length of life. Furnace 3 was made identical with Furnace 2 except that "heavy" magnesium oxide was used as the heat insulator. This lasted two and one-half hours.

Furnace 3A was made with the outer casing a 12″ x 6″ diameter iron cylinder. The heating element was a 15″ x $1^1/_4$″ bore tube covered with asbestos and wound for $7^3/_4$″ at eight turns to the inch, using about thirty feet of the same kind and size wire as used in No. 2. The space between the heating wire and the six-inch iron cylinder was filled with a double layer of asbestos pipe covering. The space between the $1^1/_4$″ bore tube and the combustion tube was filled with precipitated silica. The life of this furnace was fourteen ten-hour days. At 115 volts it took 4.1 amperes, dropping to 3.2, and yielded a temperature of about 1850° F. Furnace 4 was made identical with number 3A, except that eight inches was wound at six and one-half turns to the inch, using about twenty-five feet of the same wire. A little shorter life and higher temperature were obtained.

Furnace 5 was identical with Furnace 3A, except that $8^1/_8$″ was wound at eight turns to the inch with 18-gauge (B. & S.) Driver-Harris nichrome wire, using thirty-one feet. The life of this furnace for a fourteen-hour day was exactly four months. At 115 volts it took 4.4 amperes and yielded a temperature of 1920° F.

Furnace 8 was made like 5, except that $7^{11}/_{12}$″ was wound at twelve turns to the inch, using forty-five feet of the wire. Chip graphite was used between the two tubes. The life of the furnace here for a fourteen-hour day of constant use was five months and four days. At 112–117 volts it took 3.6 (mean) ampe es. The temperature was maintained at 1750° F. to 1850° F. with this current flow. With this furnace it was found that receding from the middle four inches of the heated zone the temperature dropped rather more sharply than is desirable. The temperature being recorded at the middle, 1800° F.; at each end of the middle seven inches, 1590° F. This is corrected in the furnace as adopted by winding for more length of tube

The Combustion Furnace as Adopted.—The outer casing consists of a piece of six-inch iron pipe A, 12″ long supported by the 1″ x $^1/_4$″ legs B, which en-



cicle the pipe and are spread at the underside, so that the angle between them is of about sixty degrees. At the bottom the feet are bent outward to the line of the horizontal. The height to the center of the furnace is ten inches. The two heads C, which are alike, are of $^5/_{16}$″ plate cut under the shears to hexagon $7^3/_4$″ between their parallel edges. They are equipped with three equidistant pins D, on a $5^3/_4$″ circle. These projected inward, are riveted, are $^3/_4$″ long x $^1/_4$″ diameter and serve to prevent the heads falling from the 6″ cylinder while the insulators and wires are being adjusted just prior to drawing the two heads together with the bolts. They also serve to hold the heads concentric with the cylinder. The heads are further equipped with five holes, having in the alternate angles $^3/_8$″ holes centered on a $7^5/_8$″ circle. Through these three holes pass the bolts E, which draw the heads together and hold them tightly in place. The joint between the head and the cylinder is made tight by a ring of asbestos board F. The center of the head has a two-inch hole, while at the intersection of the horizontal axis and a $3^1/_2$″ circle is a $^3/_4$″ hole. Through this is placed, with the flange inward, $^5/_8$″ x $1^1/_2$″ porcelain insulator G.

The heating element consists of a 15″ x $1^1/_4$″ bore quartz tube H, covered for the middle thirteen inches with one layer of "thin woven asbestos cloth" I, and wound with the resistance wire J, so that the windings are tightly imbedded in the asbestos cloth and do not touch each other and so that the ends cannot slip. For the bore given it will be found that the tubes bought in the market will yield an average winding circumference very close to $5^1/_2$″. For the 110 volt circuit approximately fifty feet 18-gauge nichrome wire is used. For the 220 volt circuit the results desired are achieved by simply connecting two furnaces in series. The tube is held in the lathe for winding by an arbor of soft wood which fits the inside of the tube, runs through it, and has projecting end enough to screw a "dog" on to. The asbestos cloth should be cut thirteen inches long by about six inches wide. Then the lengthwise threads are unraveled until the woven piece is about five and one-half inches wide, saving the ravelings for binding. The cloth is held in place around the tube preparatory to winding by tying it at each end and in the middle with some of the threads unraveled from the cloth itself. At about $2^5/_8$″ from the end of the tube the wire—which should be on a spool in case the tube is to be hand-wound—is threaded with about 3/4″ stitches through the asbestos cloth for one complete turn, and the end is drawn through so that there is a free end about 12″ long. This free end is wound around the cloth and made fast to the "dog," which couples the arbor running through the tube with the lathe. The lathe is now started by having a boy pull the belt, or after experience has been gained by a very low-speed power. The first turn is made to begin at $2^3/_4$″ from the end and the winding continued at eleven turns to the inch until $9^1/_2$″ have been wound. The wire is held firmly in its place on the tube, while it is cut leaving about seventeen inches free end. This end is threaded with about $^3/_4$″ stitches through the cloth for a complete turn as at the beginning, and the end held tight while at both ends the asbestos cloth at the place where the wire is threaded through it is bound and tied with five or six turns of the asbestos thread unraveled from the cloth. This tying of the asbestos string around the tube where the windings cease serves admirably to prevent the loosening of the wire on the tube during subsequent handling. Care should be used at all times to avoid sharp kinks in the resistance wire, as it is likely to break when straightened. The heating element is now ready for the heat insulator.

The heat insulator consist of two pieces—one for $1^1/_4$″ pipe, the other for 3″ pipe—of magnesia-asbestos pipe covering and some asbestos paper (Keasby and Mattison's "Magnabestos" and Johns-Manville 85 per cent. magnesia pipe coverings have been found highly satisfactory.) Both pieces of the pipe covering are twelve inches long. This is readily cut with any kind of saw. The 15″ x $1^1/_4$″ quartz tube, on which is wound the heating wire, is encased with equal projecting ends in the smaller piece of the asbestos pipe covering, which is in turn encased in the larger piece of the same material, so that the joints of the two sizes do not come at the same place. The loose ends of the wire must of course be kept free. The outside of the 3″ pipe covering, which has a diameter of about $5^9/_{16}$″ is wrapped with a strip 12″ wide of asbestos paper until the diameter of this heat insulating material is 6″ and just slips snugly into the 6″ iron pipe of the outer casing. When the heating element and the heat insulator have been placed in the 6″ iron pipe of the outer casing, the loose ends of the heating wire or lead wires are drawn through the $^5/_8$″ porcelain insulators in the hexagon heads. The heads are put in position and drawn tightly to the ends of the 6″ iron cylinder by the long bolts.

The furnace is now ready for the combustion tube L, which is inserted through the $1^1/_4$″ bore tube. For the middle 12″ of the two tubes the space between them is tightly packed with the *Heat Conductor M*, which is chip Ceylon graphite. The graphite is held in place by a ring N, at each end of it, made by wrapping a strip about $^1/_2$″ wide of asbestos cloth around the combustion tube. This serves also to hold the two tubes concentric. The graphite can be most easily introduced between the tubes by setting in place one of the asbestos rings, then standing the furnace on end on a tripod with the asbestos ring at the downward end and pouring the graphite

from a sheet of paper into the space between the two tubes, tapping meanwhile on the upward projecting combustion tube. When the graphite has been solidly packed in for the desired twelve inches, the asbestos ring is packed in place at the upper end. It is desirable to have these asbestos rings packed in tightly, so that large amounts of air cannot get into the graphite and effect a gradual combustion of it. The furnace is now completed and ready for connection to the power circuit and rheostat. The connection to the resistance wire is made by coiling tightly around it for ten or twelve turns copper wire of about 18 ga. Connection can be made from this copper wire to any desired conductor.

As winding for the heating element, the nichrome wire from the Driver-Harris Wire Co., Newark, N. J., seemed to give the best results.

The time required for the winding reduces itself, after some experience, to a short and easily executed operation. The writer, with the help of a boy, has repeatedly wound with hand feed, including all manipulations, three elements in an hour.

The life of the element is, of course, effected much by the care exercised in the daily use of the furnace. It is important, for instance, that the element, after it has been in use some time, should not be subjected to any sudden jar or jerk, such as is occasioned when the hand slips off the stopper when tightening it in the combustion tube just after inserting a boat. The element should not be subjected to any undue longitudinal or rotary motion in this operation of corking the tube, as such abuse tends to loosen the element from the heat insulation and also increases the possibility of short circuit of the windings. Four elements used in pairs by the writer and kept under heat for a 14-hour day, each lasted four to five months. He has now been using for about three months his third pair of elements.

Some irregularity has been noted with some lots of wire received, due to its having been heated too hot in the annealing. Such wire shows in the fracture a coarse crystalline structure with a bright lustre at the edge. It is brittle. Extreme care must be taken to avoid short kinks in it and consequent breaking. If too bad it can be annealed by passage of the electric current; or with those inexperienced in this, it should be returned to the makers, to be replaced with wire that is satisfactory.

The furnace to yield 1800 to 1850° F. should have connected in the circuit about 3 to 5 ohms rheostat resistance, depending on the voltage, and should take 3.2 to 4.0 amperes, depending also on the voltage. Where, on account of rather coarse sample, or for other cause, it is thought advisable to temporarily raise the temperature of the furnace above 1800 or 1850° F. this can be done by simply cutting out one or two ohms of the rheostat resistance. However, some judgment must be used in doing so with a heating element that has been in use some months, as the wire has become somewhat oxidized and is somewhat reduced in cross section area. The temperature may be raised at any time by cutting out some of the rheostat resistance, but with this or any other kind of wire resistance furnace excessive temperature is always at the expense of the life of the furnace.

As heat insulator many materials were used with varying degrees of success. Powdered MgO, C. P., is satisfactory. MgO of the commercial grade both "light" and "heavy" seemed to contain some agent that attacked the heating wire. This objection might be overcome by a thorough ignition of the commercial grade at high temperature before using. Of the various heat insulators tried other than that described in the furnace as adopted for general use, and MgO that which would seem to lend itself under some circumstances to a practical using, is a special form or brick made from fire clay. It is made cylindrical, so as to be, when burned, 12″ long by 7″ diameter with a two-inch hole through center of its circular cross section. This brick was made both in one piece and in two longitudinal sections. There are objections to this brick arising from the mechanical packing and the handling of the heating element with them, the breaking of the brick, and the lack of suitable equipment in most places for making them. If this form of brick should be used the iron outer casing would not be necessary. Some form of support with cylindrically hollowed top or with upward projecting pins to prevent rolling is all that would be required. However, for reasons of cleanliness and durability, the outer casing as described was adopted and for reasons of cheapness, ease with which obtained, and good results achieved, the pipe covering as described was also adopted.

While this description is given using a quartz tube, the time required for removing the combustion tube and replacing it with another is so short that any other kind of tube—porcelain, glass or platinum—may be put in service in the furnace at will. This changing of combustion tubes when not a necessity is hardly to be recommended, however, with a furnace heating element which has been in continuous service some months. The reason for this is the increased likelihood of short circuit of the turns of wire on the outer quartz tube caused by these turns becoming displaced (the asbestos cloth having shrunken) when this tube is put in the vertical position for introducing the graphite between the two tubes. On account of not being able to use red lead or any oxidizing flux in quartz tubes it is the practice in this laboratory, where carbon in a great number of all the varieties of ferro alloys is required to be determined, to keep a pair of furnaces equipped

with 24″ by $^3/_4$″ bore Royal Berlin porcelain combustion tubes ready to be connected in circuit for use whenever needed. Of course the usual precautions against breaking a porcelain tube must be observed when introducing the boat into the porcelain tube.

The furnace here given as adopted for general use has proven highly satisfactory for the uses intended. The features embodied in the use of the thin woven asbestos cloth as a bed for the wire windings and the use of the graphite in the space between the tubes as the heat conductor are highly valuable and are, so far as the writer is aware, entirely new. The asbestos cloth can be obtained from any chemical apparatus supply house; the chip Ceylon graphite from any manufacturer of plumbago crucibles.

The actual cost for the entire furnace as made is itemized as follows:

Outer casing:	
Materials	$0.76
Labor	2.26
Heating element:	
15″ x 1 $^1/_4$″ bore quartz tube	3.12
Asbestos cloth	0.15
Wire	0.53
Heat insulator	0.22
Porcelain insulators	0.01
Graphite	0.05
Total	7.10

It is worthy of note that the only parts that deteriorate so as to need replacing at the time of successive rewindings of the heating element are the asbestos cloth, the resistance wire and the inner piece of pipe covering, with an aggregate cost of ninety cents.

The laboratory treating furnace is used in two sizes. The smaller for the 110 volt circuit is made in two variations. One of these is exactly like the combustion furnace with the omission of the combustion tube. The other is identical except that 17-gauge nichrome wire is substituted, winding 10$^1/_2$″ at eleven turns to the inch. Working in temperatures higher than are needed for combustion furnace practice, this larger wire affords an increased length of life over the 18-gauge. The maximum safe carrying capacity as given by the manufacturers is 9 amperes for the 18-gauge and 10 amperes for the 17-gauge. This is doubtless true for the wire in the open air, but when encased in a heat-insulating material 50 to 60 per cent. of these figures should not be exceeded. When either this or the large furnace is in use, each end of the quartz tube is plugged tightly with asbestos wool to hold the heat.

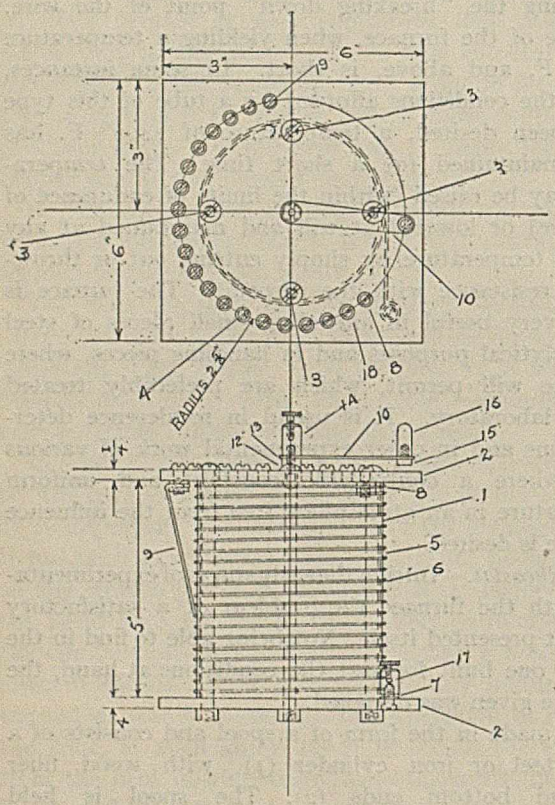
The larger size is for the 220 volt circuit. It is similar to the combustion furnace. The outer casing has an iron cylinder which is 8″ inside diameter by 17″ long. The heating element is made on an 18″ x 1$^1/_2$″ bore quartz tube. 18-gauge nichrome wire is used, winding 15$^1/_2$ inches at eleven turns to the inch, using about 90 ft. of the wire including the leads from the furnace. As heat insulator, two layers, each 1$^1/_2$″ thick, of magnesia-asbestos pipe covering of size for 1$^1/_2$″ and for 4$^1/_2$″ pipe are used.

These furnaces have value in affording a very thoroughly uniform temperature for their full length, except the extreme ends. They have also the advantage of having nothing about them which produces dirt in the laboratory. They cannot be said to be desirable for constant use in temperature approaching the "breaking down" point of the wire. The life of the furnace, when yielding a temperature 2200° F. and above, is short. In some instances, where the conditions afforded by a tube of this type have been desired, a temperature of 2400° F. has been maintained for a short time. The temperature may be raised (within the limits of endurance of the wire) or lowered at will and maintained at any desired temperature by simply cutting out or throwing in resistance with the rheostat. The furnace is found very useful in annealing small pieces of steel for analytical purposes and in handling pieces, where the size will permit, which are preferably treated in the laboratory. It is useful in recalesence determinations and in other experimental work of various sorts where a controllable, constant and uniform temperature in an atmosphere free from the influence of flame is desired.

The Rheostat.—During the early stages of experimentation with the furnace the problem of a satisfactory rheostat presented itself. Not being able to find in the market one built for just the conditions at hand, the one here given was designed.

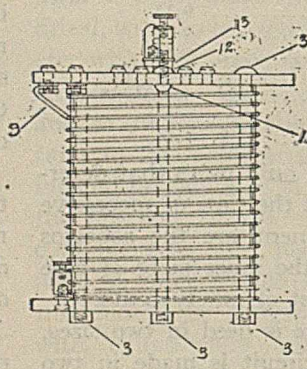
It is made in the form of a spool and consists of a sheet steel or iron cylinder (1), with wood fiber top and bottom ends (2). The spool is held together by four bolts (3), 5$^3/_4$″ long by $^1/_4$″ diameter, extending completely through the spool just inside the metal cylinder, thus serving to hold the ends in place and to keep the cylinder concentric with the coil-button circle (4). A layer of asbestos cloth or paper (5), $^1/_{16}$″ thick, is wrapped around the cylinder and is held in place by the coil of resistance wire (6). One end of this resistance wire is fastened under binding post (7), which is in the corner of fiber board bottom. The wire is then wound tightly around the cylinder in coils $^1/_4$″ apart and the other end fastened under the first screw (8) of the coil button circle. Twenty turns are thus wound on the spool. The sheet metal cylinder, which is 5″ long and 4$^1/_8$″ outside diameter, is increased to 4$^1/_4$″ diameter by the asbestos covering, giving a circumference of 13.35″. For the windings 22-ga. (B. & S.) nichrome wire, which has a resistance of 0.9 ohm per foot, is used. A coil of this size has then a resistance of one ohm per turn. The fiber top is provided with a circle of coil-buttons twenty-two in number placed $^1/_2$″ apart between centers at a radius of 2$^5/_8$″ from the center of the fiber top.

Brass bolts (round-head machine screws) 8 x 32 size and $^7/_8$″ long are used for these buttons. Holes the body size of the screws are drilled through the fiber top, the screws inserted, and one nut screwed tightly on the under side, thus holding the bolt. Each turn of the resistance wire is in succession tapped by pinching around it a piece of copper wire (9) about 18-ga., which is led upward to the lower end of the



corresponding brass bolt, where it is bent around the bolt and held against the first nut by a second nut. The switch arm (10) is a piece of sheet brass about $^1/_{16}$″ thick and $^5/_8$″ wide, having a hole with about No. 19 drill (0.166″ diameter) through each end $2^5/_8$″ between centers. Through the center of the fiber top is a No. 19 hole. Through this hole is inserted from the lower side a No. 8 x 32 brass screw (11). A brass nut (12) is screwed down tightly on the top side and a washer or jamb nut (13) is put on. One end of the brass arm (10) is placed on the bolt over this washer and a binding post (14) is screwed on. The binding post should be tight on the screw (11) and be stationary, but the brass arm (10) should be free to turn. The other end of the arm is provided with a brass screw (15) and a fiber handle (16). The switch arm should, of course, press firmly on the coil-buttons so as to give a good contact. A wire carrying the electric current is inserted at (17), the current passes through the resistance wire (6) and out at (8) through brass arm and to binding post (14), where connection is made to furnace wire. When the arm is on button (8) the entire 20 ohms are in circuit; placing arm on the next button (18) cuts out one turn of resistance wire (6), giving 19 ohms. Advancing thus each button cuts out 1 ohm. Button (19), which is connected to the first coil above (7) thus gives 1 ohm. Button (21) (not shown in drawing) is adjacent to button (19), connection from this drops directly down, through the bottom fiber board, and is connected to (7). This gives the full load without resistance. Button (20) (also not shown) is adjacent to (8). It is unconnected and breaks the circuit.

The cost of materials of the rheostat as made by the writer, has not in any case exceeded $1.02. The mechanic's time should not exceed two hours.



The rheostat as first made by the writer had for the top, slate of $^1/_2$″ thickness, and had the binding posts adjacent and on the same circle as the coil-buttons. The use of the board fiber and the arrangement of the binding posts as here shown was introduced by Mr. M. A. Allen at the time of his beginning the use of this furnace in May, 1909. The use of the board fiber has, as compared with slate, the decided advantages of being easily procured, easily cut and drilled, and of being non-breakable.

It has been the purpose in this article to give to all fellow laborers the necessary details of the information gleaned, in the hope that it may be of help to some and so that any can, by following the details given, produce at nominal cost a furnace which will do the work for which it was designed.

The writer is indebted to Mr. Myron A. Allen, Chemist to the Brown-Lipe Gear Co., for his very kind service in making the accompanying drawings of the furnace and the rheostat and also for the changes mentioned in the design and material of the rheostat.

LABORATORY OF HALCOMB STEEL COMPANY,
SYRACUSE, N. Y.,
January, 1910.

[CONTRIBUTION FROM THE LOUISIANA SUGAR EXPERIMENT STATION, AUDUBON PARK, NEW ORLEANS.]

OCCURRENCE OF FORMALDEHYDE IN SUGAR CANE JUICE AND SUGAR-HOUSE PRODUCTS.

By P. A. YODER AND W. G. TAGGART.

Received April 2, 1910.

In an investigation on some minor constituents of the sugar cane and sugar-house products, we diverged from the main branch of the problem pur-

sued (the acid constituents) to investigate the occurrence of formaldehyde and incidentally for the further elaboration of a method for quantitatively estimating small amounts of formaldehyde. We were led to this sideline investigation by a consideration of the facts (1) that formaldehyde is very convenient to use and frequently is used to preserve fresh juice in the sugar house when boiling is interrupted from any cause; (2) that it is recommended by some as a clarifying agent; (3) that formaldehyde is objectionable in food products; and (4) that it has never, as far as we know, been proved, but is generally assumed that it all boils away in the evaporation of the juice to a massecuite. Further complicating the problem are some recent reports that in caramelizing sugar or even in boiling sugar solutions, formaldehyde is formed. Trillat[1] and A. A. Ramsey[2] report thus. Chas. H. La Wall[3] calls into question the conclusions of Trillat and Ramsay, pronouncing the test which the latter used as unreliable. That formaldehyde can form unstable compounds with some of the sugars has been reported by several investigators. Lippmann[4] mentions such a compound with cane sugar.

The preliminary work on the detection of the formaldehyde in sugar-house products and on the quantitative methods for its estimation was done by us jointly, the junior author carrying out most of the laboratory tests. The working out of final details of the quantitative method used and its application to the juices and sugar-house products reported here was done by the senior author, who alone and in a private capacity is responsible for the formulation of this report and the conclusions drawn.

Methods for Detecting and Estimating Formaldehyde.—Of qualitative tests for formaldehyde there is no lack and many of them are exceedingly delicate. The reliable quantitative methods usually mentioned in text-books, *e. g.*, the KCN and $AgNO_3$ method, or the H_2O_2 acidimetric method, are not sufficiently delicate to use with the very small quantities with which we found it desirable to work. Hehner's test with milk and concentrated H_2SO_4 containing a trace of iron, as well as a similar test with HCl, seems to be characteristic of formaldehyde and so delicate for qualitative work that we were led to look hopefully to modifications of these for a quantitative method which, even if not extremely accurate, is sufficiently accurate and delicate for our purposes. F. W. Richardson[5] modified Hehner's method to make it colorimetrically quantitative, using in place of milk a clear solution containing albumose, which he prepared by incompletely digesting egg albumen with a solution of pepsin and HCl. Seeking a similar substitute for milk in the method with ferruginized concentrated HCl, we tried first a solution of dried peptone, such as is used in bacteriological laboratories. This worked so satisfactorily that we did not take further trouble to prepare partly digested albumen. Substituting this peptone solution for milk, we had a very delicate reagent and the resulting colored solutions were so clear as to be well adapted for comparisons in Nessler's tubes.

In the preliminary work, 1 cc. of the distillate or other solution to be tested was mixed with 5 cc. of a 1 per cent. peptone solution and 5 cc. of concentrated HCl containing one part $FeCl_3$ in 5000 parts acid. This mixture was gradually heated in a small flask over a free flame to from 80° to 85°, held at that temperature 2 minutes, and then allowed to cool. Thus we tested the following compounds closely related to formaldehyde or frequently accompanying it: acetic aldehyde, benzaldehyde, sucrose, dextrose, levulose, xylose, ether, ethyl and methyl alcohols, acetic, lactic, oxalic, propionic, glycolic, citric and benzoic acids, phenol, metol, pyrogallol, furfurol, potassium cyanide and acrolein. Of these the glycolic acid and the ether are the only ones that gave the same color. The same sample of ether, after being thoroughly washed, ceased to give it. We conclude that the ether was contaminated with formaldehyde and probably the glycolic acid likewise. After the publication of the article by La Wall above referred to, in which he assigns furfurol as the cause of Ramsey's supposed test for formaldehyde in caramelized sugar products, additional tests with furfurol were made according to the details as finally worked out for this method and reported below. Though applied to solutions of furfurol ranging in strength from 1 in 1,000,000 to 1 in 100, we got no reaction except the faint tint which water alone gives with the reagents. Assuming the ferruginized concentrated H_2SO_4 reacts or fails to react in the same cases, we must conclude that La Wall was in error and that his furfurol actually had formaldehyde in it, but not in sufficient quantity to show in the less sensitive test of Rimini, upon which La Wall depended to prove the presence or absence of formaldehyde. As ultimately applied to cane juice and sugar solutions, our method in detail is as follows:

The sugar solution is acidified with H_3PO_4, then distilled from a bath of boiling saturated common salt solution with a current of steam superheated to a temperature such that there will be but little change in the volume in the distillation flask. To 5 cc. of the distillate in a test tube, size 20 mm. by 180 mm., add 5 cc. of a 1 per cent. peptone solution (recently dissolved and filtered) and 10 cc. concentrated HCl containing 1 part $FeCl_3$ to 5000. Mix these with a

[1] *C. r. d. l'Acad. des Science*, **142**, 454–6. *Chem. Centr.*, **1905**, I, 18, 131, 1178; 1423; **1906**, I, 917, 1193. *Z. Ver. Rübenzucker Ind.*, **1906**, 93–103. *Bul. de l'Assoc. des Chim. de Sucr. et de Dist.*, **23**, 649–652.

[2] *Jr. Roy. Soc. N. S. W.*, (1907) **41**, 172–5. *Intern. Sugar Jr.*, **11**, 100. *Bul. de l'Assoc. d. Chim. de Sucr. et de Dist.*, **26**, 587.

[3] *Am. J. Pharm.*, **81**, 384. *Chem. Abstr.*, **3**, 2836.

[4] *Chem. d. Zuckerarten*, **2**, 1320.

[5] *J. Soc. Chem. Ind.*, **26**, 3 and 4; *Chem. Abstr.*, **1**, 750.

heavy glass stirring rod with rounded end, which may conveniently remain in the tube to weight it down and aid in mixing while heating in the water bath. Prepare likewise any number of other samples and at the same time a set of standards for comparison, which may conveniently include strengths 1 : 50000, 1 : 100000, 1 : 200000, 1 : 500000, 1 : 1000000, 1 : 20000000 and a blank. The test tubes, suspended through holes of an appropriate size in a board, are suspended in a water bath previously heated to such a temperature slightly above 82.5° C. that the cold tubes will bring it down to about 82.5°. Keep it in the bath at this temperature for altogether 5 minutes, occasionally shaking by a rotatory motion of the board so that the glass rods in the tubes will rotate and help mix the contents, then set into a bath of cold water. After cooling, the color intensities of each sample and its most nearly matching standard are matched in the ordinary way by varying the depths of the columns in Nessler's tubes. From these data the strength o the sample is determined. If the sample is stronger than 1 : 100000 it should be diluted tenfold or a hundredfold before mixing and heating, to bring it within the range 1: 100000 and 1 : 1000000. As the dilute solutions of formaldehyde do not keep well, the tests should be made not too long after distilling and the standards should be made up from strong solutions not over a day or two prior to the time of using them.

An extended study of this method developed the following facts:

Blanks with the reagents available to us always gave a slight coloration, barely distinguishable from that with a standard 1 : 5000000. Practically the method is not applicable to solutions weaker than 1 : 1000000.

With solutions of formaldehyde stronger than 1 : 100000 and reagents of same strength as before indicated, the increase in intensity of color is not correspondingly great. Instead of a deeper color, it develops a color less towards the violet and more towards the purple shade. Diluting afterwards to like strengths will not bring such pairs to like intensities of color.

Stronger solutions of formaldehyde with reagents stronger in both peptone and $FeCl_3$ will develop a correspondingly greater intensity of color.

The proportion of $FeCl_3$ to the peptone should not vary greatly from that given above to get best results.

Nitric acid may be substituted as the oxidizing agent for $FeCl_3$, using 1.6 cc. normal HNO_3 to 100 cc. concentrated HCl, as was done by Shrewsbury and Knapp,[1] but, contrary to the conclusions of these gentlemen, we did not find the HNO_3 possessing any advantage, but having the disadvantage of decomposing and losing its activity quickly on standing after mixing with the HCl.

With the water bath as low as Shrewsburg and Knapp report, *viz.*, 50°, we found the action too feeble to be satisfactory, and likewise at 66°.

The color, after cooling, changes very slowly towards blue and less intensity, allowing one or two hours after heating to make the comparisons, provided, however, that sample and standard stood equally long.

Heating the mixture over the free flame in a casserole, controlling the temperature by the aid of a thermometer, gave less good results and was far less expeditious where many samples and standards had to be prepared.

In these experiments, in which superheated steam was used, the steam was superheated, for want of a better way, by passing it through a copper spiral over a small flame. Its temperature was controlled by use of a thermometer in the current of the steam about 5 inches above the neck of the distillation flask and about 10 inches from the liquid through which it bubbled. The temperature at the thermometer was held at about 115°, never going above 120°, except in Nos. 5, 7, 9 and 10, in which it was held at 120° to 125°. With the distillation flask in a boiling water bath and the inflowing steam at 115°, the volume increased about 9 cc. for every 50 cc. distilled. With the boiling saturated brine bath and the steam at 115°, the volume decreased about 7 cc. for every 50 cc. distilled. Though we adhered in most of these tests, for the sake of uniformity and comparative results, to the one temperature, 115°, our recommendation is to choose a lower temperature, or, if necessary, to omit superheating the steam, so that the volume in the distillation flask may remain constant.

Application in Examination of Cane Juices, Sugar-House Products and Special Mixtures.—The test for formaldehyde, of course, could not be made in the presence of the sugar and other constituents of the juice, therefore distillation was necessary to separate the formaldehyde from interfering substances. Experiments were tried with and without previously acidifying and by distillations from free flame, from oil bath, by steam from oil bath, by superheated steam from water bath, and by superheated steam from brine bath.

In the preliminary work, while we were following the method of heating over the free flame and comparing samples and standards that were prepared in succession, the results were not always regular or conclusive, but among the following conclusions, those not based upon the results of the final tests reported in the accompanying table are based upon regularities in the results of the preliminary tests, such as seemed to justify the conclusions.

In all the distillations the mouth of the condensers

[1] *Analyst*, **34**, 12–14. (This report came to our attention after practically all our work on the method was completed.)

touched, or nearly touched, the narrow neck of the receiver flask, but no further provision was made to guard against the escape of formaldehyde into the air.

In tests in distilling in this manner, moderately strong formaldehyde solutions (1 per cent.), acidified with phosphoric acid, and determining the formaldehyde in the distillate by the $KCN-AgNO_3$ method, the recoveries were 84, 91, and 102 per cent., respectively, in three tests.

If water is distilled with superheated steam from a 10 or 15 per cent. sugar solution, not acidified, there are only traces of formaldehyde shown in the distillate (Nos. 5, 6 and 11 in the table).

In distilling an acidified juice or sugar solution from the direct flame (Nos. 1 and 4), the succeeding fractions of the distillate increase in the amount of formaldehyde as the caramelization point is approached. The browned residue, redissolved and again subjected to distillation, yields distillates relatively strongly charged with formaldehyde Nos. 1*a*, 2*a* and 3*a*). These results seem to bear out the conclusions eached by Trillat and Ramsey, cited above, with reference to the formation of formaldehyde in the caramelization of sugar. However, we are still not quite sure that this caramelization product, the distillate from which gives the formaldehyde reaction, is actually formaldehyde, though we are satisfied it is not furfurol. It does seem strange, if formaldehyde is formed by very slight caramelization in such large quantities as indicated by Nos. 1*a* and 2*a* in the table, that jams, caramel candies, and many other sweetmeats can be eaten with such impunity as they are.

In distilling sugar solutions with superheated steam, the distillates show only traces of formaldehyde and succeeding fractions are nearly constant in formaldehyde content (Nos. 7 and 12). In 250 cc. of distillate with superheated steam through a solution of 15 grams sugar in 100 cc. water, only 0.143 mg. formaldehyde was formed.

A number of other samples of fresh juice not recorded in the table, including one from green top joints of cane, gave results not remarkably different from No. 1 here reported.

In preliminary tests in which formaldehyde was added to water and to sugar solutions, there was evidence that sugar tended to hold back a small portion of the formaldehyde from distilling over.

Adding formaldehyde to cane juice or sugar solutions in the proportion of 1 mg. per 100 cc., it is recovered in the distillate either from direct distilla-

TABLE OF FORMALDEHYDE DETERMINATIONS.

No. of test.	Composition of mixture.	Manner of distillation.	Formaldehyde found in fractions of distillate. In 1st 50 cc. mg.	In 2nd 50 cc. mg.	In 3rd 50 cc. mg.	In 4th 50 cc. mg.	In 5th 50 cc. mg.	CH_2O recovered mg.
1.	200 cc. juice + 5 cc. H_3PO_4[2]	Direct overflame	0.025	0.100	0.250	.....	.....	0.375
1*a*.	Residue from 1 + 170 cc. water	" "	0.50	0.50	0.50	.....	.....	1.50
2	200 cc. juice + 2 mg. CH_2O + 5 cc. H_3PO_4	" "	0.86	0.94	0.96	0.30 in 15 cc.	0.16 in 6 cc.	3.22
2*a*.	Residue from 2 + 170 cc. water	" "	0.50	0.50	0.50	.....	.....	1.50
3.	200 cc. juice + 2 mg. CH_2O	" "	0.39	0.81	0.66	0.19 in 15 cc.	0.08 in 6 cc.	2.13
3*a*.	Residue from 3 + 170 cc. water	" "	0.62	0.63	0.57	.....	.....	1.82
4.	20 g. sugar I[3] + 200 cc. water + 5 cc. H_3PO_4	" "	0.059	0.190	0.270	.....	.....	0.519
5.	10 g. sugar I + 100 cc. water	Superheated steam and in water bath	0.009	0.010	0.009	.....	.....	0.028
6.	Duplicate of 5	Superheated steam and in water bath	0.012	0.011	0.011	.....	.....	0.034
7.	10 g. sugar I + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in water bath	0.025	0.028	0.027	0.027	.....	0.107
8.	Duplicate of 7	Superheated steam and in water bath	0.021	0.027	0.028	.....	.....	0.076
9.	10 g. sugar I + 100 cc. water + 1 mg. CH_2O	Superheated steam and in water bath	0.36	0.35	0.20	0.21	.....	1.12
10.	10 g. sugar I + 100 cc. water + 1 mg. CH_2O + 5 cc. H_3PO_4	Superheated steam and in water bath	0.53	0.37	0.21	0.18	.....	1.29
11.	15 g. sugar II[4] + 100 cc. water	Superheated steam and in brine bath	0.008	0.008	0.008	.....	.....	0.024
12.	15 g. sugar II + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.025	0.025	0.028	0.033	0.032	0.143
13.	15 g. sugar II + 100 cc. water + 1 mg. CH_2O + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.46	0.27	0.14	0.09	0.08	1.04
14.	15 g. sugar run, after 5, made without CH_2O + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.000[1]	0.025[1]	0.028	0.043	0.047	1.43
15.	15 g. sugar, run 6, made with CH_2O + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.007[1]	0.030[1]	0.047	0.054	0.054	0.192
16.	15 g. molasses, run 5, made without CH_2O + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.000[1]	0.008[1]	0.031	0.028	0.025	0.092
17.	15 g. molasses, run 6, made with CH_2O + 100 cc. water + 5 cc. H_3PO_4	Superheated steam and in brine bath	0.027[1]	0.100[1]	0.118	0.123	0.100	0.468

[1] In these fractions of the distillate there was a slight cloudiness and probably interference with the test.
[2] The H_3PO_4 solution in each case was an 85 per cent. sol.
[3] Sugar I is commercial refined sugar from the local market.
[4] Sugar II is commercial sugar from India.

tion or from distillation with steam, in such amounts that the tests, quantitatively applied, can serve easily to distinguish between products to which it has, and those to which it has not been added (Nos. 2, 10 and 13, and Nos. 1, 4, 7 and 12). From these acidified formaldehyde solutions, the formaldehyde comes off most copiously in the first fractions. When not acidified this is less marked and the total recovery is less in the same total volume of distillate (cf. Nos. 3 and 9). When made alkaline with NaOH, as we did in some preliminary trials, the tendency to hold back formaldehyde in the sugar solution was many fold greater.

Coming now to the main question which concerned us, *viz.*, Does formaldehyde added to juice in the sugar-house all boil away or does it persist in any final salable products? we seek the answer in tests Nos. 14 to 17.

Runs 5 and 6 were made at the small mill of the Louisiana Sugar Experiment Station, the former without the addition of any formaldehyde either in that or the immediately preceding run, and the latter with the addition of formaldehyde to the fresh juice in the proportion of about 1 part of formalin (40 per cent. sol. of formaldehyde) to 160,000 parts of juice, or 25 parts CH_2O to a million. The clarification in each run was as usual with sulphurous acid, followed by liming back almost to neutrality. The concentration was accomplished as usual with reduced pressure in the "effects" and vacuum pan. The sugars used in these experiments (Nos. 14 and 15) are the first sugars, testing about 96 per cent., and the molasses samples (Nos. 16 and 17) are of the first molasses in each case, testing about 43 per cent. sucrose and 58 purity. In the distillation with superheated steam and the formaldehyde determination in these samples, carried out as above described, a peculiar condition developed which was not noted in the previous samples with pure sugar solutions. The first one, or two fractions of the distillate, were slightly cloudy, and these same fractions, which should have been highest in formaldehyde, gave no reaction, or only very weak ones for that substance. This leads us to suspect that our test in these cases does not show the total quantities of formaldehyde present. Suspecting that the interfering substance may be sulphurous acid, or possibly other sulphur compounds, tests were made and it was found that the addition of sodium sulphite strongly interfered, that sodium thiosulphate completely prevented the color development, and that hydrogen sulphide but slightly affected the intensity of the reaction. Notwithstanding these probable shortages in the total formaldehyde recovered, we still find evidence of an excess of formaldehyde in the products from juice to which it had been added, very small in the case of the 1st sugar, but more pronounced in the case of the 1st molasses. In the 1st sugar it amounts to 12.8 parts CH_2O per million as against 9.5 parts per million in 1st sugar from juice without added formaldehyde, or an excess of 3.3 parts per million. In the first molasses it amounts to 31.2 parts per million as against 6.1 parts per million in 1st molasses from juice without added formaldehyde, or an excess of 25.1 parts per million. The molasses is thus found to be as strongly charged with this excess of formaldehyde as was the juice from which it was made. Assuming that the yields of 1st sugar and 1st molasses are 9.5 per cent. and 6 per cent., respectively, of the juice, then the amounts of formaldehyde retained by them are about 1.2 per cent. and 6 per cent., respectively, of that added to the juice, or a total of 7.2 per cent., which, as far as these tests show, was not boiled away. It is probable, as pointed out above, that these tests show only part of that actually retained. The small quantity left in this 96 per cent. sugar may justify the conclusion that in refining the sugar this excess is all eliminated.

If the sugar is the only product used for food, then there need be no hesitation, on the score of health considerations, in using formaldehyde as a preservative in juice in the sugar mill. If, however, the molasses is also to be used for food, or if table syrup is to be manufactured, then the question of the permissibility of its use may reasonably be raised. To this question we deem the data now at hand to be insufficient basis for a definite answer. We should have the results from further tests of final and of intermediate products. We should develop a method to circumvent the interference of sulphurous acid or other substanes in the distillates, in the formaldehyde determination. We should make comparative tests also with syrup or molasses and sugar made by the open kettle method of boiling, with and without formaldehyde. We should, moreover, know in what form or combination the formaldehyde is held back in these sugar solutions, and whether it is deleterious to health in this form or combination.

SOME EFFECTS OF FEEDS UPON THE PROPERTIES OF LARD.

By C. L. Hare.

Received April 11, 1910.

It is well known that in the feeding of hogs different feeds produce varying effects upon the carcasses of the animals and upon the characteristics of the fats produced.

The Department of Animal Industry of the Alabama Polytechnic Institute has through a series of years made extended experiments in pork production, particularly from an economic standpoint.

Working in coöperation with that department, there have been encountered lards which show interesting effects of the feeds used in their production.

The following is a preliminary account of the investigation undertaken to point out some changes in properties so brought about.

Among the available pork producing feeds some of the most important economically are corn, peanuts, soy beans, cottonseed-meal and tankage, the three last being relatively rare as constituents of rations for hogs.

The results here given were secured on lards resulting from three series of feeding experiments in each of which series these feeds were used.

In the first series of experiments examination was made of lards from thirty-six hogs.

The pigs in this series were divided into six lots and the feeding so conducted a to show the effect upon the lards of corn, cottonseed-meal, tankage, soy beans and peanuts. The lots were further subdivided so as to show the effect of corn following peanuts, of cottonseed-meal following peanuts, and of tankage following soy beans and peanuts.

In the second feeding trials results were again obtained on thirty-six pigs—the feeding in this series being intended to show the effects of, 1st corn, 2nd cottonseed-meal, 3rd tankage, 4th soy beans with varying rations of corn, 5th soy beans and peanuts, 6th soy beans and peanuts with a finishing ration of corn, 7th soy beans and peanuts with a finishing ration of corn and cottonseed-meal, 8th soy beans and peanuts with a finishing ration of corn and tankage.

The third experiment included twenty-three pigs and data were secured illustrating the effects of, 1st, corn; 2nd, tankage, 3rd, cottonseed-meal; 4th, soy beans with varying amounts of corn; 5th, soy beans with a finishing ration of corn; 6th, soy beans with a finishing ration of corn and cottonseed-meal; and 7th, soy beans with a finishing ration of corn and tankage.

Corn being the universal hog feed, one corn-fed lot was carried in each series as a basis of comparison—the corn lards being used as standards.

In every series of experiments the feeding of each lot was so conducted and the slaughtering so regulated in point of time that the full effect of the ration might be observed. Thus, in the corn-fed lot of series No. 1 the pigs were slaughtered at intervals—the first at the end of thirty-five days and the last at the end of one hundred and forty-seven days.

Slaughtering one pig from each lot at stated intervals furnished lards on which comparable results could be secured from all pigs in the different lots as well as in the same lot.

The period of feeding in days for each pig is indicated in the tables.

The rations of corn, cottonseed-meal and tankage were fed soaked.

The pigs were made to graze the soy beans and peanuts.

All pigs in each series entered the feeding trials at a fairly uniform age and weight.

All lards were rendered from the kidney fat and thus represent uniformly the firmest fat obtainable from the pig.

Since the melting points and iodine values of lards are more notably affected by feeds than are the other characteristics, and at the same time probably furnish a more accurate index to the qualities of lards than do the other constants, these values were selected as giving a sufficient showing of the changes produced.

In Table I are found results on lards from hogs which had been fed on corn for periods varying from 35 to 150 days. The results include lards from three feeding trials.

The lards in series 2, with the exception of those numbered 61, 42, 53, 15, 23, and 34, had become slightly rancid when the iodine values were determined, but it is not thought that the oxidation had proceeded so far as to seriously affect those values.

TABLE I.

No. days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
63	101	43.5	53.87		
91	103	43.4	58.68		
119	106	44.2	57.60	1	Cornmeal
140	105	41.6	57.37		
147	104	40.5	57.10		
		Av.,	56.92		
35	72	43.1	56.50		
70	71	44.8	51.50		
84	73	44.0	49.70	2	Cornmeal
112	75	43.0	56.00		
134	74	....	56.57		
		Av.,	54.05		
75	69	....	64.79		
110	36	....	63.07	3	Cornmeal
125	42	....	60.04		
150	8	....	60.07		
		Av.,	61.98		
		Average,	57.35		

Examination of these figures seems to show that corn as fed in these trials has not the effect of softening pork to the extent indicated by results secured by some investigators, notably those of Shutt[1]

On the other hand, the iodine values are somewhat below the average value of that constant for lards—this being particularly true of the lards in series 2, which gave an average iodine value of only 54.05. Not only do the melting points and iodine values indicate relatively firm lards throughout but the pigs which were fed corn continuously for a period of five months show no greater degree of softness than those fed for shorter periods on this ration.

In fact, the pigs in series 3 show an increasing firmness in the fat, though this may be attributed to the increasing age of the animal.

Table II shows the effect upon the two constants under consideration of a ration containing much cottonseed-meal.

[1] Canada Cent. Ex. Sta., *Bull.* 38.

TABLE II.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	112	47.7	61.00	1	Cornmeal 2/3, cottonseed-meal 1/3.
63	109	49.8	53.57		
91	111	49.3	53.57		
119	110	48.3	57.58		
140	108	50.0	55.16		
147	107	46.8	55.95		
35	61	49.2	48.44	2	
70	65	50.8	51.20		
84	64	50.0	51.60		
112	62	49.6	50.22		
		Average,	53.80		

This mixture contains a very little more oil than the corn ration but constitutes a much higher protein ration. It will be observed that the melting points are materially elevated, while the iodine values suffer a corresponding depression.

This tendency has been often observed in this as well as in other rations where the protein content has been increased—*e. g.*, corn and skim-milk, and is even more apparent in a ration containing much smaller amounts of cottonseed meal than the above.

Table III gives results on lards produced by a ration consisting of corn 9/10 and cottonseed-meal 1/10.

TABLE III.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
70	45	48.6	53.80	2	Cornmeal 9/10, cottonseed-meal 1/10.
84	41	48.4	50.60		
112	44	47.6	55.0		
134	40	49.0	52.0		
99	42	49.7	41.85		
75	39	....	49.23	3	
		Average,	52.13		

Here we find the results on iodine values lower than where a more concentrated cottonseed-meal ration was fed. It is, however, probable that with results on a larger number of lards from this ration more comparable figures would be secured, as there is no apparent explanation of this slight difference in properties.

In order to test further the effects of a feed containing more protein than corn, one lot of pigs in each series was fed a mixture consisting of corn 9/10 and tankage 1/10. Table IV gives analytical results on the lards produced.

TABLE IV.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	131	43.1	59.08	1	Cornmeal 9/10 Tankage 1/10
63	132	45.6	50.06		
91	136	42.5	56.59		
119	135	41.6	57.80		
140	133	45.1	57.77		
35	53	....	49.85	2	
70	54	43.0	56.80		
84	51	42.9	56.53		
112	52	....	56.53		
91	50	42.2	52.40		
91	55	41.4	58.80		
75	1	....	57.02	3	Same
110	43	....	61.25		
125	37	....	52.26		
150	2	....	53.61		
		Average,	55.67		

The figures in this table again seem to indicate that the introduction of a high protein feed into the ration produces an elevation of the melting point and depression of the iodine value of lards. While the effect upon these two constants is not so pronounced as in the case of cottonseed-meal they are nevertheless significant and would seem to point to the presumption that the changes in properties brought about in fats by cottonseed meal are, at least in part, due to the protein content of that feed.

For purposes of comparison, the averages on all lards produced from the four rations so far discussed are presented in Table V:

TABLE V.

Ration.		Iodine value.	Average of
Cornmeal		57.35	14 lards
Cornmeal 2/3, Cottonseed-meal 1/3		53.83	10 lards
Cornmeal 9/10, Cottonseed-meal 1/10		52.13	5 lards
Cornmeal 9/10, Tankage 1/10		55.67	15 lards

The increasing use of soy beans as a hog feed makes necessary the determination of the effect of this ration upon the finished product and a study of rations which may be suited to finishing hogs which have been fattened thereon.

Table VI gives figures obtained on lards from pigs grazed on soy beans and at the same time fed part rations of cornmeal:

Table VI.

No. of days fed.	No. of pig.	Melting point.	Iodine value.	Series.	Ration.
35	34	33.6?	100.5	2	Soy beans and 1/4 ration of corn
75	76	?	94.86	3	
35	125	41.8	71.09	1	Soy beans and 1/2 ration of corn
35	23	40.0	80.60	2	
75	87	?	82.70	3	Soy beans and 3/4 ration of corn
35	15	40.7	79.0	2	
75	68	?	84.32	3	
		Average,	84.72		

Representing as these values do results on lards the firmest obtainable from the pigs—that rendered from the kidney fat—they illustrate the very great softening effect of this feed upon the fat.

Some of the lards in this lot remain semi-fluid throughout the winter months and are too soft for melting point determinations.

Whether the softness is due solely to the oil in the feed or in part to the fact that it is grazed as a green feed has not yet been determined. It is probable, however, that both factors influence the properties of the lard. This would be in keeping with Shutt's results on pigs grazed on clover. Further, his observations that certain other green crops, as turnips and sugar beets, have no softening effect upon lards are confirmed by data secured in this laboratory from pigs grazed on sorghum.

This leads to the suggestion of the possibility that

the legumes when fed green to hogs have a softening effect upon the fat.

While the soy bean feed is high in oil content, it is also relatively high in protein. The results therefore in a measure contradict the assumption that protein in the feed induces hardness in the fat. This further suggests the question whether the protein molecule in this feed breaks down into cleavage products differing from those formed by cleavage of the protein molecule of corn and tankage and, in turn, produces radically different effects upon the fat.

In order to determine the persistence of the softness of fat produced by soy beans, three different finishing rations were employed: corn, cottonseed-meal and tankage.

Table VII illustrates the effect of corn in hardening the fat:

TABLE VII.

Ration—Soy bean grazing and 1/4 ration of cord followed by corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	76	94.86		
75	98	83.92		Corn 35 days
75	88	69.77	3	Corn 50 days
75	7	70.31		Corn 75 days
Average of corn-fed lot in this series		61.98		

The limited number of pigs in this lot renders the results none the less valuable, inasmuch as they are fully confirmed by the figures in Table XI, which show the effect of corn following soy beans and peanuts.

Although these results show that corn produces a marked hardening effect, yet a comparison of the iodine values on numbers 88 and 7 with the average value of the corn-fed lot of this series, indicates that the properties conferred by the soy bean ration have in some measure persisted even after a period of 75 days' feeding on corn.

Some difficulty was experienced in testing the hardening effect of cottonseed-meal as in this series nearly all pigs on a ration of this feed died of cottonseed-meal poisoning.

However, two cottonseed-meal pigs in this trial made good growth and Table VIII sets forth the results secured on these:

TABLE VIII.

Preliminary ration soy bean grazing and 1/2 ration of corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	87	82.70		
75	88	73.41	3	Cornmeal 2/3 Cottonseed-meal 1/3 for 35 days
75	56	65.46		Cornmeal 2/3 Cottonseed-meal 1/3 for 50 days
Average of corn lards of this series.		61.98		

The effect of the cottonseed-meal ration is what was expected and the hardening effect would possibly have been greater could the time of feeding cottonseed-meal have been extended.

The softness induced by the soy bean ration is somewhat in evidence after 50 days' feeding on cottonseed-meal.

The effect of tankage, the third finishing ration used in these experiments, is set out in Table IX:

TABLE IX.

Preliminary ration—Soy bean grazing and a 3/4 ration of corn.

No. of days fed soy beans.	No. of pig.	Iodine value.	Series.	Finishing ration.
75	68	84.32		
75	57	68.83	3	Cornmeal 2/3 Tankage 1/3 for 35 days
75	66	72.67		Cornmeal 2/3 Tankage 1/3 for 50 days
75	77	74.0		Same 75 days
Average values corn lards.		61.98		

Here again there is illustrated the pronounced hardening effect of a high protein ration.

For some unexplained cause the hardening effect in this trial with tankage seems to be greatest at the end of 35 days' feeding period and the lards to increase in softness for longer periods of feeding. This is probably due to individual peculiarities of the pigs. There still appears a persistence of the properties originally contributed by soy beans.

A study was also made of the persistence of the properties conferred upon lards by a ration of soy beans followed by peanut grazing.

There is first given in Table X values obtained from pigs slaughtered off peanuts following soy beans:

TABLE X.

Ration—Soy bean grazing followed by peanut grazing.

No. of days fed soy beans.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
35	127	40.6	79.61	1	Peanuts 28 days
35	25	31.2?	89.84	2	Peanuts and 1/2 ration corn 35 days
35	14	37.0	76.94	2	Same
35	33	?	89.70	2	Same
		Average,	84.02		

A comparison of these lards with those from the soy bean fed pigs, as shown in Table VI, demonstrates that while the average results of the two sets are practically the same, yet some of the individual soy bean lards are very materially softer than the softest of this lot, and that as between soy beans and peanuts the former has probably the greater softening effect.

In efforts to harden the fat of the pigs fed upon both soy beans and peanuts, use was again made of corn, cottonseed-meal and tankage.

The effect of corn is shown in Table XI:

TABLE XI.

Ration—Soy beans followed by peanuts followed by corn.

No. days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	14	37.0	76.94	2	
70	10	36.9	82.80	2	Corn 14 days
70	12	36.8	73.93	2	Corn 42 days
70	11	39.0	70.1	2	Corn 64 days

There is found here a confirmation of the results recorded in Table VII, which illustrate the hardening effect of corn as well as the difficulty of hardening the fats to a normal firmness—using the corn lards as standard.

The effect of the corn is progressive and is greatest as in Table VII during the first forty to fifty days.

Still further confirmatory results on the effect of corn were secured from a third trial with four pigs. The results are recorded in Table XII:

TABLE XII.

Ration—Sorghum and 1/2 corn 35 days. Peanuts and 1/2 corn 28 days (preliminary).

No. days fed preliminary ration.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
63	113	40.8	70.08	1	
63	116	41.8	62.15	1	Corn 28 days
63	117	42.3	60.67	1	Corn 56 days
63	118	42.7	60.60	1	Corn 77 days

In Table XIII are given results secured on the soy bean peanut pigs, finished on a ration of $^2/_3$ corn and $^1/_3$ cottonseed-meal.

TABLE XIII.

Days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	25	31.2	89.84	1	
70	22	42.4	76.1	2	2/3 corn and 1/3 Cottonseed-meal for 42 days
70	21	41.5	79.22	2	Same for 64 days

These results are not so striking as those found in Table VIII, but the one set is confirmatory of the other. Cottonseed-meal in the ration exercises its usual function of firming the fat.

The lot in this series finished on tankage puts this feed in a most favorable light as a finishing ration, as will be observed by inspection of the figures in the following table:

TABLE XIV.

Preliminary ration—Soy beans 35 days followed by peanuts 35 days.

No. days fed soy beans and peanuts.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
70	33	....	89.70	2	
70	35	39	74.35	2	Corn and 1/3 tankage 42 days
70	31	41.0	70.65	2	Same 49 days
63	127	40.6	79.61	1	Corn and 1/6 tankage 28 days
63	126	41.9	66.40	1	
63	130	42.9	64.69	1	Same 77 days

While, as before stated, these results point to tankage as a desirable ration for hardening the fat of soft hogs yet, on considering them in connection with the results in Table IX, it is seen that confirmatory feeding trials are necessary before the results in Table XIV can be accepted.

Tankage, however, is free from the toxic effect which renders cottonseed-meal a dangerous hog feed and the data secured are sufficient to emphasize its value as a finishing ration. The results too show that it compares favorably with cottonseed-meal in its hardening effect on the fats. This, however, is not verified by examination of the carcasses nor by the results on pigs fed these rations without a prior softening ration—see Table V—and further comparative feeding trials are in progress.

Below is given a further comparison of lards from the two feeds:

TABLE XV.

Preliminary ration—Soy beans 35 days. Peanuts 35 days. Corn 14 days

Days fed soy beans, peanuts and corn.	No. of pig.	Melting point.	Iodine value.	Series.	Finishing ration.
84	32	36.9	82.80	2	
84	10	39.2	71.60	2	Corn 2/3, tankage 1/3 for 14 days.
84	20	44.4	71.80	2	Corn 2/3, Cottonseed-meal 1/3 for 14 days.

The results on this lot of three pigs but serve to further confirm results recorded in the foregoing tables illustrative of favorable changes produced in the properties of lards by these two rations.

Summarizing the results, it is found that corn may be fed without regard to time limit in so far as concerns any unfavorable effect on the properties of the lard.

Soy beans and peanuts both produce oiliness in the hogs and the lards resulting are extremely soft.

The fat of oily hogs can be hardened by rations of corn, cottonseed-meal or tankage—the two latter producing unusually firm lards.

The possibility is suggested that legumes when fed green may produce soft fats.

In connection with the general subject here discussed, there are presented below results which accentuate the extreme differences in properties which may be conferred upon lards by different feeds:

No. of pig.	Melting point.	Iodine value.	Iodine value of liquid fatty acids.	Saponification value.
34	?	100.5	119	197.5
100	48.2	40.35	78	203.2

Pig No. 34 is selected from the soy bean fed lot.

No. 100 was fed throughout its life on slaughter pen refuse and weighed about 200 pounds when slaughtered.

This lard presents much the appearance of beef tallow and its constants possess much the same value as those of beef fat. It further responds readily to the Belfield test for beef fat.

ALABAMA POLYTECHNIC INSTITUTE.

[Contribution from the Laboratory of Soil Chemistry, University of Tennessee, Agricultural Experiment Station.]

SOIL HUMUS AS DETERMINED BY DIFFERENT METHODS.

By Sherman Leavitt.

Received April 6, 1910.

From the wide variation in analytical results on samples of several different types of soil when analyzed for percentage of humus by five well-known methods, the writer has been led to believe that these variations may be partly accounted for by the fact that the several methods may individually include or exclude certain organic substances as humus.

The Official method for humus,[1] based on that of Grandeau, is, to my knowledge, followed by most of the soil chemists in this country at least to the completion of the extraction of organic matter with four per cent. ammonia. This method determines the organic matter by evaporation of a clear aliquot free from clay (a difficult result to obtain) and by burning off the organic matter in a platinum dish. We may therefore assume that soil humus is emperically the total organic matter, combined with a little inorganic matter, soluble in a solution of four per cent. ammonia at ordinary temperature. Thus far, I believe, all methods agree, however they disagree from this point.

As is well known, the Official method, when followed literally, is very unsatisfactory and gives abnormally high results This is due to the presence of clay which cannot readily be removed by the method as given. Different investigators have accordingly modified this method more or less to overcome this difficulty. Among the modified methods may be mentioned those of Cameron and Breazeale;[2] Peter and Averitt;[3] Mooers and Hampton;[4] and C. W. Stoddart.[5] Briefly, the principal modification of each of these four methods is as follows:

Cameron and Breazeale filtered off the clay by means of a Pasteur-Chamberland filter and determined the humus in the filtrate free from clay.

Peter and Averitt used the Official method in connection with a correction factor of ten per cent. of the residue which is left after burning off organic matter and which must be subtracted from the total loss in weight. This factor seems to apply fairly well in some cases but, as Mooers and Hampton have shown, it does not apply to all soils.

Mooers and Hampton devised the method which is in use in this station. Briefly, the clay is partially removed by settling for several days, the supernatant liquid being then siphoned off. An aliquot portion of this liquid is then evaporated to dryness and baked for some hours on the steam bath. It is re-dissolved in four per cent. ammonia, filtered, re-evaporated, baked again, dissolved in four per cent. ammonia, and filtered.

The solution should then be absolutely clear. When this method is properly handled, the insoluble residue remaining after burning off the organic matter in a platinum dish is not much over 0.20 per cent. of the total weight of soil taken.

C. W. Stoddart's method, as given in the article referred to, depends upon the use of a strong solution of ammonium sulphate to flocculate and precipitate the clay on standing twelve hours. The humus, as humic acid, is then precipitated out by the addition of strong hydrochloric acid to a clear aliquot of the solution free from clay and by whirling in the centrifuge, the resulting precipitate being filtered, washed, dried at 105° C., and weighed on a tared gooch crucible. This method would seem to be the ideal one for simplicity and the writer has striven to make this applicable to the soils of Tennessee, but without success.

Several of these methods have been respectively tried on the same soils by two chemists in this laboratory, working over a year apart, the results of each method being comparable. I shall take the liberty of quoting the results on two very different types of soils taken from the paper of Messrs. Mooers and Hampton and of placing them alongside the results obtained by the writer to better illustrate the point.

In the soils which they examined, Mooers and Hampton found the Official method unreliable; the method of Peter and Averitt only partially reliable; and the method of Cameron and Breazeale practically of no value. The writer finds that excellent results can be obtained with the Mooers and Hampton method after a little practice and has little trouble duplicating results on the same samples of soils which they used.

As stated before, the writer hoped to make use of Stoddart's method, which commends itself on account of its simplicity and ease of manipulation, but, as can be easily seen from the last column in the above table, the results obtained by Stoddart's method are not comparable to those obtained by the modified official method. This fact was also shown in the following way: Duplicate aliquots of ammonium humate solution from soil No. 602, freed from clay according to the method in use in this laboratory (Mooers and Hampton), were evaporated to dryness in platinum dishes, being heated in the oven for three hours and weighed. The weight of extract in each case was the same. One aliquot was burned and the organic matter as humus determined by loss on ignition, giving 1.22 per cent. humus. The other aliquot was completely dissolved in 50 cc. of four per cent. ammonia, the humus precipitated by hydrochloric acid, giving only 0.45 per cent. of humus as humic acid.

[1] *Bull.* **107** (revised edition) Bureau of Chemistry.
[2] *J. Am. Chem. Soc.*, **26**, 29–45.
[3] Kentucky Station, *Bull.* No. **126**, p. 63–126.
[4] *J. Am. Chem. Soc.*, **30**, No. 5.
[5] *J. Ind. Eng. Chem.*, **1**, 72.

A qualitative test was made of this filtrate after removal of the excess of acid by evaporation and baking on the steam bath, and it was found to yield in a faintly acid solution a considerable quantity of greenish copper salt, which was organic. This showed qualitatively that all of the organic matter was not precipitated by the hydrochloric acid. That this wide variation between the weights of humic acid and the ammonium humate could not be accounted for by the presence of the ammonium radicle, was shown by dissolving the humic acid on the gooch crucible in four per cent. ammonia, evaporating, drying and weighing as ammonium humate, very little increase of weight being noted.

The writer has attacked this problem in a slightly different manner. Four large samples of ammonium humate, prepared from distinctly different important types of soils, were used. The samples were made from 500 grams of air-dried soils by the Official method and were freed from clay by repeated treatments of baking on the steam bath to flocculate the clay and to bring about its removal by filtration, this operation requiring about six weeks on account of the large amounts of soils taken. These residues were finally dissolved in water and made up to 500 cc. each and allowed to stand about two months tightly stoppered to further clarify the solution.

The clear solutions were pipetted off for analysis and the amount of humus as ammonium humate and of ash present were determined in each cubic centimeter by evaporation and loss on ignition. Known amounts of each soil humus were diluted to 50 cc. and treated with 2 cc. of concentrated hydrochloric acid, whirled in the centrifuge, filtered, washed with 1 per cent. hydrochloric acid, and dried according to Stoddart's method. The following tabulated results were obtained:

In the above table is a column (No. 5) marked "percentage of humus compounds precipitated by copper after hydrochloric acid treatment" (the excess of acid having been removed by evaporating to dryness and baking on the steam bath). Several years ago it was shown by S. Suzuki[1] to be possible to obtain copper salts from humic acid derived from natural sources. Two of these salts were identified, one being a salt of active prolin, and the other probably a salt of inactive prolin. There was also formed a considerable quantity of copper salts of unknown acids. The same investigation brought out the fact "that the nitrogen in the humus is not as amino compounds but chiefly as a kind of protein which may be connected more or less intimately with the black substances."

The writer of the present article has been led to believe from the type soils that have come under this investigation that many of them contain their humus largely in the form of protein or like proteins. This would account, in part, for some of the very low determinations of humus by Stoddart's method. As some of the proteins can be precipitated as copper salts, the results given in column 5 probably represent the total organic matter as protein or like proteins (the actual weight of copper in combination having been determined in each case and subtracted), including some organic acids precipitated as copper salts which have failed of precipitation by hydrochloric acid. Column 8 gives the percentage of organic matter by difference, not precipitated by hydrochloric acid and copper collectively. Column 7 gives the percentage of total humus and protein bodies which can be salted out from the humus solutions by means of an excess of ammonium sulphate. This method is given as a quantitative one[3] for removing all protein bodies except peptones from solution.

TABLE I.

		Peter and Averitt.				Cameron and Breazeale.		Mooers and Hampton.		By the writer.			
		Official.		Factor 10,	Factor 14,					Official.		Mooers and Hampton.	Stoddart's.
Sample.	Character of soil.	Humus.	Ash.	per cent.	per cent.	Filtration.	Ash	Humus.	Ash.	Humus.	Ash.	Humus.	Humic acid by HCl.
	Fertile clay loam	2.04	5.23	1.52	1.31	0.64	0.22	1.36	0.28	1.61	0.96	1.33	0.34
636	" " "	2.34	6.75	1.66	1.40	0.65	0.18	1.33	0.19	2.15	0.75	1.45	0.38
	" " "	2.64	7.97	1.84	1.51	0.77	0.21	1.38	0.23	....	....	....	0.39
	" " "	2.55	8.78	1.67	1.32	0.59	0.24	1.26	0.33	....	....	....	0.37
602	Poor clay loam	1.28	1.95	1.08	1.01	0.76	0.23	1.08	0.29	1.65	3.99	1.22	0.45
	" " "	1.26	2.06	1.05	0.97	....	....	1.11	0.18	1.67	3.93	1.22	0.45
	" " "	....	....	....	....	....	....	....	....	....	....	1.40[2]	0.45
	" " "	....	....	....	....	....	....	....	....	....	....	0.97	....
	" " "	....	....	....	....	....	....	....	....	....	....	0.94	....

TABLE II.

Locality.	Sample.	Per cent. humus in soil.	Wgt. of humus used.	Ash in humus used.	Per cent of total by HCl.	Per cent. humus compounds by copper.	Per cent by HCl + Cu.	Humus by salting with $(NH_4)_2SO_4$.	Organic matter not precipitated.
Cookeville	1096	0.93	0.0369	0.0066	45.81	34.83	80.64	70.4	19.36
Crossville	1101	0.90	0.0238	0.0012	26.05	25.22	51.27	33.6	48.73
Jackson	1266	0.39	0.0280	0.0025	64.28	19.29	83.57	75.0	16.43
Gallatin	1267	1.66	0.0392	0.0021	49.74	50.00	99.74	57.9	0.26

[1] Bulletin College of Agriculture, Tokyo Imperial University, 7, (No. 4) 513–529.

[2] This result was abnormally high due to a little clay left in solution before the writer had become thoroughly familiar with the method.

[3] *Watts' Dictionary*, "Proteids."

As Stoddart's method calls for the use of considerable ammonium sulphate to flocculate and precipitate the clay, we have another explanation of the low results obtained when this method is used on soils of this type, *i. e.*, where the humus is probably largely of a protein nature.

The above table shows very clearly that the humus matter in each of the soils given is quite different. This can be shown distinctly to the eye in the case of soils 1101 and 1266. If we use the same weight of humus from each soil and dilute them to the same volume, say 50 cc.; the solution made from the humus from soil 1266 will be black and cannot be seen through in a 250 cc. beaker, while the same weight of humus from soil 1101 will be a light amber, perfectly transparent (see column 4 of table for corresponding percentages precipitated by hydrochloric acid).

We notice in column 8 of this table for soil 1101 that about 49 per cent. of the organic matter is unaccounted for, whereas in soil 1267 apparently nearly all of the organic matter has been precipitated by hydrochloric acid and as a copper salt. The writer is inclined to believe that the humus from soil 1101 is in a higher state of oxidation than that from the other soils and that it is partly present as highly oxidized organic acids. This study is being continued in this laboratory.

The writer wishes to express his thanks to Professor Charles A. Mooers, of this station, for introducing the writer to the chemistry of soil humus and for kindly reading and criticizing this paper.

Mr. H. H. Hampton, now at the Johns Hopkins University, Baltimore, Md., gave the writer many helpful suggestions regarding the technique of the Mooers and Hampton method for humus.

Professor William R. Orndorff, of Cornell University, has very kindly gone over many points on this subject with the writer.

KNOXVILLE, TENNESSEE,
March 31, 1910.

ON THE COMPOSITION OF LIME-SULFUR SPRAY.

By H. V. TARTAR AND C. E. BRADLEY.

Received February 5, 1910.

Introduction.—The literature on the composition, properties, and use of the commercial lime-sulfur spray solution, now so widely employed as an insecticide and fungicide, consists in the main of the details of field experiments which have been carried out in various localities by entomologists and horticulturists. In the majority of these tests but little attention has been given to the composition of the spray. The solution has been made by boiling, either by direct heat or with live steam, sulfur and freshly slaked lime in water. These materials have been used in varying proportions. In some instances the quantity of lime and of sulfur used, together with the specific gravity of the resulting solution, have been stated. Other than this, it has been the prevailing practice to give but little attention to the composition of the spray, and up to the present time there have been no definite systematic field experiments to show the relative insecticidal and fungicidal value of its constituents. The real chemical investigations dealing directly with the lime-sulfur solution have been carried out by Avery, Haywood, Thatcher, Giboney, and Wellington.

Avery[1] modified standard methods of analysis to suit the conditions so that the total sulphur and total lime could be determined.

Haywood[2] was the first investigator to point out the real constituents of the spray solution now in use. He showed that it contained considerable amounts of polysulfids and thiosulfate, and but small quantities of sulfate and sulfite of calcium. A small amount of calcium hydroxide was supposed to be present. It may be stated here that the compounds which are formed when sulfur and calcium hydroxide are boiled in aqueous solution had been quite thoroughly investigated by Divers[3] and others previous to Haywood's work on the commercial spray solution. Standard methods of analysis were modified by Haywood so that quantitative estimations could be made of the sulfur combined as sulfids and polysulfids, as thiosulfate, as sulfate and as sulfite, respectively. The presence of sodium chloride was found not to affect the composition nor the amount of the sulfur compounds in the solution. Different formulas for the preparation of the spray were tried and the use of 1 part of lime to $1^1/_4$ parts of sulfur was suggested for practical purposes. Solutions made from commercial materials were found to be of the same composition as those made from chemically pure materials. One hour of cooking was demonstrated to be sufficient time to effect the combination of the sulfur with the lime.

Perhaps the most valuable part of Haywood's work was his study of the decomposition of the spray by the use of artificial experiments approximating the conditions on the tree. He found that the principal immediate products of decomposition were calcium thiosulfate and free sulfur, and that the thiosulfate gradually decomposed to form sulfite and liberate more sulfur. The calcium sulfite finally oxidized to the sulfate. From the results obtained, a theoretical explanation of the action of the wash on insects was made. Haywood also suggested the preparation of a spray in which sodium hydroxide was substituted for slaked lime.

Thatcher[4] showed previous to Haywood that sodium

[1] *Bull.* **90**, Bureau of Chemistry.

[2] *J. Am Chem. Soc.*, **1905**, page 244. *Bull.* **101**, Bureau of Chemistry.

[3] *J. Chem. Soc.*, **1884**, page 270.

[4] *Bull.* **56**, Washington Station.

chloride did not affect the quantity of sulfur compounds in solution. Later[1] Thatcher demonstrated that 1 part of lime to 1.95 parts of sulfur was the proper proportion of chemically pure materials to be used. The present extended commercial use of 1 part of lime to 2 parts of sulfur in the preparation of the spray attests the correctness of Thatcher's conclusion. In 1908[2] he endeavored to work out the exact reaction between lime and sulfur when boiled in aqueous solution. It was found that perhaps the following primary reaction takes place:

$$3Ca(OH)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O.$$

The analysis of concentrated lime-sulfur spray solutions revealed the fact that a secondary reaction occurs in which the amount of thiosulfate decreases while the polysulfids increase. Thatcher made some suggestions regarding the nature of this reaction but, because of the lack of sufficient analytical methods, was unable to present any definite results.

Giboney,[3] from the results of laboratory experiments, suggested that 40 minutes is the proper length of time for boiling the solution. He also gave analytical methods for estimating the "sulfid" and "polysulfid" sulfur in the polysulfids. Prolonged boiling was found to effect the solution of a little more calcium and thus cause the formation of somewhat lower sulfids. Giboney also demonstrated the harmful effects of magnesia on the composition of the solution and pointed out the necessity of using lime which is comparatively free from this substance.

Wellington[4] stated that lime-sulfur-salt wash contains 25 per cent. to 30 per cent. of calcium monosulfid and hydrosulfid collectively. This view has not been upheld by any other investigator and is, no doubt, erroneous. Wellington assisted by Fernald showed, however, by field experiments, that calcium thiosulfate does possess some insecticidal value.

Experimental.—At the suggestion of Prof. A. B. Cordley, of the Entomological Department, a chemical study was taken up at this station with the view of obtaining a wider knowledge o the nature and composition of lime-sulfur spray solution. At the outset it became evident that some additional analytical methods must be devised which would enable us to ascertain more definitely the nature and composition of the polysulfid and also to estimate the calcium hydroxide which might be present.

It is a well-known fact that when an acid is added to a metallic polysulfid, sulfur equivalent to form the monosulfid of the metal is liberated as hydrogen sulfid, while the remainder of the sulfur is deposited as free sulfur, *e. g.*:

$$CaS_4 + 2HCl = CaCl_2 + H_2S + 3S.$$

For the sake of convenience, the sulfur equivalent to form the monosulfid is here spoken of as "sulfid" sulfur, while the remainder is spoken of as "polysulfid" sulfur. It can be readily seen that when the amount of "sulfid" and "polysulfid" sulfur are known the simplest formula of the polysulfid can be easily calculated.

Method for "Polysulfid" Sulfur.[1]—Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. For analysis 10 cc. aliquots are used. The aliquot is placed in a small beaker and about 30 cc. of distilled water is added. Tenth-normal hydrochloric acid is then run from a burette into the solution, drop by drop, with constant stirring until the yellow tint has practically disappeared. Two drops of methyl orange indicator is then added and the addition of the acid continued until the first permanent pink tint appears. (After standing for some time this tint will gradually disappear.) The solution will be milky white from the finely divided sulfur present, but it is not difficult to ascertain the exact end point of the reaction. After the solution is allowed to stand a few moments to permit the sulfur to settle and collect together, the sulfur may then be filtered on a weighed gooch crucible, thoroughly washed, dried at a low temperature (about 40°) and weighed directly as free sulfur. It has been found somewhat more accurate to filter the sulfur on a small filter paper and, after thoroughly washing, gently boil the paper and its contents in 50 cc. of 10 per cent. potassium hydroxide solution until all the sulfur is dissolved. Upon cooling, 50 cc. of a 3 per cent. solution of hydrogen peroxide free from sulfates is added. Heat on the steam bath for exactly 30 minutes and then acidify with hydrochloric acid, precipitate with barium chloride in the usual manner in boiling solution, and finally weigh as barium sulfate.

The precipitation of the sulfur by means of the weak acid does not decompose the thiosulfate in solution.

Method for "Sulfid" Sulfur.—For the determination of "sulfid" sulfur a well-known analytical method[2] has been but slightly modified. However, because of the manner of manipulation, it is deemed advisable to give it in detail. As it is used here, the zinc is not precipitated as the normal sulfid, but as the polysulfid.

An ammoniacal zinc chloride solution is prepared by dissolving 3.253 grams of pure zinc (or 4.0488 grams of pure zinc oxide is somewhat more convenient for use) in hydrochloric acid, supersaturating with ammonia and diluting to 1 liter. Each cc. of the solution is equivalent to 0.0016 grams of sulfur, or, in other words, it is a decinormal solution.

[1] *Bull.* **76**, Washington Station.
[2] *J. Am. Chem. Soc.*, **1908**, page 63.
[3] *Circ.* No. **1**, Virginia State Crop Commission.
[4] *Bull.* **116**, Massachusetts Experiment Station.

[1] The methods here given for "polysulfid" and "sulfid" sulfur do not involve any new principle. They are specially adapted to the conditions involved and have been found to be simple and accurate.
[2] *Sutton's Vol. Analysis*, Ninth Edition, page 325.

Measure 10 cc. of the clear lime-sulfur solution into a 100 cc. volumetric flask and make up to the mark. Use 10 cc. aliquots for analysis. The zinc solution is run in from a burette until the filtered solution is colorless and no dark color is shown when a drop is brought in contact with an almost saturated solution of nickel sulfate spread in drops on a white porcelain tile. This titration will give the approximate end-point of the reaction. Several aliquots (four or five) are then placed in beakers and a series of determinations made by adding to the first the exact amount of zinc solution required in the above titration; to the second add 0.2 cc. less of the zinc solution; to the third, 0.4 cc. less, and so on. These should be then allowed to stand about 30 minutes to insure complete precipitation of the zinc. The aliquots are then filtered. The amount of zinc solution which just suffices to remove all of the yellow color so that the resulting filtrate is colorless, is the correct titration. The great tinctorial power of the polysulfid serves adequately as an indicator in this determination.

The writers have been able to attain an accuracy of within 0.2 cc., or 0.0003 gram of sulfur, which is as close as could be determined gravimetrically.

For greater accuracy larger aliquots (say 20 cc.) may be taken for the final titrations.

Method for Calcium Hydroxide.—Attempts have been made to devise a method for the direct determination of the hydroxide by the use of a copper or zinc salt as suggested by Bloxam[1] in his work on ammonium polysulfids. None of these have been successful.

The amount of calcium hydroxide in the lime-sulfur solution may be calculated, however, from the data obtained in the above-described methods for the determination of "polysulfid" and "sulfid" sulfur. The amount of tenth-normal acid used in the precipitation of the sulfur in the first method is the amount necessary to react with both the polysulfid and the hydroxide present, while the number of cc. of zinc solution used in the "sulfid" sulfur method is the decinormal titration of the polysulfid only. The difference between the two titrations will represent the amount of tenth-normal acid required to neutralize the hydroxide.

[1] *Jour. Chem. Soc.*, **1895**, page 289.

The final titrations with the zinc solution in this determination should be made on 20 cc. aliquots.

Results of Analyses.—The analytical methods devised by Haywood[1] and Avery[2] have been used somewhat extensively during this investigation and have been found to be quite satisfactory. Some of the analyses made by the use of Haywood and Avery's methods in conjunction with our own are given in Table I. The solutions are representative, consisting of commercial samples, together with samples prepared in the laboratory by the use of different formulas and having different concentrations. Many other analyses have been made, but the general relationships found were the same as in those here recorded and the analytical data are omitted to economize space. The results are calculated as grams per 100 cc. solution.

TABLE I.

		Grams per 100 cc. original solution.					
No.	History of sample.	Total CaO.	Sulfid sulfur.	Polysulfid sulfur.	Thio-sulfate sulfur.	Sulfite and sulfate sulfur.	Calcium hydroxide.
1.	Commercial sample "Rex" lime-sulfur spray	12.12	5.92	23.06	1.47	0.08	None
2.	Commercial sample mfgd. by Oregon Spray & Gas Co., Portland, Oregon	12.86	7.04	25.30	1.78	0.12	None
3.	Commercial sample mfgd. by Niagara Spray Co., Hood River, Or.	12.38	6.79	23.90	0.82	0.08	None
4.	Laboratory sample made by boiling 55 grams CaO, 110 gram sulfur, and 400 cc. of water under reflux condenser for 1¼ hours	9.49	3.93	14.82	2.98	None	None
5.	Laboratory sample made by boiling 55 grams CaO, 55 grams of sulfur, and 450 cc. of water under reflux condenser 1 hour.	4.99	1.80	6.25	2.43	None	Trace
6.	Laboratory sample made by boiling 60 grams CaO, 110 grams sulfur, and 450 cc. water under reflux condenser 1 hour	9.45	3.60	12.43	3.84	None	None

The laboratory samples were made by boiling the stated length of time, then allowed to cool, and after standing 12 hours, the clear supernatant liquid was drawn off into glass-stoppered bottles. Upon standing a day or two longer the analyses were made. In the case of samples No.5 and No. 6, orange-red, needle-shaped crystals separated out of the solution. A considerable excess of lime was used in the preparation of No. 5, and a slight excess in No. 6, and the crystals formed were undoubtedly the oxysulfids of calcium. These compounds seem to be of variable composition, as they have been stated by various investigators to be $3CaO.CaS_4.12H_2O$, $2CaO.CaS_3.10$ or $11H_2O$, $5CaO.CaS_5.20H_2O$, $4CaO.CaS_4.18H_2O$, or $3CaO.CaS_3.14$ or $15H_2O$.

The amount of calcium hydroxide in the clear spray solution is only a trace, if any. It appears that if there is hydroxide in the freshly prepared solution it either unites with some of the sulfur already in combination to form more polysulfid, or it unites directly with the polysulfids to form oxysulfids which crystallize out of the more concentrated solutions.

The spray solution is always alkaline. Its alkalinity must be due to the hydrolysis of the polysulfid as the thiosulfate is not hydrolyzed to any extent. Küster and Heberlein[3] have found the sodium poly-

[1] *Jour. Amer. Chem. Soc.*, **1905**, page 244.

[2] *Bull.* **90**, Bureau of Chemistry.

[3] *Zeit. anorg. Chem.*, **1905**, page 53.

sulfids to be strongly hydrolyzed in solution. The case of calcium polysulfid is analogous.

From Table I we are able to get an idea of the polysulfid. Thatcher[1] has stated unreservedly that the polysulfid is the pentasulfid. If this were correct, the amount of "polysulfid" sulfur would be exactly four times that of the "sulfid" sulfur. In nearly every instance our results show that the "polysulfid" sulfur is approximately $3^1/_2$ times the amount of the "sulfid" sulfur, proving that the polysulfid in solution is not one compound only, but probably a mixture of the tetrasulfid and the pentasulfid of calcium.

The Absence of the Hydrosulfid.—In order to thoroughly establish the above given "sulfid" sulfur method and tabulated results it is necessary that the absence of the hydrosulfid should be proven. Wellington[2] and others have suggested the presence of this compound.

Divers and Shimidzu[3] showed that calcium hydrosulfid reacts very rapidly with sulfur to form polysulfid and liberate hydrogen sulfid, the action being as brisk as that of a strong acid with marble. When a solution of the hydrosulfid is heated with sulfur on a water bath the reaction is complete, only a trace of hydrosulfid remaining. Since free sulfur is always present in the preparation of lime-sulfur solution, it seems not probable that the hydrosulfid could be present in appreciable quantity.

Divers and Shimidzu[4] employed a manganous salt for the detection of basylous hydrogen, the test being based upon the following reaction: $Ca(SH)_2 + MnSO_4 = CaSO_4 + MnS + H_2S$, half of the sulfur present being liberated as hydrogen sulfid. Similar tests on the lime-sulfur solution with manganese sulfate have failed to reveal the presence of any hydrosulfid.

Again, when the spray solution is dried in hydrogen over sulfuric acid, hydrogen sulfid would be liberated by the decomposition of any hydrosulfid which might be present. Only the merest trace of hydrogen sulfid has been found to be liberated under these conditions.

In the "sulfid" sulfur determination, any hydrosulfid would in all probability be precipitated as zinc hydrosulfid and, since it is calculated as the normal sulfid only one-half of the sulfur present as hydrosulfid would be shown by the titration with the zinc solution. A comparison of the amount of "sulfid" sulfur found by this method with the amount of sulfur which could be liberated from the solution as hydrogen sulfid was made. The determination of the hydrogen sulfid was effected by adding exactly enough tenth-normal acid to completely react with the sulfids present and passing the gas liberated into an ammoniacal zinc chloride solution. The zinc sulfid thus obtained was digested in a small amount of concentrated potassium hydroxide solution, oxidized with hydrogen peroxide, and precipitated in the usual manner as barium sulfate. The comparative results of one of the determinations made in this way are as follows:

By "sulfid" sulfur method, 3.42 grams sulfur per 100 cc.

Sulfur liberated as H_2S, 3.44 grams sulfur per 100 cc.

If the hydrosulfid were present in any quantity there would be an appreciable difference found in the amounts of sulfur obtained by the two different methods. No such difference has been found in the determinations made.

From the above data it may be said that only a trace of hydrosulfid, if any, is present in the lime-sulfur solution. What little there may be is perhaps that which might be formed by the hydrolysis of the polysulfid.

The Nature of the Polysulfid.—When the spray solution is brought in contact with benzene or with chloroform sulfur is extracted in considerable amount. This fact led to a rather extended study of the polysulfids, for it seemed that some of the sulfur was held in very feeble combination if not in physical solution. An endeavor was made to ascertain just the exact amount of sulfur which could be extracted from a definite quantity of the spray solution. Preliminary tests showed that carbon disulfid cannot be used for making such an extraction because it reacts rapidly with the polysulfid to form a thiocarbonate.

Small quantities (5 and 10 cc.) of the solution were shaken in separatory funnels with benzene and with chloroform, the solvent in each instance being removed occasionally and new quantities added. The combined extractions made by the two solvents respectively were then distilled and the residual sulfur determined. A considerable quantity of sulfur was obtained from both the chloroform and the benzene extraction. However, a definite end-point to the extraction could not be obtained, for even after several days' extraction some sulfur continued to be gradually dissolved. Upon investigation it was found that during the extraction an oxidation of some of polysulfid to the thiosulfate had occurred, due to the contact with air in the separatory funnel, and some of the free sulfur was constantly liberated by this reaction. A very small amount of calcium carbonate was formed from the carbon dioxide present.

An extraction apparatus similar to that devised by A. H. Fiske[1] was arranged so that a quantity of the lime-sulfur solution could be extracted with benzene without coming in contact with the air. An ex-

[1] *Jour. Amer. Chem. Soc.*, **1906**, page 63.
[2] *Bull.* **116**, Mass. Exp. Station.
[3] *Jour. Chem. Soc.*, **1884**, page 270.
[4] *Loc. cit.*

[1] *Amer. Chem. Jour.*, **41**, page 510.

traction was made using 10 cc. of lime-sulfur solution. At the beginning a much larger quantity of sulfur was extracted than near the close of the experiment, which required several days' time. A definite end-point to the extraction could not be obtained and an examination of the extracted solution showed that there had been a considerable increase in the amount of thiosulfate, besides the formation of a very small quantity of what appeared to be calcium carbonate. The experiment was repeated, using 5 cc. of lime-sulfur solution diluted with 5 cc. of water. The details were carried out much more carefully than in the previous trial, but the results were the same. It was evident that either the benzene absorbed enough oxygen and carbon dioxide from the air in the apparatus to effect the composition of the solution, or else there had been a decomposition of the polysulfid with the formation of more thiosulfate as well as small amounts of other products.

Previous to the benzene extraction described above, an attempt was made to evaporate some of the lime-sulfur solution in partial vacuo, extract the dried residue with some sulfur solvent and ascertain what definite polysulfid, if any, remained. An experiment was tried drying 10 cc. of the solution in partial vacuo over calcium chloride. The quantity of thiosulfate increased enormously during the evaporation, indicating that an oxidation of the polysulfid had taken place.

Drying the solution in hydrogen sulfid was next tried, but the gas reacted rapidly with the solution, precipitating sulphur and forming hydrosulfid of calcium.

It was found after many trials that the solution could be successfully evaporated in pure hydrogen over sulfuric acid. Because of the conflicting data on the polysulfids in general, the details of the following experiments are given quite fully:

A lime-sulfur solution was made by boiling 55 grams of calcium oxide, 110 grams of sulfur and 450 cc. of water under a reflux condenser for one hour. Pure hydrogen was prepared from pure zinc and dilute sulfuric acid and washed, first with a potassium permanganate solution, then with a saturated solution of mercuric chloride, and finally with a strong solution of potassium hydroxide. The hydrogen was dried by passing it first through a calcium chloride tube and then through sulfuric acid.

Ten cc. of the lime-sulfur solution was placed in each of three glass mortars, which were immediately placed over sulfuric acid in different desiccators, and hydrogen passed into each until all traces of air were removed. The desiccators were then stoppered tightly, placed in a dark room where the temperature did not rise above 16°, and the solutions allowed to dry for three weeks. During this time the sulfuric acid became slightly turbid, indicating that a trace of hydrogen sulfid had been liberated. The dried residues had a light yellow color and contained some crystals of thiosulfate. Before opening the desiccators the hydrogen in them was tested and found to be practically pure. The dried residues were then removed, one by one, and immediately covered with pure, freshly distilled, dry carbon disulfid, previous tests having shown that this substance does not react with the dried material. The residues were ground to a fine powder while still under the solvent. The carbon disulfid was then decanted off and the residues carefully washed with a fresh supply. That a considerable amount of free sulphur was extracted was certain from the yellow color of the solvent after the extraction. The powdered residues were then transferred to wide-mouthed glass-stoppered bottles and covered with more carbon disulfid. Long standing failed to extract any more sulfur. After the solvent was decanted off the residues were dried in a current of hydrogen and then analyzed. The analyses of the residues and the original material are given in Table II, the results being calculated as grams per 100 cc. original solution:

TABLE II.

Grams per 100 cc. of original solution.

No.	Sample.	Total CaO.	Thio-sulfate sulfur.	Poly-sulfid sulfur.	Sulfid sulfur.	Sulfate and sulfite sulfur.	Sulfur extracted with CS_2.
1.	Original solution. ..	9.68	3.39	15.05	3.85	None	...
2.	Dried residue[1].....	9.25	3.43	3.64	3.58	None	11.25
3.	Dried residue.....	9.52	3.71	3.82	3.72	None	11.21
4.	Dried residue.....	Lost	3.84	4.43	3.60	None	10.28

The above-described experiment was repeated, using a lime-sulfur solution made by boiling 60 grams of lime, 110 grams of sulfur, and 450 cc of water under a reflux condenser for $2^1/_2$ hours. The method of procedure was the same with the exception that a fresh supply of hydrogen was passed into the desiccator every day or two in order to keep the supply pure and also to remove all traces of hydrogen sulfid which might be liberated. The results, calculated as grams per 100 cc. original solution are given in Table III:

TABLE III.

Grams per 100 cc. original solution.

Sample.	Total CaO.	Thio-sulfate sulfur.	Poly-sulfid sulfur.	Sulfid sulfur.	Sulfite and sulfate sulfur.	Sulfur extracted with CS_2.
Original solution.....	8.24	1.41	14.71	4.16	None	...
Dried residue.....	8.11	1.76	3.70	4.00	None	11.05

From the results given it appears that there is a more stable, primary polysulfid of calcium. Although the analyses given do not permit of a definite statement regarding its composition, it does correspond, however, very closely to the formula CaS_2. The slight variability in the results obtained may be

[1] A small amount of residue No. 2 was lost after the extraction with carbon disulfid had been made, hence the low results on lime, etc.

due to the fact that some of the higher polysulfid may not have been entirely decomposed in some instances. The writers have not found any indication whatsoever of the presence of the monosulfid in the dried residue.

Other investigators have found similar cases. Bloxam[1] discovered that of the potassium polysulfids, there was a more stable one having the formula K_4S_5. Küster,[2] in his work on the sodium polysulfids, found that after the polysulfid Na_2S_4 is formed the remainder of the sulfur in solution is not so firmly combined.

This lower primary polysulfid of calcium is amorphous, and mustard-yellow in color. It is readily soluble in water and 95 per cent. alcohol. When dry it is stable in the air.

An attempt was made to separate the polysulfid from the thiosulfate in the dried residue by the use of a solvent which would dissolve only the polysulfid. Trials were made using 80 per cent., 90 per cent., 95 per cent. and 98 per cent. alcohol, respectively, as the solvent, but the thiosulfate was found to be somewhat soluble even in 98 per cent. alcohol. The polysulfid is not soluble in absolute alcohol. No solvent has been found which will effect the complete separation of the thiosulfate from the polysulfid. All efforts to prepare a pure solution of calcium polysulfid from which a residue free from thiosulfate might be obtained have been unsuccessful, some thiosulfate being always present, though in some instances in very small amount.

Viewed in the light of previous investigations, it seems evident that all of the sulfur found in the lime-sulfur solution must be in chemical combination. The latest extensive work on this question was done by Küster and Heberlein on the sodium polysulfids.[3] These investigators state that the polysulfids are analogous to the polyiodides and are the salts of hydrogen sulfid acids of the ormula $H_2S.S_x$. They found that the more sulfur there is present, the less the hydrolysis of the polysulfid. This fact is indicative of chemical combination, for, if after a certain definite polysulfid is formed the remainder of the sulfur is simply in physical solution, there would be but ittle change in the amount of hydrolysis after enough sulfur had been added to form the primary compound.

These experiments with the polysulfid reveal a fact of practical significance in regard to the spray solution. It is not necessary for the polysulfid to oxidize in order that free sulfur be deposited, as has heretofore been stated. If the polysulfid is not oxidized completely before the spray dries on the tree, there will be left a lower polysulfid and some sulfur will be deposited which is not the result of oxidation. A considerable amount of the sulfur in lime-sulfur solution is in very feeble combination and for the practical purposes to which it is applied might be considered as sulfur in physical solution.

Effect of Time of Boiling.—Previous work on the lime-sulfur spray has shown that one hour is sufficient time for boiling in the preparation of the solution. Prolonged boiling has been found not to effect materially its composition. This latter statement has been found by us to be true only for certain conditions.

Solutions were prepared using different formulas and different lengths of time for boiling. The cookings were made under a reflux condenser and the samples were analyzed after standing 24 hours. The results calculated as grams per 100 cc. original solution are given in Table IV:

TABLE IV.

		Grams per 100 cc. original solution.				
No.	History of sample.	Total CaO.	Sulfid sulfur.	Poly-sulfid sulfur.	Thio-sulfate sulfur.	Sulfate and sulfite sulfur.
1.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. of water for one hour.....	5.15	1.84	6.49	2.43	Trace
2.	Boiled 55 grams lime, 55 grams sulfur, and 450 cc. water for 2½ hours	5.10	1.82	6.32	2.45	Trace
3.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 1 hour...	9.45	3.60	12.43	3.84	Trace
4.	Boiled 60 grams lime, 110 grams sulfur, and 450 cc. water for 2½ hours	8.39	4.16	14.71	1.40	Trace

In the case of samples No. 1 and No. 2, prolonged boiling did not effect the composition of the spray. With No. 3 and No. 4, where a larger proportion of sulfur was used, there was, however, a decided decrease in the amount of thiosulfate and an increase in the polysulfid present. There was also less lime in the solution. These results indicate that when the sulfur used is approximately double the quantity of lime, continued boiling does exercise a much more marked effect on the composition than when equal parts of lime and sulfur are used. The writers have been unable to furnish a complete, satisfactory explanation for the occurrence of this phenomenon. It may be said, however, that when the clear lime-sulfur solution is boiled hydrogen sulfid is liberated in considerable quantity, because of the hydrolysis of the polysulfid. As the hydrogen sulfid is liberated a deposit of calcium sulfite is obtained. The formation of the sulfite is due, no doubt, to the decomposition of the thiosulfate in the boiling solution.

Effect of Carbon Dioxide on the Lime-sulfur Solution.—It has been conjectured by some that the carbon dioxide of the atmosphere may have an influence in the decomposition of the diluted lime-sulfur solution when sprayed upon the tree. Some

[1] *Jour. Chem. Soc.*, **1900**, p. 753.
[2] *Zeit. anorg. Chem.*, **1905**, p. 53.
[3] *Ibid.*, **1905**, p. 53.

work has been done by the writers to test out this point.

Pure carbon dioxide was passed into some of the concentrated lime-sulfur solution. A large quantity of hydrogen sulfid was rapidly liberated; apparently as much as if some strong acid were used. The following reaction occurs:

$$CaS_x + H_2CO_3 = H_2S + CaCO_3 + S_x.$$

Two experiments were made by passing air through first a dilute lime-sulfur solution and then through a 10 per cent. solution of copper sulfate. Any hydrogen sulfid liberated would react to form copper sulfid in the latter solution. The air was passed through until the dilute spray solution no longer possessed a yellow color, the polysulfids present being completely decomposed. In one instance the air was used directly and in the other the carbon dioxide was removed by passing through a potassium hydroxide solution.

There was a distinct precipitate formed where the normal amount of carbon dioxide was present. However, the precipitate was quite small. The decomposed lime-sulfur solution had a strong odor of hydrogen sulfid. Paper moistened with lead acetate solution was gradually darkened, showing the presence of the gas.

In the instance where the air free from carbon dioxide was used there was only a trace of copper sulfid precipitated. The decomposed lime-sulfur solution had an odor of hydrogen sulfid. Evidently some hydrogen sulfid is formed during the oxidation, whether carbon dioxide is present or not, probably due to the hydrolysis of the polysulfid. The solution decomposed more rapidly when carbon dioxide was present, showing that it does exercise an influence in the decomposition of the spray, but our results indicate that this influence is comparatively small. The presence of hydrogen sulfid should not be overlooked in the consideration of the immediate insecticidal value of the spray.

In conclusion, it may be said that the above results are presented as derived from a limited study made in this laboratory, and with a full realization that the lime-sulfur solution is a complex equilibrium subject to the influence of many varying conditions.

Summary.—1. Simple and accurate methods for the determination of the composition of the polysulfids and the amount of calcium hydroxide have been perfected.

2. Free dissolved calcium hydroxide is not a constituent of the lime-sulfur solution, its alkalinity being due to the hydrolysis of the polysulfid.

3. The polysulfids in the solution are probably a mixture of the tetrasulfid and pentasulfid of calcium.

4. Our tests show the absence of appreciable quantities of hydrosulfid. Should any be present, it is that which might be formed by the hydrolysis of the polysulfid.

5. There seems to be a more stable polysulfid of calcium which our results indicate to be CaS_2. A considerable amount of the sulfur in the solution is very feebly combined and for practical spraying purposes may be considered as sulfur in physical solution.

6. It is not necessary for the spray to oxidize in order that free sulfur may be deposited from the same.

7 Prolonged boiling when approximately one part of lime to two parts of sulfur are used causes an increase in the amount of polysulfids and a decrease of thiosulfate.

8. Carbon dioxide reacts with the lime-sulfur solution, liberating hydrogen sulfid. Our laboratory experiments indicate that the carbon dioxide of the air exercises some influence in the decomposition of the spray upon the tree.

LABORATORY AGRICULTURAL EXPERIMENT STATION,
CORVALLIS, OREGON.

[CONTRIBUTION FROM THE LABORATORY OF THE HAWAII EXPERIMENT STATION. PAPER NO. 2.]

THE AVAILABILITY OF SOIL PHOSPHATES.

By W. P. KELLEY.

Some time after the announcement of the "Mineral Theory" of agriculture by Liebig, it began to be recognized that, while absolute analyses of soils are of value in agricultural practices, the larger part of the mineral substances of the soil is in a state in which it cannot be absorbed by most plants. The recognition of this fact has led to the development of a number of methods for the determination of the so-called available plant foods of the soil. It is generally considered that substances, available for plant growth, must either be in solution in the soil moisture or readily soluble in the secretions from root surfaces. Other factors, such as the physics and biology of the soil, play an important part in the question of fertility, however, and unless due consideration is given these factors entirely erroneous conclusions may be drawn from solubility determinations. Nevertheless, any step which leads to a knowledge of the state of solubility of the substances in the soil is an important one.

While some attention has been given to the determination of available plant foods in general, by far the larger part of these investigations has dealt with the phosphates. Some years ago the Association of Official Agricultural Chemists adopted the use of N/5 hydrochloric acid for the determination of the more active forms of P_2O_5. In this determination 200 grams of soil are digested with 2000 cc. of N/5 hydrochloric acid at 40° for five hours, due allowances

being made for the neutralization of the acid by soil carbonates, etc. More recently some chemists have substituted N/5 nitric[1] acid in this determination. In the publications bearing on this point but little field data has been submitted,[2] and therefore the reader is left with uncertainty as to whether or not the results given are of purely theoretical importance. No one claims, however, to be able to imitate natural conditions and extract from the soil the plant food that is immediately accessible to growing crops. The availability probably depends on the rate of solubility as much as on the absolute amount dissolved at any one time. On the contrary, it is only hoped to secure results of comparative value.

In the course of some investigations at the Indiana Experiment Station, the author had occasion to compare both the official and the nitric acid methods in the determination of available phosphates in a large number of soils in Indiana on which field experiments had been conducted. Some of these showed a response to the application of phosphatic fertilization; others did not. The following table,[3] selected from a large number of these determinations, shows the total P_2O_5 and the percentage soluble in N/5 hydrochloric and nitric acids, respectively.

TABLE I.—TOTAL P_2O_5 IN INDIANA SOILS, AND PERCENTAGE SOLUBLE IN N/5 ACIDS.

Soil No.	Description of soil.	Total P_2O_5. Per cent.	P_2O_5 soluble in N/5 HCl. Per cent.	P_2O_5 soluble in N/5 HNO_3. Per cent.
1.	Gray silt loam.....	0.08	0.0050	0.0060
2.	Gray silt loam.....	0.05	0.0030	0.0025
3.	Yellow silt loam.....	0.13	0.0028	0.0034
4.	Brown silt loam.....	0.11	0.0016	0.0022
5.	Sandy loam.....	0.10	0.0080	0.0078
6.	Dark sandy loam.....	0.20	0.0605	.....[4]
7.	Peaty soil.....	0.34	0.0380	0.0360
8.	Peaty soil.....	0.40	0.0500	0.0530

The above table shows that the solubility of the phosphates in these soils varies between very wide extremes, and that the differences between the solubility in N/5 hydrochloric and nitric acids are too slight to be of any consequence. On these various soils field experiments, involving the use of phosphates, etc., have been conducted for many years. Various crops have been grown, although the principal ones are corn and wheat. The following table shows the solubility of the soil phosphates in N/5 hydrochloric acid, and the effects on the yield of certain crops brought about by the application of phosphate. While it is true that the application of any given fertilizer does not always produce the same effects in different seasons, the data submitted fairly represents the action of phosphate on these soils.

[1] Peter and Averett, *Bull.* **126**, Ky. Expt. Sta.; Whitson and Stoddard, *Research Bull.*, No. **2**, Wisc. Expt. Sta. Snider, *Bull.* **102**, Minn. Expt. Sta.

[2] Snider gives some data bearing on this point; also Fraps gives some results from pot experiments in an article entitled "Availability of Phosphoric Acid in the Soil," *Jour. Am. Chem. Soc.*, **28**, 824.

[3] This data is taken from a thesis for a Master's degree presented to Purdue University in 1907, and published by permission.

[4] Not determined.

TABLE II.—PERCENTAGE OF P_2O_5 SOLUBLE IN N/5 HYDROCHLORIC ACID AND THE EFFECTS OF THE APPLICATION OF PHOSPHATE UNDER FIELD CONDITIONS.

Soil No.	P_2O_5 soluble in N/5 HCl. Per cent.	Crop grown.	Effects of the application of phosphate.
1.	0.0050	Corn	Yield increased 10 bu. per acre
2.	0.0030	Wheat	Yield increased 5 bu. per acre
3.	0.0028	Potatoes	Yield increased 50 bu. per acre
4.	0.0016	Corn	Yield increased 14 bu. per acre
5.	0.0080	Corn	Yield increased 6 bu. per acre
6.	0.0605	Corn	No increase
7.	0.0380	Corn	No increase
8.	0.0500	Corn	No increase

In all these soils, except the sandy loam and peaty soils, we find that the application of phosphate produced an increase in the growth of the crop in question. The total P_2O_5 in the sandy loam and peats is considerably greater than in the other types, but the percentage dissolved in N/5 hydrochloric acid is likewise very much greater. With but few exceptions, the soils of Indiana that contain less than 0.01 per cent. P_2O_5, soluble in N/5 hydrochloric acid, are benefited by the application of soluble phosphate, and seldom do those containing more than this amount respond to its application.

In order to maintain a strictly N/5 acid solution in the determination of available phosphate it is necessary to determine the amount of acid the soil is capable of neutralizing under the same conditions that are employed in the actual determination of the soluble phosphate. Some soils contain large amounts of carbonates; others do not, and if the phosphate solubilities are comparable, they must be made by the use of the same strength solvent. In the preliminary digestion for the determination of this neutralizing power it was noticed that those soils which neutralized a large amount of acid contained a correspondingly large percentage of soluble P_2O_5, whereas, soils having a slight neutralizing power were found to contain a small percentage. For a number of years soils that neutralized but little acid in the preliminary digestion have been considered as being in need of lime, since it is generally accepted that the presence of carbonate of lime promotes bacterial activity, as well as neutralizes soil acidity. The following table will show the neutralizing power of these soils and the percentage of P_2O_5 soluble in N/5 hydrochloric acid:

TABLE III.—THE N/5 HCl NEUTRALIZED BY ONE GRAM OF SOIL, AND THE PERCENTAGE OF AVAILABLE P_2O_5.

Soil No.	Acid neutralized. cc.	P_2O_5 soluble in N/5 HCl. Per cent.
1.....	0.37	0.0050
2.....	0.25	0.0030
3.....	0.50	0.0028
4.....	0.50	0.0016
5.....	0.44	0.0080
6.....	....[1]	0.0605
7.....	3.87	0.0380
8.....	6.00	0.0500
9.....	4.00	0.0420

[1] Not recorded.

The above table shows that a low solubility of phosphates is associated with a slight neutralizing power in the soil; and that there is a casual relation between the absence of active bases, on the one hand, and the low solubility of phosphates, on the other, seems likely. Whitson and Stoddard[1] have recently pointed out that acid soils in Wisconsin need phosphates. In Indiana the same conditions prevail.

The author recently pointed out that while the litmus test for soil acidity is unreliable,[2] the amount of N/5 hydrochloric acid which the soil is capable of neutralizing offers a very trustworthy indication of the needs of lime, and while the neutralization factor gives valuable indication of the need of lime, it is also very useful as a rapid means of determining phosphate deficiencies;—not that it could be relied upon as a definite indication, but is valuable as a suggestion. The fact that the N/5 hydrochloric acid method gives reliable indications concerning the application of phosphates, with such soils as prevail in the central west, led to an inquiry concerning its applicability to the soils of Hawaii, which are of a vastly different origin and type.

The entire island group of Hawaii is of volcanic origin, and from a geological standpoint, of a recent formation. The soils of Hawaii, being very largely derived from disintegrated basaltic lava, are characterized by a very high percentage of iron and alumina, and a relatively small percentage of calcium. As an average of a large number of determinations, these soils have been found to contain about 40 per cent. iron oxide and alumina, soluble in concentrated hydrochloric acid, whereas the combined iron and alumina of American soils probably do not exceed 6 per cent. In this investigation it was thought well to compare the solubility in both N/5 hydrochloric and nitric acids. The following table will show the results:

TABLE IV.—HAWAIIAN SOILS, SHOWING SOLUBILITY OF PHOSPHATES.

Soil No.	Total. Per cent.	Soluble in N/5 HCl. Per cent.	Soluble in N/5 HNO_3. Per cent.	Acid neutralized by one gram soil. cc.
10	0.07	Trace	Trace	0.90
11	0.35	Trace	Trace	1.80
12	0.20	Trace	Trace	1.30
13	0.55	0.1128	0.1025	3.50

Soils Nos. 10, 11 and 12 are found to contain only a trace of soluble P_2O_5, being, in each instance, not more than 0.0005 per cent., while No. 13 contains a very large percentage of available phosphate. The first three samples are representative of the upland soils of Oahu, having been taken from an elevation of 650 feet or more. Soil No. 11 is highly manganiferous. Each of these has been derived from primary lava. No. 31, however, is a coast-wise soil, derived from the disintegration of volcanic ash and cinders, having been subsequently submerged by the sea, during which time a considerable portion of coral limestone was incorporated with what is now the soil. Just as with the Indiana soils, we find that the neutralization coefficient bears a direct relation to the state of solubility of the phosphate.

It has been considered for some time that calcium phosphate is available for plant growth, whereas the basic phosphates of iron and alumina are not. Some years ago Fraps[1] pointed out that the solubility of the basic phosphates of iron and alumina in N/5 hydrochloric and nitric acids is very slight, whereas the solubility of calcium phosphate is complete. The Wisconsin investigators have recently shown that soils which respond to the application of phosphates contain not only a much smaller percentage of P_2O_5 soluble in N/5 nitric acid but also relatively more of the basic phosphates of iron and alumina than do the soils which do not respond to the application of phosphate.

While N/5 hydrochloric acid has been shown to completely dissolve calcium phosphate, and to effect only a slight solution of the basic phosphates of iron and alumina, Stoddard[2] points out that a one per cent. solution of sodium hydroxide is capable of dissolving the basic phosphates of iron and alumina while possessing only a slight solvent power for calcium phosphate. With soils that contain such large percentages of iron and alumina as prevail in Hawaii, it seems likely that a correspondingly high percentage of the phosphates would be combined with these bases, and hence be unavailable for plant growth.

With a view of testing this point, 100 grams of air-dried soil were digested with 1000 cc. of a one per cent. sodium hydroxide solution at 40° for five hours; the solution filtered and the P_2O_5 determined in the filtrate For the sake of comparison, the solvent powers of N/5 hydrochloric acid and one per cent. sodium hydroxide are given; and also the effects of the application of phosphate:

TABLE V.—SHOWING THE P_2O_5 DISSOLVED BY N/5 HCl. AND 1 PER CENT NaOH FROM FERRUGINOUS SOILS.

Soil No.	Soluble in N/5 HCl. Per cent.	Soluble in 1 per cent. NaOH. Per cent.	Crop grown.	Effects of the application of phosphate. Per cent. increase.
10	Trace	0.0060	Pineapples	50[3]
11	Trace	0.0219	Pineapples	100[3]
12	Trace	0.0089	Cotton	200
13	0.1128	0.1858	Rice	No effects

The above results show that while these soils contain considerable P_2O_5 as basic phosphates of iron and alumina, in the case of soil No. 13, there is also a large percentage of the phosphoric acid combined with calcium. These results show that the N/5 hydrochloric method is of value in determining phosphate deficiencies in soils of widely different types,

[1] *Loc. cit.*

[2] Soil Acidity, *Sugar Planters' Monthly*, May, 1909.

[1] *Loc. cit.*

[2] "Soil acidity in its relation to available phosphates," *Research Bull.* No. 2, Wis. Expt. Station.

[3] Estimated.

although there is an indication that the strength of the acid is not sufficiently great for highly ferruginous soils.

It is generally considered that apatite (soluble in N/5 HCl), and wavellite and dufrenite (soluble in 1 per cent. NaOH solution), constitute the principal mineral phosphates of the soil (soil No. 10 may contain some triplite), and yet the combined P_2O_5 dissolved by the two solvents, constitutes but a small percentage of the total phosphate in the soil. It is true that the dissolving power of a given solvent toward a pure chemical may be greatly modified when the same body is associated with numerous other substances, such as occur in soils. Furthermore, these soils contain a large percentage of finely divided ferric hydrate which so permeates and surrounds the soil particles that a complete dissolution can be brought about only by use of agents that are capable of dissolving the iron also.

It[1] has been suggested that the amount of P_2O_5 recovered from a soil by the use of a given solvent is not a true measure of the dissolving power of this solvent towards the phosphates in the soil, since some of the P_2O_5, after being dissolved, is refixed by the soil. In this connection it has been shown that these soils possess a high fixing power for soluble phosphates. It seems more likely, however, that only a small percentage of the phosphates present was dissolved by the solvents employed.

We should expect soils which contain from ten to twenty times as much iron and alumina as calcium to hold the phosphoric acid, combined largely with iron and alumina, rather than calcium; and the behavior of crops on these soils, together with their solubility, indicates the correctness of this view.

[CHEMICAL LABORATORY, NORTH CAROLINA DEPARTMENT OF AGRICULTURE.]

A RAPID METHOD OF DETERMINING CRUDE FIBER.

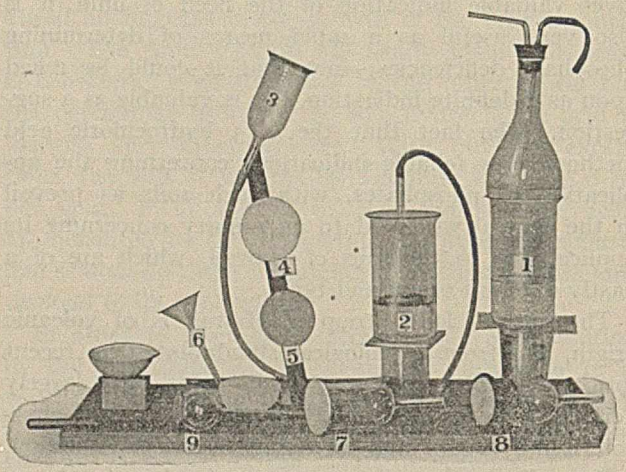
By J. M. PICKEL.

Received January 17, 1910.

This is, in the main, a method of filtering and washing the fiber. The filtration is effected by *upward* suction of the fiber against linen. The method was first used by the writer in the summer of 1902, since when it has been in constant use in this laboratory. A bare outline of the method was published in *Science* (Jan. 8, 1904).

Figure 1 (accompanying illustration) shows the manner of digesting the fiber: a beaker 7 to 8 cm. in diameter, about 15 cm. deep, capacity 600 to 800 cc., covered by a round-bottom flask through which flows cold water. Any convenient number of such digesters may be connected in series by rubber tubes 25 to 30 cm. long, and the water run through the series from first flask to last. There is no loss of digesting liquid by evaporation; and if the boiling is started and conducted slowly, no great trouble from foaming, since each digester may, without disturbing its neighbor, be lifted and swirled.

Figures 3, 6, 7, 9 show suitable forms of filters—broad mouth tube, funnel, thistle tube—each provided with a rim or flange over which the linen disc is drawn taut. Convenient dimensions of these tubes (Figs. 3, 7) are, large end, diameter 5 to 6 cm., length 6 to 9 cm.; total length, including stem, 18 to



20 cm; diameter of stem, inside, about 0.5 cm. The rim or flange should be about 0.5 cm. wide, turned at nearly right angle to the axis of the tube or funnel and uniform in diameter. Note the rims (Figs. 3 and 6). The linen disc (Fig. 4) is attached to the tube by means of a strong, but not too coarse, flax thread. This thread is passed in short running stitches through the linen in a circle (Fig. 4) whose diameter is greater than that of the rim of the tube (or funnel), but not so much greater that, when the linen is drawn over the rim and the thread tied, it (the thread) will press against the side of the tube—the entire "pull" of the thread should be exerted on the linen. This adjustment is easily made once for all, and permanently fixed in the shape of a pasteboard (or metal) disc (Fig. 5) which shall serve as a pattern; any needlewoman can then make the linen discs by the score or hundred, according to need. As each linen will serve for a half dozen or more fiber determinations, these filters are inexpensive. In addition to the larger filter, 5 to 6 cm. diameter, a smaller one, diameter about 2.5 cm., is needed. A perforated disc (copper) over the mouth of the tube, under the linen, is useful but not indispensible.

Operation.—The filter having been connected by

[1] Fraps, *Loc. cit.*

heavy rubber tube to a Bunsen suction pump and suction turned on, the surface of the filter is put in contact and kept in contact with the surface of the liquid in the beaker (Fig. 2) until all the liquid is drawn into the filter-tube, when the latter is withdrawn and reversed (Fig. 3) to permit the liquid to be sucked out. The suction is then discontinued, the fiber washed with 50 to 75 cc. of boiling water back into the beaker, stirred thoroughly, allowed, if need be, to subside a few moments, and the liquid sucked out through the filter, as above described. Three or four such washings will free the fiber of acid or alkali. When freed of acid, the fiber is washed back into the beaker with the requisite quantity of 1.25 per cent. alkali and digested. Finally, when filtered and washed (as above described) free of alkali, the fiber is washed with distilled water into a 50 cc. tared evaporation dish (royal Berlin porcelain in absence of platinum), the water evaporated on steam bath, the fiber dried, weighed, incinerated, the ash weighed, the fiber obtained by difference in the usual way. A small flexible steel spatula is often useful in removing the fiber from the linen and in bringing it into the dish. It will not infrequently happen that the dish will get full of water before all the fiber is washed into it; in such case, the excess of water is removed by suction through the small filter above referred to.

Experiments with filtering materials other than linen—hardened filter paper, flannel, chamois skin, unglazed porcelain discs (Fig. 8) were made—but the first and last are out of the question because of slowness, the two others are not suitable with hot alkali.

Results Obtained by the Method.—Duplicates on peanut hulls, corn bran, rice chaff, corn cobs, and peanut middlings gave results differing by 0.01 per cent., 0.14 per cent., 0.32 per cent., 0.20 per cent., 0.12 per cent., respectively. In the case of six samples of cocoas, duplicates were obtained differing by 0.02 per cent., 0.33 per cent., 0.03 per cent., 0.02 per cent., 0.06 per cent., 0.13 per cent. in each case. The fiber of cocoa, a fine powder, is one of the most difficult to filter and wash—next to impossible with a Gooch filter, but comparatively easy and quick by this method.

The filtrates and wash-water from the second or alkaline digestion were, after having passed through the linen filter, put through gooches (asbestos). It was found in six fiber determinations (wheat bran, shorts, cornmeal, "ship stuff") that the gooches retained 0.21 per cent. to 0.37 per cent. of solids, reckoned as fiber, that had passed through the linen; in the case of seven cocoas, filter paper (the hardened variety) retained 0.02 per cent., 0.02 per cent. 0.02 per cent., 0.26 per cent., 0.27 per cent., 0.35 per cent., 0.46 per cent., respectively, of solids which had passed through the linen.

The filtering (from the second or alkaline digestion), washing and transferring of the fiber to the evaporating dishes in the case of six cocoas consumed sixty-six minutes, an average of eleven minutes to the determination; the filtrates from these determinations were then put through hardened filter paper under suction, the shortest time of filtering in any of the six cases was one hour, the longest seven hours.

The above tests of the method were made several years ago. The author has hoped from year to year to make more extended and searching experiments, but has not been able to do so.

The official method of the U. S. Dept. of Agr. (Bur. of Chem., *Bull.* 107, p. 56, revised) for crude fiber says: "Filter through linen, asbestos or glasswool"—nothing as to particular grade of linen. One naturally selects, if linen, that of finest, closest mesh obtainable. Old filters of the author, still on hand, are 32 x 32 per square cm., that is, contain about thirty-two threads each way to the cm.; the threads are apparently about 0.2 to 0.3 mm. in diameter. Undoubtedly *standard*, or *better standardized* linen—if that material be finally found to be best—should be adopted.

There is a kind of felt, composed mainly of cotton, comparatively thin, uniform in texture; it would probably make an excellent filter. It is to be had at tailoring establishments.

RALEIGH, N. C., Jan. 10, 1910.

THE DETERMINATION OF CRUDE FIBER.

By G. M. MACNIDER.

Received February 17, 1910.

In carrying out the method of the A. O. A. C. for the determination of crude fiber in cattle feeds[1] we have tried a good many modifications of the apparatus to shorten the time required and to make the determination less laborious. As the apparatus in use in this laboratory at present has proved satisfactory, some of the modifications in use may be of interest to chemists engaged in agricultural work.

The digestions with 1.25 per cent. sulphuric acid and 1.25 per cent. sodium hydroxide are done in 600 cc. Jena glass beakers, 16.5 cm. in height and with a uniform diameter of 8 cm. During the digestion a clock glass is placed over the beaker to condense the steam. This is fairly satisfactory, but considerable trouble is frequently caused by the frothing of the liquid, thereby necessitating the washing of the

[1] Bureau of Chemistry. *Bull.* No. 107 (revised).

substance from the sides of the beaker, and by the loss by evaporation which varies the strength of the solution. A number of different forms of condensers were tried to overcome both of these difficulties, but with only a fair amount of success. The author has found the following apparatus very satisfactory: this consists of an upright Liebig condenser, the lower end of which passes through a large rubber stopper which fits into the beaker described above. The stopper also carries a small tube for the introduction of a stream of air. (The use of a stream of air is suggested in the official method.) When the digestions were done in this apparatus is was found that with the use of only a weak stream of air the frothing even on the most difficult samples, *i. e.*, low-grade cotton-seed-meals, could be so controlled that no error was introduced from this source. By using the Liebig condenser in place of a glass tube condenser or a flask containing water placed on the beaker there was so little loss of steam that the volume of the liquid remained practically constant throughout the digestions.

A great many different forms of filters have been tried for filtering the fiber. The most satisfactory form is by reverse filtration, using linen as a filtering medium. (The official method directs to use either linen, asbestos or glass wool.) Any good grade of linen is satisfactory. The first form of this filter was made as follows: A circular piece of linen was fastened over the mouth of a glass funnel by means of a draw string around the edge. The stem of the funnel is connected with the suction apparatus and the linen immersed in the liquid and the liquid sucked up into a waste bottle. The fiber adhering to the linen is washed off with a jet of water.[1] This form of funnel was used for a while, but was found unsatisfactory and was discarded on account of the fact that the linen was not supported and consequently sucked back into the funnel, causing trouble in washing. It also required a considerable amount of time to prepare the lined filters and attach them to the funnel. To overcome this difficulty Mr. Harris (formerly of this laboratory) designed a funnel made of sheet copper, the mouth of which is closed by a perforated copper plate, which supports the linen. The linen filter is fastened over this by a copper band about 1 cm. in width which fits closely around the edge of the funnel. This keeps the linen stretched taut over the copper plate and makes it very easy to wash off any adhering fiber. By this arrangement the linen filters can be changed very rapidly. The funnel, as used at present in this laboratory, is made 7 cm. in diameter, or so as to just fit into the fiber beaker, thus giving as large a filtering surface as possible. When the fiber is finally washed free from alkali it is transferred from the beaker to a crucible or poreclain dish and evaporated to dryness in the usual manner. The only objection to the funnel just described is that in transferring the fiber it requires a large volume of water, usually 120 to 150 cc., to wash the fiber from the filter and wash out the beaker. To overcome this the author has designed a small copper funnel 3.5 cm. in diameter, made very similar to the large one. This can be used for the entire filtration, but the work can be done faster if the acid washings and the first few washings of the alkali are done with the large copper funnel, then on the last washing of the alkali use the small funnel. As the liquid is sucked up the funnel is carefully moved around in the beaker and the greater portion of the fiber can be collected on the linen attached to the funnel and can then be washed into a small crucible with a very small amount of water. It requires only a small amount of water to wash out the fiber remaining in the beaker. It was found that by using this method the fiber could be transferred to a small crucible with from 25 to 40 cc. of water as compared to 120 to 150 cc. with the large funnel. Where a large number of determinations are to be made this is a great saving in time as well as in the amount of gas burned in evaporating the fiber to dryness.

A number of tests were made, using Gooch crucibles for both the entire filtration or for the alkali filtration. The nature of the material causes the filters to clog so readily that it requires too much time to filter in this way when a more rapid method is available. Very satisfactory results were, however, obtained when all the washings except the last washing of the alkali were done with the copper funnel and the fiber then washed into the gooch. With wheat products and similar materials this procedure is fairly rapid, but with cottonseed-meal and similar products the filters clog very readily and it requires a considerable amount of time to complete the filtration.

Tests were also made with the Monroe crucible, prepared according to the directions given by Snelling.[1] When the filtrations were divided as described for the Gooch crucible, the Monroe crucible gave very satisfactory results. The time of filtration is, of course, longer than with the copper funnel, but this will be more than compensated for by the time saved on the evaporations. Snelling suggests the use of a platinum wire gauze in the platinum felt to prevent cracking and curling of the felt when heated. This would probably be of considerable advantage in this class of work. After the fiber has been ignited and weighed the ash can be very easily removed with a camel's hair brush without injuring the platinum felt.

FEED AND MICRO-CHEMICAL LABORATORY,
N. C. DEPARTMENT OF AGRICULTURE,
RALEIGH.

[1] This form of filter was first gotten up by J. M. Pickel of this division. See preceding paper, THIS JOURNAL.

[1] *J. Am. Chem. Soc.*, **31**, 4, 1909.

PLANT AND MACHINERY.

RECOVERY AND PURIFICATION OF SOAP LYE GLYCERINE BY THE GARRIGUES PROCESS.

By G. A. Moore.

Received April 15, 1910.

Glycerine is so closely associated with the soap industry that no soap plant is complete without its department for saving the glycerine contained in the fats and oils used by the soap maker.

For a number of years chemists and engineers have been directing their energies toward improved processes and machinery for the recovery of glycerine from spent soap lye. Many patents have been granted and many processes developed, each having the common object of glycerine recovery. A gradual evolution can be traced, the plants in successful operation to-day being but combinations of the old principles with new ideas, resulting in greater efficiency of procedure and improved design of apparatus.

Metallic salts, such as sulfate of iron and aluminum, were used in the early stages of lye treatment for coagulating and purifying agents, as in the processes of L. M. Brochon, in 1882, and Jesse P. Battershall, in 1883, and later by Jos. Van Ruymbeke, in 1891. The Van Ruymbeke process for recovering the glycerine from the still foots was an important step taken in 1894. In 1904 Garrigues developed his process for eliminating volatile fatty acids previous to distillation.

Domeier and Hagemann, in 1890, first used the closed salt separator later applied to vacuum evaporators by Foster, in 1899. O. Laist, in 1883, applied the air condenser to glycerine stills, but the first use of vacuum had been made in 1882 in connection with the apparatus of F. Armandy. In 1891 Van Ruymbeke combined the use of high vacuum with heating the still by means of saturated steam and injecting saturated steam and in 1894 applied the injection of expanded and reheated steam to glycerine stills. In 1904 Garrigues utilized the heat of the glycerine vapor from the still for superheating the low pressure steam injected into the still.

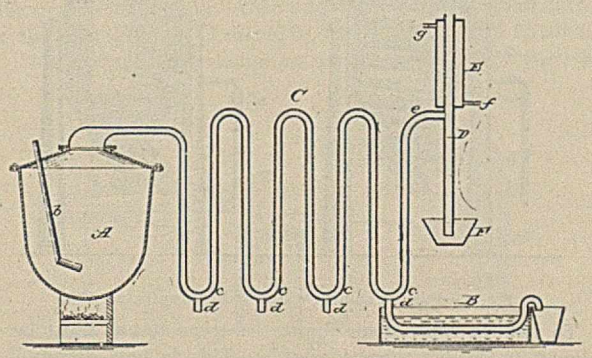


Fig. 1.—Apparatus of O. Laist, 1883. Air condenser applied to glycerine still.

With the Garrigues process the crude glycerine is of first quality, dynamite grade glycerine can always be produced in one distillation, and it is possible to obtain from even the blackest soap crudes a colorless, odorless, salt-free glycerine in two distillations, and there is never a time when the glycerine is off and has to be re-distilled.

Crude glycerine from soap lyes is a saturated solution of various alkaline salts in glycerine together with varying amounts of water, organic impurities and coloring matter. It is sold on a basis of 80 per cent. glycerine content and must contain but a small percentage of salts and organic matter in order to present but little difficulty in refining.

Refined glycerine must meet more stringent tests. Dynamite grade must have a gravity at 60/60 F. of not less than 1.2602 and must contain not more than 0.01 per cent. chlorine as determined in the water solution of the ignited residue. Some

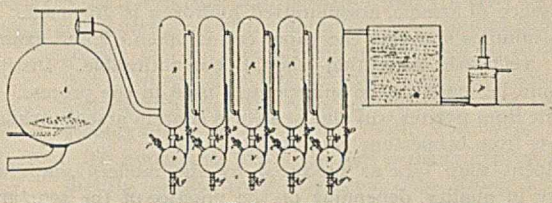


Fig. 2.—Apparatus of F. Armandy, 1882. Vacuum still.

buyers lay particular stress on the following silver nitrate test: Mix 10 cc. of glycerine with 10 cc. of 10 per cent. silver nitrate and stand in the dark 10 minutes. No precipitation or marked darkening in color must take place.

For chemically pure glycerine the tests as given in the United States Pharmacopoeia are official. C. P. glycerine must contain not less than 95 per cent. absolute glycerol, must be odorless and colorless, and conform to tests for mineral impurities, sugars, acids, salts, etc. Of the several tests designated in the Pharmacopoeia, that for butyric acid is most stringent and no glycerine will meet it. Also the silver nitrate test for acrolein is open to suspicion. In making this test the temperature must be taken into consideration, as any variation in temperature will invalidate the test. A good test is to mix equal volumes of glycerine and a 20 per cent. solution of silver nitrate and stand in the dark for thirty minutes. The solution should show no color in that time. The temperature must be kept constant by immersion in water at 15° C.

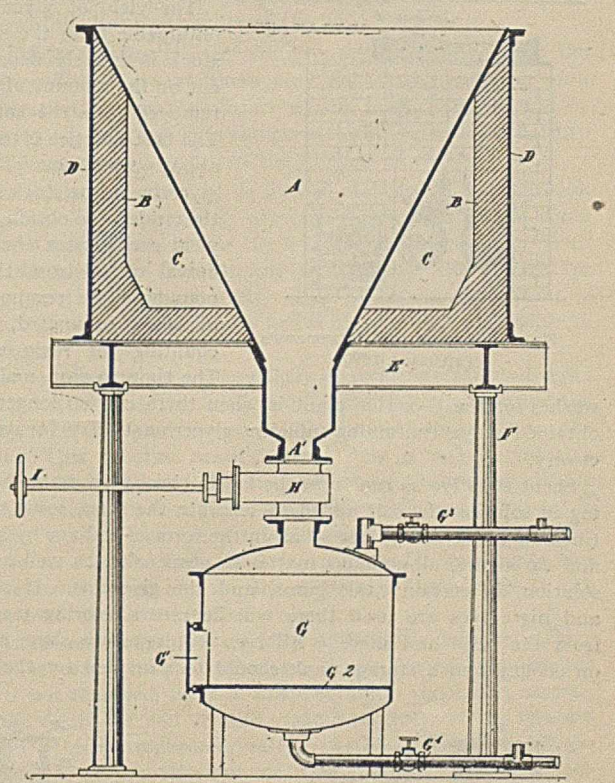


Fig. 3.—Domeier and Hagemann's salt pan, 1890.

The presence of arsenic in glycerine used for medicinal purposes is extremely dangerous and pure glycerine should not show any reaction for arsenic by the following modification of the Gutzeit test. Place 2 cc. of sample in a high test-tube; add some zinc free from arsenic and a few cc. of pure dilute

sulfuric acid. The test tube is then covered with a tightly fitting cap of filter paper, two or three layers thick, the innermost layer having been previously moistened by the aid of a glass rod, with a 50 per cent. solution of silver nitrate. In presence of arsenic, arseniuretted hydrogen is given off. After ten minutes standing the paper cap is taken off and examined. No yellowish coloration should be noticeable. Distinction should be made in the sulfuric acid used in the process. That made from pyrites will almost always contain arsenic, while that made from brimestone does not.

Spent soap lyes as produced by the modern soap factory vary in quality, depending on the practice of the soap maker. The refiner would, of course, prefer to receive lyes free from organic impurities and coloring matter, but the object of passing water through the kettle is to remove the dirt and coloring matter from the soap as well as to obtain a good yield of glycerine. It is advisable, however, to avoid running nigre and rosin lye to the glycerine plant. This, of course, can only be done if the glycerine has been properly removed from the soap before the nigre and rosin are added.

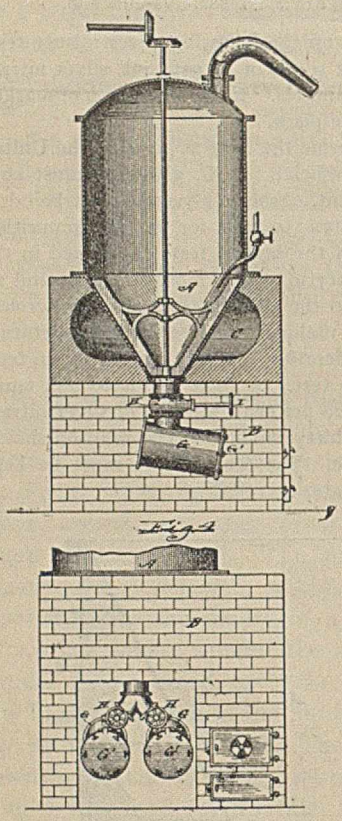


Fig. 4.—Domeier and Hagemann's evaporator, 1890.

The yield of glycerine obtainable from the soap stock is entirely dependent on the amount of lye removed from the kettle. The best practice is to get about 90 per cent. of the glycerine in the stock into the crude. To obtain this yield necessitates the removal of at least three pounds of lye per pound of stock saponified, not counting the rosin used. The time to stop making washes for the glycerine plant is when there can no longer be obtained a lye containing sufficient glycerine to pay for its recovery.

Spent soap lye as run from the kettle consists of water holding in solution the salt added to separate the soap, some soap (including lime soap), free alkali in the form of sodium hydrate and carbonate, albuminous matter in suspension as well as in solution, in certain cases gums, and the glycerine. If rosin and nigre lyes are used there will be much coloring matter from the rosin and nigre. All lyes will separate some soap on cooling and a storage tank should be provided for the lye waiting to be treated and from which the separated soap can be skimmed. No lye need be drawn for the glycerine plant containing sufficient strength to raise the average of all the lyes to more than 0.4 per cent. total alkalinity. This low figure will result in a large saving both in caustic soda in the soap factory and acid used to neutralize the alkalinity of the lye in the glycerine plant.

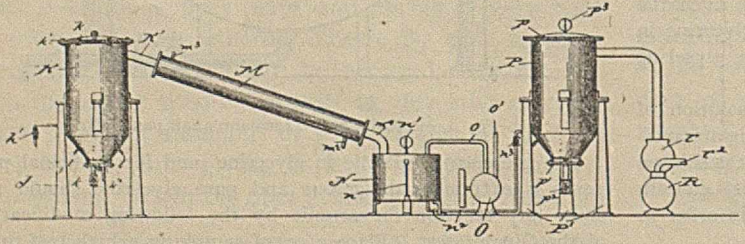


Fig. 5.—Van Ruymbeke's still and concentrator, 1891.

After the lye has cooled and all separated soap been skimmed off, it is taken to the glycerine plant, where it is to be treated before going to the evaporators. The alkali in the lye must be neutralized and the organic impurities removed.

The neutralization of the alkali is effected by the addition of an acid, either hydrochloric or sulfuric. The use of the former is open to objection because of high cost. It has the advantage, however, of producing as a result of the chemical action, sodium chloride, and the salt recovered from the evaporator can be used continuously in the soap kettles. It also contains no arsenic—an advantage where C. P. glycerine is manufactured.

Sulfuric acid is most generally used. Its use introduces sodium sulfate into the lye, which salt is recovered with the common salt from the evaporator. Sodium sulfate is practically useless for graining soap, its graining qualities being but three-fifths that of sodium chloride and the grain produced is soft and often hard to separate from the lye. When the recovered salt has been used a sufficient number of times to bring the percentage content of sodium sulfate to 25 per cent. or 30 per cent., it is advisable to waste it, as with anything over this proportion so much is required to grain the soap that the large amount of salt is liable to give trouble in the evaporator by coating the tubes. The number of times recovered salt can be re-used depends on the amount of alkali left in the lyes.

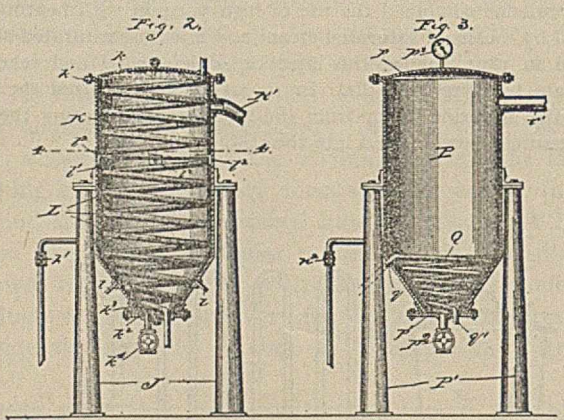


Fig. 6.—Van Ruymbeke's still and concentrator, 1891.

To remove the organic impurities some means must be employed to render them insoluble. This is best accomplished by the addition of metallic salts, forming insoluble metallic compounds, which are coagulated when the lye is brought to neutral. There are a number of compounds on the market for which special advantages in lye treatment are claimed. For this work, however, the lower grades of aluminum sulfate are amply efficient and cheap enough to offset any advantage of the special chemicals.

The amount of aluminum sulfate to be used depends on the cleanliness of the lye and its freedom from soap and gelatinous matters. The least amount that will give a good cake in the filter press and not gum the cloths is the amount to use. This chemical can be added either dry or dissolved in water and will neutralize about one-third its weight of caustic soda. An excess of free caustic

in the lye has a tendency to form aluminum hydrate which will retard filtering.

Some operators prefer to determine the amount of alkali in the lye by chemical analysis and then estimate the weight of acid to be added to bring the lye to neutral, making proper deduction for the amount of alkali neutralized by the aluminum

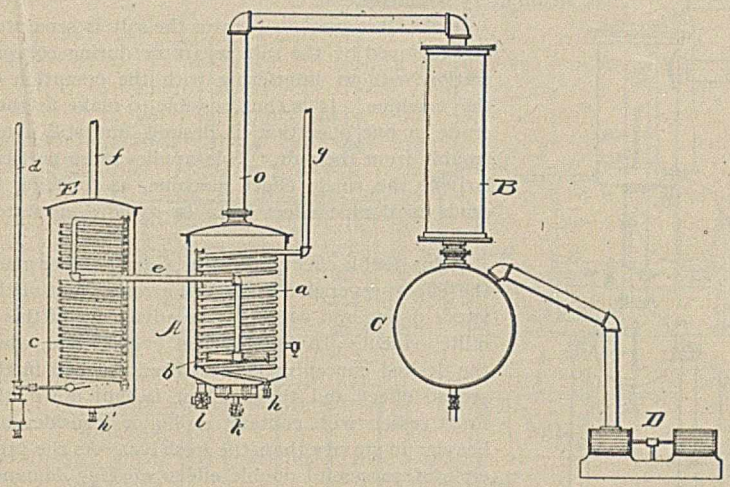


Fig. 7.—Van Ruymbeke's still, 1894.

sulfate. This, however, is unnecessary, as by means of a good neutral litmus paper in the hands of a careful worker the lye can be readily brought to between neutral and 0.01 per cent. alkaline (tested by the method given below, using phenolphthalein).

All lyes will contain some carbonate of soda. Carbonates in the lye have a tendency to cause foaming in the evaporator and as the action of carbonates on litmus is somewhat misleading the best procedure is as follows:

The lye is placed in the treating tank in which some means has been installed for agitating with air. With the air turned on, a portion of the acid is added—preferably just sufficient to take up the free caustic—then add the sulfate of aluminum. After the chemical is well mixed in, the lye should still be alkaline. Now enough acid should be added to just carry the lye

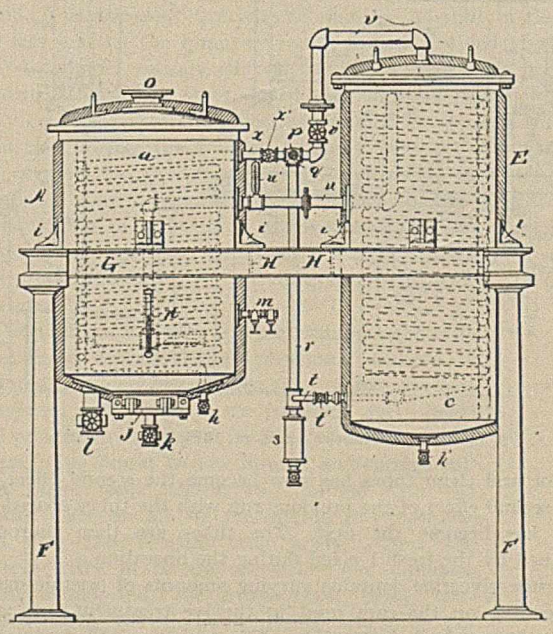


Fig. 8.—Details of Van Ruymbeke's superheater and still, 1894.

beyond the neutral point to the acid side, as indicated by its giving to neutral litmus paper a faint pink tinge. Care should be taken to thoroughly agitate the lye during all stages of the treatment.

If the lye were left in this acid condition there would be a tendency to re-convert some of the aluminum soap to aluminum sulfate and set the organic matter free, in which case both would go into solution in the acid liquor and pass through the press, producing a dark and gummy crude.

To avoid this state, the lye is made neutral or slightly alkaline by the addition of a strong solution of caustic soda. If the second addition of acid has been carefully made no more than one pint of 30° Bé. caustic need be added in treating 30,000 pounds of lye.

If the lye is just neutral it is well to make sure no chemical is still in solution. Filter a small sample and add a few drops strong ammonia. If there is any precipitate, add some more caustic to the lye and repeat the test. Usually the proper condition will be reached when the lye is between neutral and 0.01 per cent. alkaline. If desirable to know the exact condition of the lye, it is best determined by the following test: To about 20 grams of the filtered lye add 25 cc. distilled water and 5 cc. quarter-normal sulfuric acid. Boil for a few minutes to expel carbonic acid and titrate with quarter normal caustic soda, using phenolphthalein as indicator. If more acid is used the lye is alkaline. If more alkali it is acid. The difference between the acid and alkali used, multiplied by 0.01, divided by the weight of sample used and then by 100, is the per cent. alkalinity or acidity of the lye.

If the lyes being treated contain rosin lye or lye from the lower grades of grease, there may be an accumulation of a gummy material on the surface of the tank. This should be skimmed off, as it will gum the press cloths and make it hard to clean them, as well as retard the filtering of the lye.

The lye is now ready to be filtered and should pass through the press with little or no pressure. The press should drain into the tank from which the evaporator takes feed. With this treatment but one filtering is necessary, the filtered lye being practically water white. Lye containing an excess of alkali will have a yellow color and is often all but impossible to filter clear.

The practice of some soapmakers of returning silicated scrap to the kettles is to be condemned, unless all the lyes for the glycerine plant have been previously withdrawn from the kettle. This practice results in not only a loss in valuable filler but also a loss in acid neutralized by the sodium silicate in the lye treatment. The strongest objection, however, is that in treating the lye the addition of acid sets free silicic acid in its colloidal form, and any appreciable amount of this will retard filtering, and sometimes prevent the passage of any lye at even excessive pressures.

All lyes will contain nitrogenous matter, the amount varying with the care used in rendering. When the lyes are treated this is not removed, most of it appearing in the crude, increasing the figure for non-volatile organic residue. If the lyes are alkaline this nitrogenous matter partly decomposes in the evaporator, giving off ammonia. In the still this decomposition continues, the crude being always distilled alkaline, the ammonia passing out through the vacuum pump. There is no accumulation of nitrogen in the still foots when these are returned to the lyes, showing ultimate decomposition of all nitrogenous matter.

Crudes from cottonseed soap stock lyes contain nitrogenous acid bodies that resist this decomposition, necessitating waste

of the still residues. The same applying to crudes obtained by autoclave or Twitchell process from cottonseed soap stock black grease.

Lyes stored, free from caustic, ferment, the nitrogenous matter decomposing, producing sulfides which give off hydrogen sulfide on acidifying, and some glycerine is converted to trimethylene glycol.

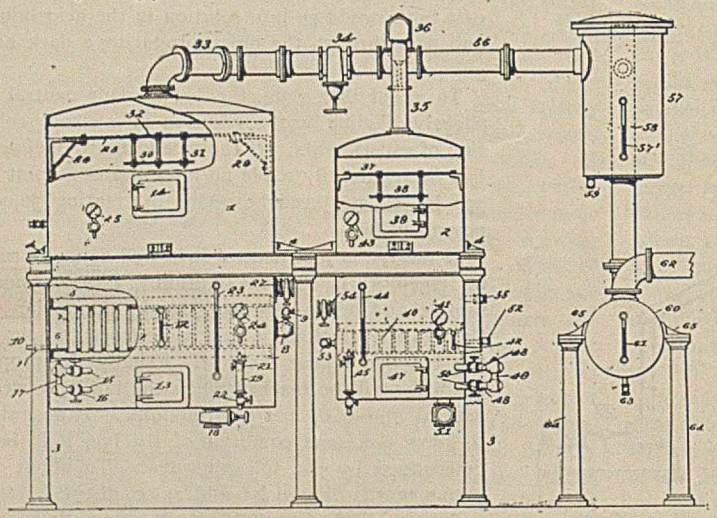


Fig. 9 —Van Ruymbeke's evaporator, 1894.

Fermented lyes give considerable trouble in the evaporator by foaming. It is sometimes impossible to evaporate them. The sulfides also corrode the iron of the apparatus.

After filtration the lye is ready for the evaporator, and is to be concentrated to crude glycerine. This concentration may be accomplished in various types of evaporators, which may be operated either single or double effect. The use of evaporators of more than double effect is not practical in glycerine lye concentration, because of the difficulty encountered with the salt. In double effect work salt will often deposit in the first effect. If a triple effect machine were used, salt would always deposit in the second effect and because of the low vacuum under which the boiling in the second effect is accomplished, the tubes would become coated and interfere seriously with the proper operation of the machine.

If evaporators of the horizontal tube type are used or any type machine in which the salt from the entire run is accumulated and emptied after the machine is shut down, it is preferable to operate in two stages. That is to concentrate the lye to half crude containing from 30 per cent. to 40 per cent. of glycerol, and when sufficient of the half crude has accumulated to finish to crude containing 80 per cent. or more actual glycerol.

The large body of salt obtained when finished crude is produced in one operation is difficult to handle as the crude salt is harder to separate from the more viscous liquor. The large amount of salt obtained also gives trouble by salting the machine so that eventually it is found necessary to boil out with water to thoroughly clean the machine. Particularly is this so when sodium sulfate has accumulated to any extent.

By operating in two stages about 80 per cent. of the salt recovered is obtained from the half crude and the tubes at the end of a half crude run have only a slight coating of salt, which is effectually removed by the light lye when starting the next run. Then when finishing to crude, if the machine is filled with fresh lye and brought to a boil before any half crude is fed, the tubes are thoroughly cleaned for the final concentration.

A finished crude can be obtained by double effect working, but there will be a big saving of time by working double effect to the half crude stage and then separating the double into two single effects and finishing the half crude, to crude using live steam at 15 pounds pressure.

In the Garrigues' evaporator the salt is separated and removed by the salt separator during concentration without interfering with the operation of the machine. It is thus possible to make finished crude in one operation, if desired, and still avoid trouble from the salt. This applies more particularly to the single effect machine, as finishing to crude in double effect is to be avoided, as stated above.

In his double effect apparatus, Garrigues has made the effects reversible by special arrangement of the vapor piping and valves. The advantage of this is quite evident. In double effect evaporation, when the desired concentration has been reached in the second effect and the machine is shut down, the first vessel will contain a liquor considerably heavier in gravity than the fresh lye. As the principle of successful double effect working demands a light liquid in the first effect, it is necessary to empty the first effect of this heavy liquor and start with fresh lye. Also the tubes of the second effect would have a coating of salt, and if this partly concentrated lye, which might be at the salting point, was transferred to the second vessel it would not dissolve the salt from the tubes. The salt would then accumulate on the tubes and the machine would eventually have to be shut down for cleaning.

Now, if at the end of a run it is possible to reverse the effects, the machine is in ideal condition to start a new run. What was formerly the first effect containing a partly concentrated

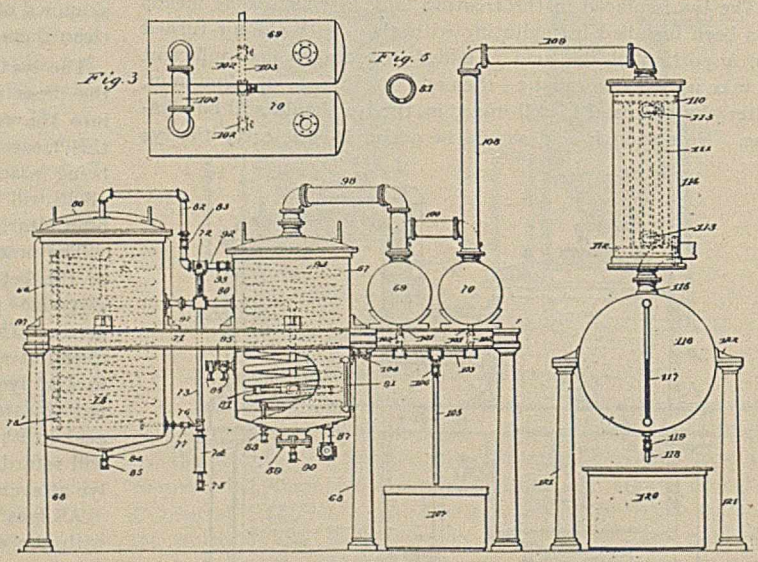


Fig. 10.—Van Ruymbeke's still set, 1894.

liquor and clean tubes has now become the second effect, and the second effect of the previous run with the tubes coated with salt has become the first. The tubes are then thoroughly cleaned by the fresh lye fed during the operation.

Crude glycerine contains varying amounts of organic matter, depending on the care used in the lye treatment, and alkali salts of the volatile fatty acids. The term "volatile fatty acids" is used among chemists to mean such fatty acids as vaporize

with water vapors at a temperature not exceeding 212° F. These include acetic, butyric, caprylic, etc., acids.

The presence of organic matter and alkaline salts materially retards distillation of the crude and increases the still residue. Furthermore, it is impossible to completely separate the glycerine from the alkali salts of the volatile fatty acids, some of the fatty acids passing over to the distillate and some glycerine being retained in the still, the amount of glycerine retained increasing in proportion to the quantity of the alkaline salts in the still. In some instances the residues contain 50 per cent. of glycerine which cannot be readily distilled.

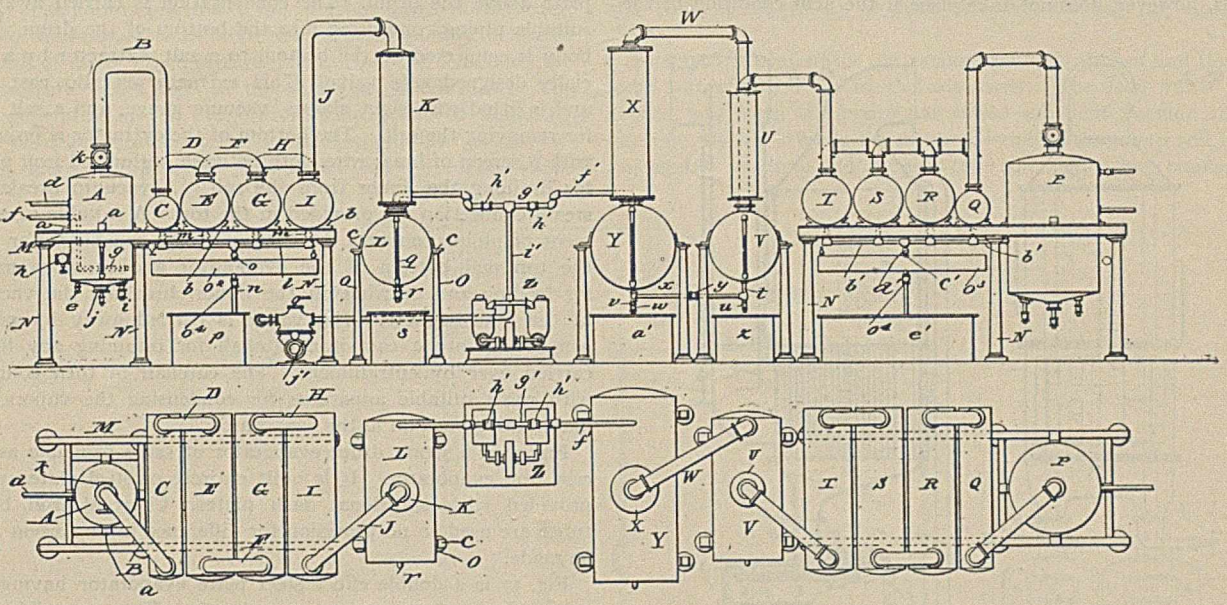


Fig. 11.—Van Ruymbeke's distilling plant, 1896.

Garrigues has developed a process which by a sequence of various steps, concentrations, and addition of alkali largely eliminates the volatile fatty acids previous to distillation. There is thus in the still a very small amount of fatty acids as compared with the quantity of glycerine. As these volatile acids are partly distilled with the glycerine from even an alkaline liquid, it is apparent that the smaller the amount in the still the less will be the quantity found in the distilled glycerine. Also by almost entirely eliminating the volatile acids previous to distillation there is produced a residue so low in volatile fatty acid salts that the glycerine retained by them is trifling.

In this process the lyes, as received from the soap factory, are treated as has already been described. The insoluble aluminum soap is separated by filtration but the soluble fatty acids remain in solution as alkali salts and pass into the filtrate. After filtering, the lye is evaporated to half crude, containing 30 per cent. to 40 per cent. of glycerol.

The half crude liquor is separated from the salts crystallized during the evaporation. Sulfate of alumina is added in sufficient quantity to produce aluminum soap from all the insoluble fatty acids still present in the liquid in form of soluble alkali soaps. The liquid is now filtered and enough sulfuric acid then added to combine with the greater part or all of the alkali in combination with the volatile fatty acids. Thus the volatile fatty acids are set free. The liquid is again evaporated, the evaporation being continued until the liquid contains above 80 per cent. of glycerol. During this operation a further crystallization of salt takes place, and at the same time the greater part of the volatile fatty acids is eliminated.

As the glycerine becomes more concentrated by the evaporation, a combination takes place between some glycerine and part of the remaining fatty acids producing glycerides, which are identical with those contained in the original fat. Therefore it is not feasible to eliminate all the volatile fatty acids present during one evaporation.

The next step is to distil off the glycerine. At the high temperature necessary for doing this the glycerides of the volatile fatty acids contained in the liquid would again be decomposed by the steam into free fatty acids and glycerine. Both would distil and some glycerides would also distil unchanged. To avoid this contamination of the distillate a sufficient quantity of alkali is added to the still. This combines with the fatty acids present, holding the greater part of them in the still, probably in the original condition in which they existed in the lye. The liquid is now distilled. The operation is continued until nearly all the glycerine is distilled and only a small residue remains in the still. This consists essentially of sulfate and chloride of sodium, the alkaline salts of the fatty acids and some coloring matter, together with a small quantity of glycerine, and may be returned to the lye and again put through the process.

Theoretically considered, the elimination of volatile fatty acids may be brought about if in the first treatment the spent

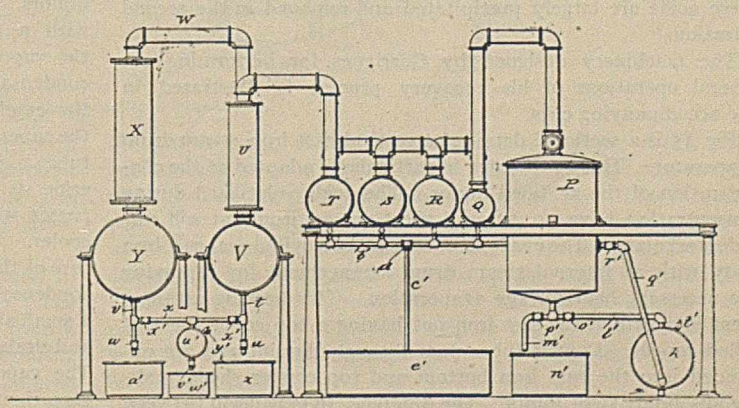


Fig. 12.—Van Ruymbeke's still set, 1896.

lye is made acid to such an extent that the volatile fatty acids are set free. These would then pass over with the water vapor during the subsequent evaporation of the lye. This plan is open to objection because the dilute liquid will froth violently during the evaporation if it contains free volatile fatty acids. This, however, does not take place if the acid condition of the

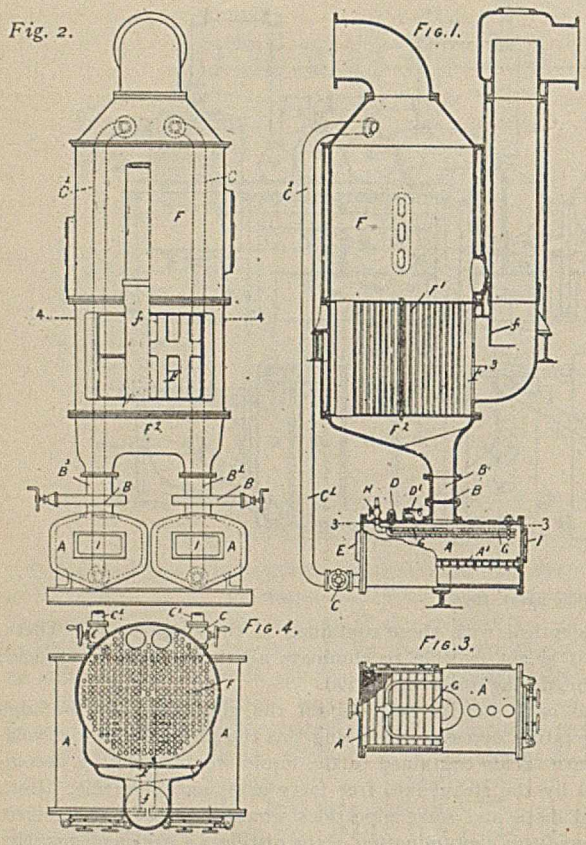


Fig. 13.—Foster's evaporator, 1899.

liquid is produced after partially concentrating the same, making it more viscid, due to a greater percentage of glycerine. Also the amount of dilute liquid to be handled would be so great that it would not be so easy to obtain the required conditions as when a small quantity of more concentrated liquor is treated. Waste lyes also contain some fatty acids which are sparingly soluble in water, but not readily volatile with water vapor. If the dilute liquor is acidified these acids pass into the filtrate because of the large amount of water present. If, however, a small quantity of concentrated liquid be acidified, these acids are largely precipitated and removed in the second filtration.

The machinery designed by Garrigues for performing the several operations of his recovery process is illustrated in the accompanying cuts.

Fig. 15 is a sectional detail of a vertical cast iron, steam drum evaporator. This evaporator is particularly adapted to the concentration of the acidified liquor. The acids volatilized during concentration have no material effect on cast iron, but will corrode steel plate. The evaporator consists of a cylindrical cast iron body with an internal steam drum arrangement for supplying the necessary heat for the evaporation. This heating arrangement is a cylindrical cast iron pot having a top cover sheet of rolled copper. Copper tubes pass through the pot and are expanded into the cast iron bottom and top copper sheet, making absolutely tight joints. The difference in expansion between the copper tubes and cast iron is amply provided for by the use of the copper tube sheet and the construction of the iron pot as shown, thus avoiding leaky tubes. Steam is admitted into the drum by a pipe through the top of the evaporator and surrounds the tubes. This pipe is sufficiently large to allow the use of exhaust steam and is fitted with a curved conical dash plate above the drum. The condensation is carried away by suitable piping connecting into the bottom of the drum. The body is connected at the bottom to a salt extractor by a specially designed gate valve. This extractor is also cast iron and is fitted with sight glasses, vacuum gauge, and a salt odor for removing the salt. The bottom of the extractor is provided with a screen of brass wire cloth between perforated iron plates for draining the liquor from the salt. A vacuum break and steam connection are provided in the top. A suitable arrangement of piping connects the bottom of the salt extractor with the top and bottom of the evaporator and provides means for feeding and drawing off the liquor, breaking the vacuum in the machine, etc. The vapor is carried away by piping connecting into a cast iron catchall for retaining any liquor carried over by entrainment. The catchall in turn connects with some suitable apparatus for condensing the vapors and maintaining vacuum in the evaporator.

Fig. 16 is a steam drum evaporator of same principle as the cast iron evaporator. It is built entirely of steel plate and is provided with additional dash plates. Charcoal iron boiler tubes are used so no provision for difference in expansion need be made.

Fig. 17 is a double effect steel plate evaporator having the vapor pipes so arranged as to make the effects reversible.

Fig. 18 is a complete plant for producing crude glycerine, showing the several tanks with the filter press for treating and filtering the liquors, a Koerting exhauster for agitating the liquor, and the evaporator with the salt extractor, condenser and vaccum pump.

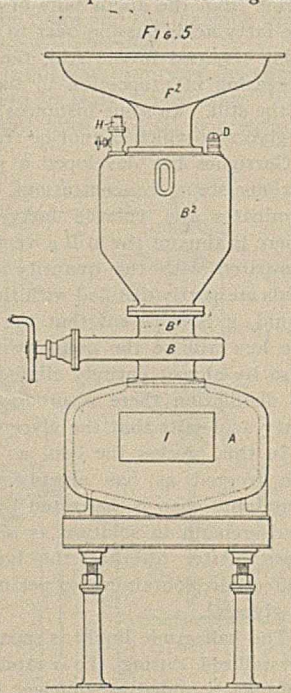


Fig. 14.—Foster's salt pan, 1899.

Fig. 19 shows a complete distilling set arranged to illustrate the principle. The still into which the crude glycerine is fed is heated by means of high pressure steam in the closed coil, the temperature in the still being maintained at above 300° F. A pipe into the bottom of the still connects with a perforated cross through which superheated steam is injected into the liquid. The vapors pass off at the top through a pipe into a catchall for retaining any entrained liquors. The catchall is provided with a steam coil for keeping the vapors hot and preventing condensation at this point. From the catchall the vapors pass to the superheater, surrounding the tubes. A large part of the glycerine is here condensed and passes with the remaining vapors into the pipe leading to the cooler. The cooler is operated with hot water and the temperature of the water regulated by means of the cooling tank so as to condense nearly all the remaining glycerine in the vapors with but a small amount of the steam. The condensed liquor drops down and drains with that from the superheater into the concentrator. The vapors which pass the cooler contain a small amount of glycerine and are all condensed in the surface condenser and collected in the receiver below. A connection is made from

this receiver to a vacuum pump for maintaining vacuum in the entire apparatus. The liquor condensed in the superheater and cooler collects in the concentrator and is finished to gravity by high pressure steam in the closed steam coil, the water vapors driven off passing to the condenser with the vapors from the cooler. The liquor collected in the receiver, called sweetwater, is fed to the evaporator as produced. The evaporator is heated by means of a coil which receives steam from the outlets of the high pressure steam coils in the still and concentrator. The vapor generated in the evaporator being produced under reduced pressure because of the vacuum maintained in the apparatus has a temperature well under 212° F. This vapor passes to the superheater and through the tubes. Here it is superheated by the hot vapors from the still which surround the tubes. The superheated steam then passes to the still and is injected into the liquor through the perforated cross, causing the glycerine to distil.

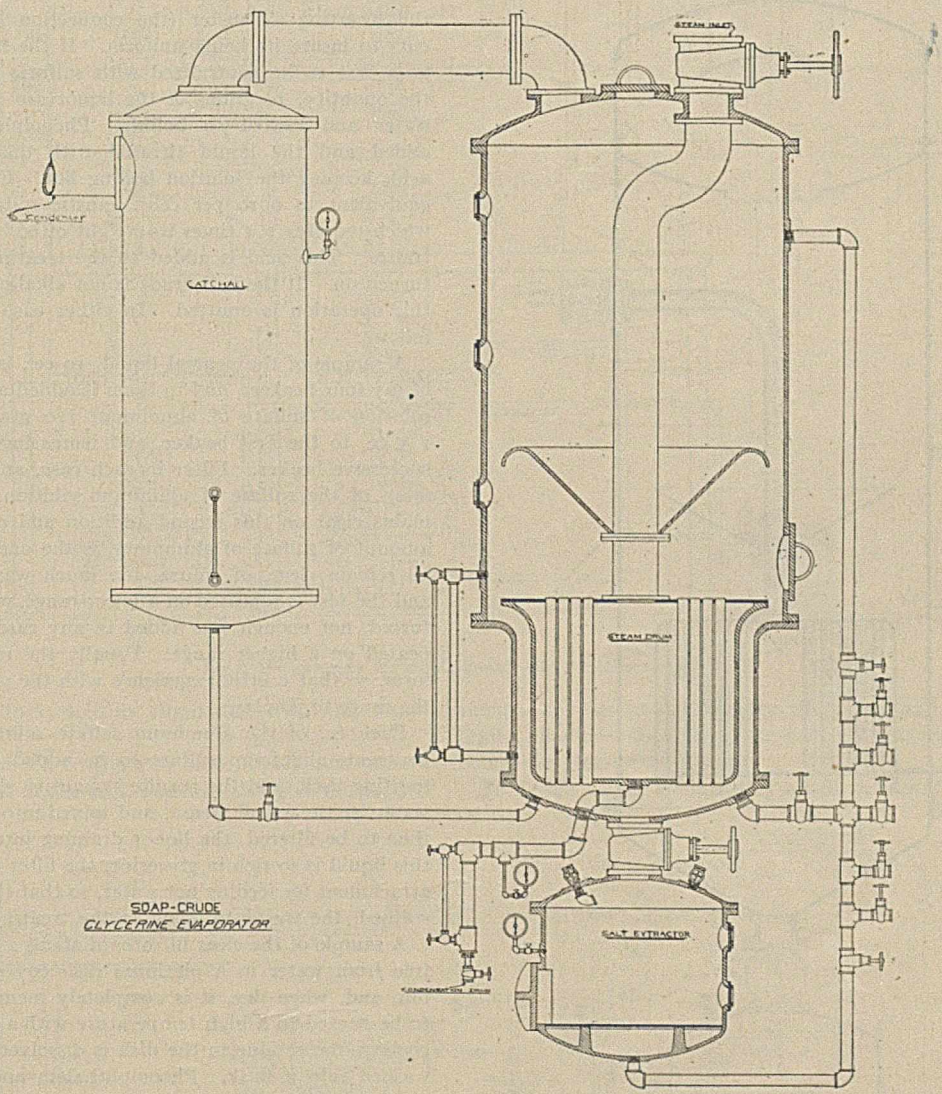


Fig. 15.—Garrigues' cast-iron evaporator.

In describing the complete operation, reference is made to the complete crude plant, Fig. 18, and the still set, Fig. 19. The lye from the soap factory, with which the still residue from a previous run may have been mixed, is placed in the treating tank and treated with sulfuric acid and aluminum sulfate as already described, agitation being produced by means of the Koerting exhauster. The liquor is then passed through the filter press by means of the pump, draining into the feed tank. When the entire charge is filtered the press is steamed out till live steam blows free from all the cocks, the liquor steamed out draining to the treating tank. After steaming, the press is opened and cleaned. The cake should be hard and dry and easily removed by wooden scrapers, leaving the cloths clean.

To start the evaporator the vacuum pump is started and then some water turned on to the condenser. The feed valve is opened and when the pump has raised sufficient vacuum the machine will fill. While the machine is filling the pump will be raising the vacuum and by the time the liquor has reached the proper level, preferably about the top of the tubes, the vacuum will be about 25". The feed valve is closed and steam turned on, letting the liquor come to a boil slowly. The vacuum will fall at first and then recover quickly. Now more injection water will be needed and the full amount is turned on to the condenser. If the evaporator is given all the steam it will take without raising the pressure at the start to more than two pounds, the evaporation will be quite rapid. The feed valve is again opened and so regulated as to maintain a constant level in the machine.

As the evaporation continues, salt will begin to crystallize out and settle down into the salt separator through the gate

valve, which is open from the start. When the separator is filled with salt, as can be seen through the sight glass, the gate valve is closed. The connection from the bottom of the salt separator is then opened and the liquor drawn from the salt into the evaporator. This is accomplished by introducing an atmosphere of steam into the separator at the top, the vacuum then drawing the liquor into the machine by difference of pressure. After the liquor is all drained off the salt the atmosphere

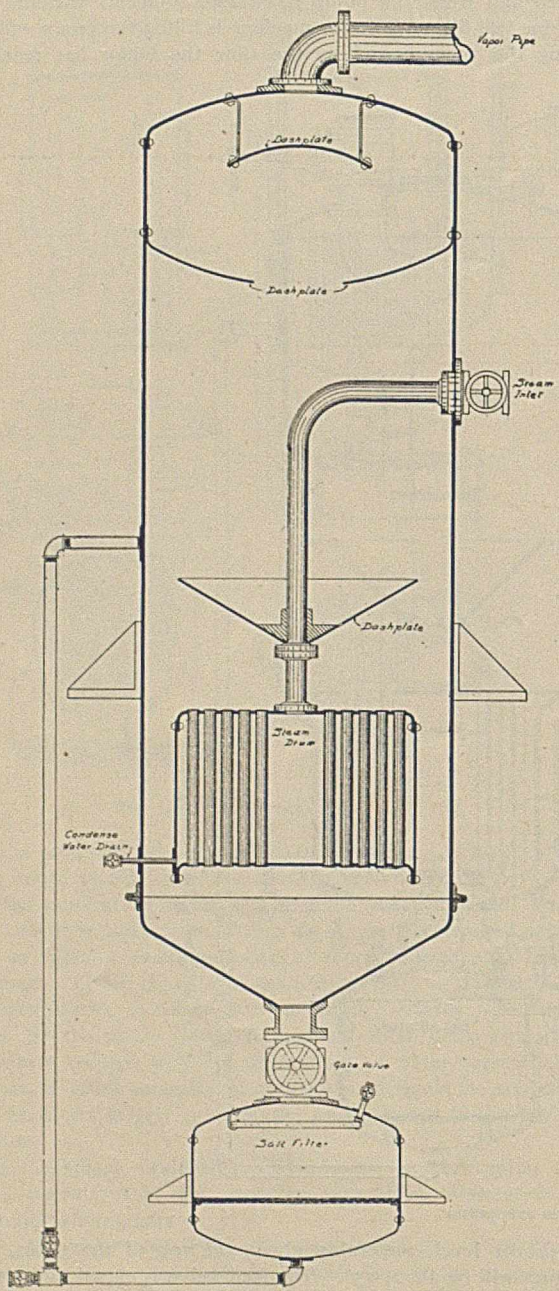


Fig. 16.—Garrigues' steel plate evaporator.

of steam is maintained in the separator for ten or fifteen minutes until the salt is thoroughly washed free of glycerine and dried. The steam is then turned off, the connection to the evaporator closed, and the salt removed through the salt door. The salt should be ready to be returned to the soap factory. Now the separator is closed and the connection to the top of the evaporator opened slowly to exhaust the air from the separator. Then the gate valve is opened slowly and the liquor allowed to run into the separator, the feed valve being opened wide to maintain the level. This operation is repeated as often as the separator fills with salt. When the entire charge is fed to the machine, which will be near the end of the day, it is allowed to boil down to half crude of about 28° to 30° Bé. The evaporation is then stopped by first closing off the steam, then stopping the water to the condenser and shutting down the pump. The liquor is drawn off and pumped to the receiving tank.

When a sufficient amount of half crude has accumulated it is to be treated for eliminating the volatile fatty acids and finished to crude. The half crude is thoroughly agitated by the Koerting exhauster (the connection is not shown in the cut) to insure its being uniform. If the half crude is alkaline it is first to be neutralized with sulfuric acid. To determine the quantity, 10 grams of the liquor are diluted with distilled water and heated to boiling. Phenolphthalein indicator is added and the liquid titrated with quarter-normal sulfuric acid, keeping the solution boiling hot. Each cc. acid used is equivalent to 0.10 per cent. caustic soda in the half crude, which requires 1.4 times its weight of 66° sulfuric acid to neutralize. This acid is added to the treating tank with the air turned on. If the half crude is not alkaline to phenolphthalein this operation is omitted. In either case the procedure is as follows:

A sample of the neutral liquid, 10 cc., is measured into each of, say four beakers, and to them is added a 12 per cent. filtered solution of sulfate of aluminum, 120 grams per liter—about 1.5 cc. to the first beaker, and increasing by 0.5 cc. in each successive beaker. Filter in each case, and to the filtrate add more of the sulfate of aluminum solution. The test which remains clear on this second addition and contains the smallest amount of sulfate of aluminum, is the one to be accepted. If all remain clear, of course, too much was used in each case, and the test is repeated on a lower range, whereas if all becomes turbid, not enough was added in any case, and the test is repeated on a higher range. Usually the results are fairly uniform, so that a little experience with the process will determine the range to employ.

Each cc. of the aluminum sulfate solution used cells for 1 per cent. aluminum sulfate to be added to the liquid in the treating tank, and the required quantity should be dissolved in water by the aid of steam, and mixed into the charge, which is then to be filtered, the liquor draining into the feed tank. As this liquid is so rich in glycerine, the filter press should have an attachment for feeding hot water, so that the press cake may be washed, the washings going to the treating tank.

A sample of the clear filtrate, of about 2 grams, is evaporated free from water in a platinum dish covered with a platinum foil, and, when dry, it is completely incinerated. The dish is to be heated to a high temperature with a good gas flame; after cooling, the residue in the dish is dissolved in warm water and washed into a flask. Phenolphthalein and excess of quarter-normal acid are added. The solution is then boiled for a few minutes and titrated with quarter-normal alkali; making the test exactly as described for the spent lye, and also making the calculation the same way.

For each per cent. alkali, calculated as caustic soda present, add 1 per cent. 66° sulfuric acid, which will produce no separation in the liquid, if the previous treatment with aluminum sulfate was properly done. The liquor is now evaporated to crude glycerine, operating exactly the same as in making half crude except that steam at 15 pounds pressure is used, during which evaporation the soluble acids are expelled with the vapor. There must never be free sulfuric acid present, as this would corrode the evaporator.

All the soluble acid set free is not volatilized. As already

explained, when a certain concentration is reached, the free fatty acids combine with glycerine to form esters, and these are not volatile. In practice about two-thirds of the soluble acid distillate. As the esters are saponified by the alkali to be added to the crude, as soon as boiling in the still begins, it is not sufficient that free alkali is present in the crude, but that

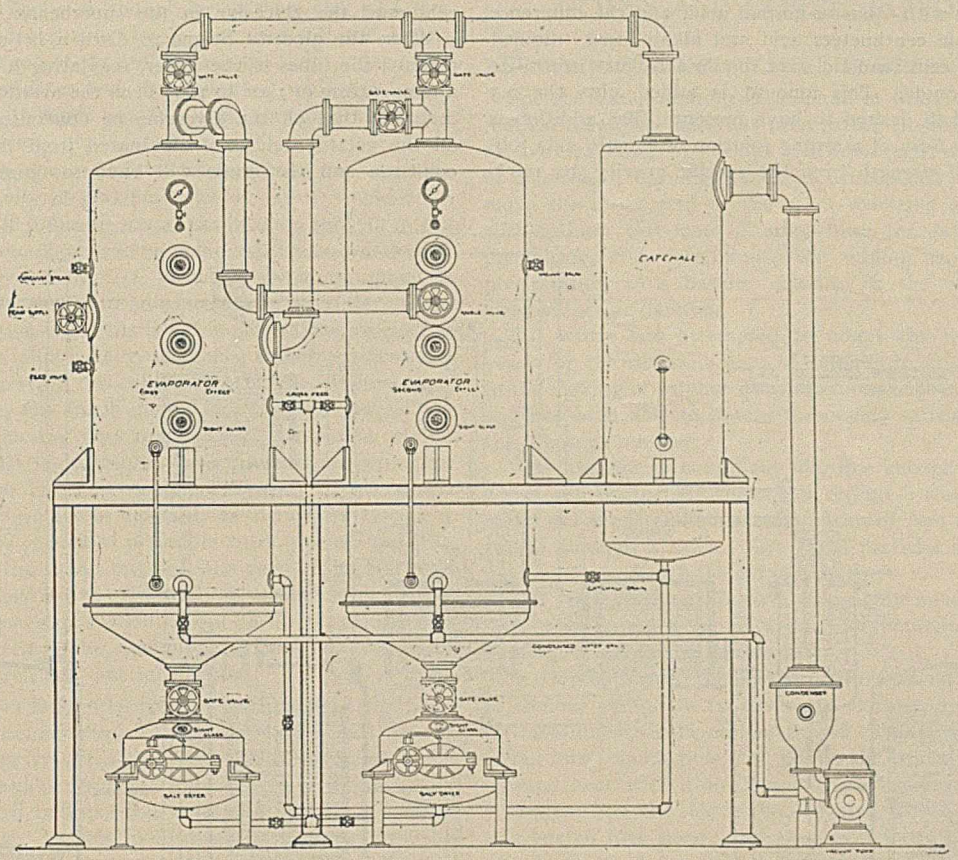


Fig. 17.—Garrigues' reversible double effect evaporator.

liberated by the sulfuric acid is eliminated with the water vapors.

The crude glycerine fed to the still must be alkaline, otherwise it may prime out of the still, and will also give an impure enough be present to saponify the esters and still leave the liquid alkaline—about 0.3 per cent. of this excess alkalinity being the best amount.

To arrive at the quantity of alkali necessary to add to the

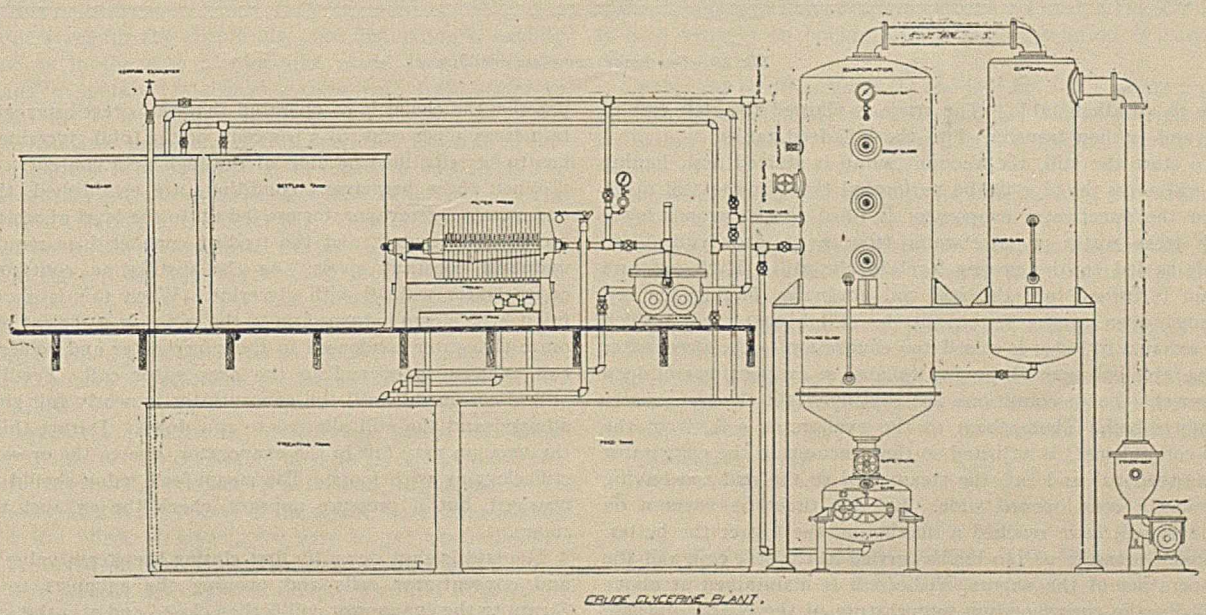


Fig. 18.—Garrigues' complete soap lye, crude glycerine plant.

crude, the esters must be saponified in making the test, which is done by boiling two grams of the crude glycerine, diluted with 100 cc. distilled water, with ten cc. quarter-normal caustic soda, for about fifteen minutes, and then adding phenolphthalein and titrating with quarter-normal acid, and the difference between the cubic centimeters acid and alkali used, divided by 2, is the per cent. caustic soda required to just neutralize the acid in the crude. This amount is added, plus the 0.3 per cent. free alkali desired to have present. The addition is best made in the form of a strong solution of caustic soda, obtaining the alkali strength from the specific gravity, by reference to an alkali table. The crude is allowed to settle free of salt and is then transferred to the still feed tanks.

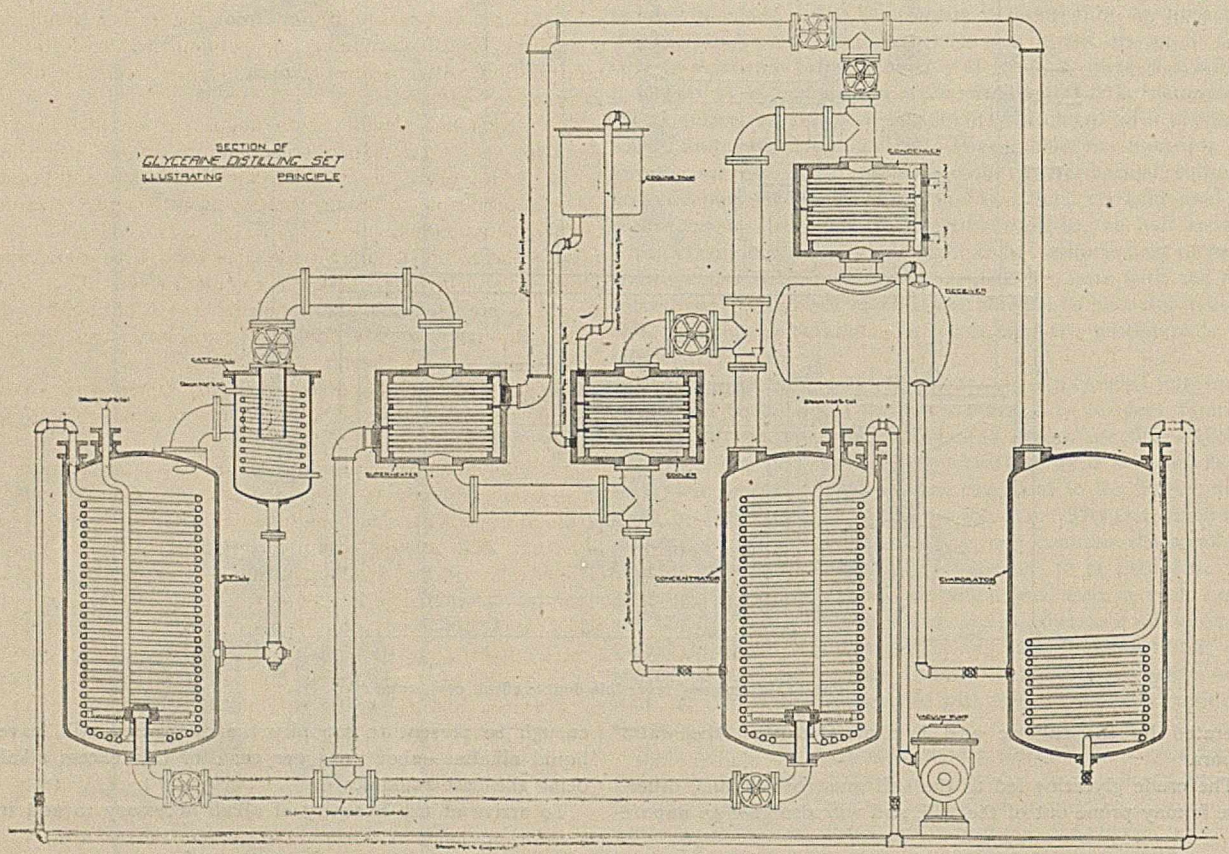


Fig. 19.—Garrigues' complete distilling set.

To start the still, the vacuum pump is started first, having the valve on the pipe to the perforated cross in the still open. Then the sweetwater evaporator is filled to the proper level, with fresh water or sweetwater from a previous run. Also crude is fed to the proper level in the still. High pressure steam is turned into the still coil gradually, having the coil exhaust open to the sewer, till the still becomes hot. Then coil exhaust to sewer is closed and connection to the sweetwater evaporator coil opened, having exhaust of evaporator coil open to sewer. These conditions are continued till the sweetwater begins to boil. Then steam to the evaporator coil (from the still coil exhaust) is adjusted so that vacuum in the evaporator is between 22″ and 24″, the steam feed to the still coil having previously been opened wide. By this time the vacuum on the still will have reached a maximum, the higher the better.

Steam pressure of 140 lbs. is carried in the still coil, and the temperature of the vapors in the still is maintained at above 300° F., the corresponding temperature of the charge likewise being maintained by that part of the coil immersed in it. The hot vapor from the still superheats the vapor from the evaporator so that it is delivered into the still at a temperature of about 300° F. (having received about 160° F. of superheat) and at a vacuum of 22″ to 24″. This abstraction of heat from the vapors condenses the glycerine in the superheater.

When the glycerin beigns to distil a little water is started through the tubes of the cooler, regulating it so as to maintain a temperature of 140° to 160° F. in the overflow pipe. It is not desirable that all the glycerine be condensed here, otherwise all the volatile acids not eliminated from the crude will also condense and the crude will have too high an acidity. In practice the cooler is so operated that the sweetwater will contain from 3 per cent. to 5 per cent. of the total glycerine which has to be redistilled because of the high acid content.

When these permanent conditions are established, the still and sweetwater evaporator are fed up to the level at which they are to be operated, and the feeding continued as required to maintain constant levels. As the distillation continues the concentrator will fill with glycerine. When this is about half full a little steam is turned on to the coil, just sufficient to evaporate the water condensed in the superheater and cooler. The coil exhaust is opened to the evaporator coil. Feeding the still is continued until the concentrator is nearly full and then stopped and the still allowed to run down. During this stage the vacuum may fall in the evaporator, due to the cross in the still clogging with foots. The steam-feed valve should not be changed, but if pressure appears, check the exhaust to save steam.

The still is shut down by first closing the steam valve to still and concentrator coils and opening the exhausts to sewer. Steam to the evaporator coil is then closed and also the valve on the injection pipe to still. The vacuum brake is opened and the

pump stopped. As soon as the vacuum is broken, the still drain should be opened and the residue allowed to drain into the foots tank, in which there should always be a few inches of liquid, and this should be mixed with the foots to keep them from hardening. The still should be washed out with hot sweetwater. The hot sweetwater is first pumped into a perforated pipe in the top of the still having the drain valve open. The drain is closed later and the still filled with sweetwater which is boiled with open steam. This operation to be repeated till still is clean.

If chemically pure glycerine is to be made, the first distillate should have a gravity of about 29° Bé. at 60° F. When the still is shut down, if sufficient steam has been on the coil in the concentrator, the distillate will be sufficiently heavy and need not be concentrated more. If, however, dynamite grade is to be made, the distillate is to be concentrated to gravity while the still is being washed. This is accomplished by closing the valve on the vapor pipe next to the cooler before breaking the vacuum, thus separating the concentrator and condenser from the rest of the set, the small connections from the vapor line below the cooler having also been closed. Operation of the pump and condenser is continued, having full steam turned on to the concentrator coil and the exhaust open to the sewer. When the desired gravity is reached, as shown by testing a sample removed by means of a sample tube (not shown), the steam is shut off, the pump stopped, the vacuum broken, and the distillate pumped to the dynamite bleaching tank. Here it is mixed with beaching carbon (about $^1/_4$ to $^1/_2$ pound per 1000 pounds glycerine—the amount depending on the color desired), then filtered and put into drums.

Crudes made from fermented lyes or lyes from fats that have not been washed before going to the soap kettle will always contain more or less trimethylene glycol. The gravity of chemically pure trimethylene glycol is only 1.05 and if present in sufficient quantity it is impossible to obtain gravity in making dynamite glycerine. In this case steam is injected into the concentrator the same as into the still and the glycol distilled off.

In making chemically pure glycerine, the first distillate is bleached with carbon the same as in the case of dynamite grade and redistilled. If the same still is to be used for the second distillation, it is necessary to remove all trace of the foots in washing the still. The best practice is to have a second still for this redistillation.

The operation for the chemically pure distillation is exactly the same as in the case of dynamite grade except that the sweetwater evaporator is always started with fresh water to avoid the odor of sweetwater from the crude. Not so much steam is required, however, in this operation and the sweetwater evaporator is operated so as to maintain vacuum in the evaporator from one to two inches less than at the pump. The slower the distillation is, the purer will be the distillate. Steam is turned on to the concentrator coil so that the distillate at the end of the run will have a gravity of about 1.253, at which it will contain at least 95 per cent. absolute glycerol. This distillate is pumped to the bleaching tank and mixed with bleaching carbon by means of air. About five pounds of carbon per 1,000 lbs. of glycerine are added. It is then filtered and drummed.

Here again the presence of trimethylene glycol will cause trouble. While not objectionable in pure glycerine on account of gravity, it gives the product an acrid taste, which cannot be gotten rid of, as it is a property of the glycol. When redistilling to avoid bad effect of glycol, the first 10 per cent. distilled should be taken off and kept separate. In this manner any butyric acid present is also gotten rid of. The first 10 per cent. can be mixed with the crude and again be distilled, but unless dynamite grade is produced and some glycol gotten rid of that way, the first 10 per cent. of the second distillation would eventually become chemically pure glycol.

NOTES AND CORRESPONDENCE.

DETERMINATION OF SULPHUR IN BRASS AND BRONZE.

For the determination of sulphur in brass and bronze, the method heretofore used has been rather circuitous by oxidizing the borings, filings or sawings with aqua regia, or with a solution of chlorine or bromine, repeated evaporation with HCl to remove the nitric acid or the other oxidizing agents, digesting with sodium carbonate filtering from the rather voluminous precipitate, and determining the sulphur in the filtrate by precipitation with barium chloride in the ordinary manner after proper acidulation.

The writer has attempted to adapt the method used for years for the determination of sulphur in organic compounds to the making of sulphur determinations in brasses and bronzes, and has been able to obtain thoroughly satisfactory results in the following manner.

With the aid of a mill-cut file, fine enough to make filings which will easily pass through a 100-mesh sieve, filings of the metal are prepared (file across machined face of test bar) and passed through a sieve. Any small particles of iron from the file are removed with the aid of a magnet.

One gram of these filings is thoroughly mixed with 6 grams of a powder consisting of 2 parts of potassium chlorate and one part of sodium carbonate.

In a wrought iron crucible there is first placed a small quantity of sodium carbonate to cover the bottom, then the mixture of the filings with the carbonate and chlorate is carefully transferred into this crucible, and finally the whole mixture is again covered over with a small quantity of sodium carbonate and chlorate. The crucible is then covered with a porcelain cover, and heated first slowly and then to a fairly high temperature over a Bunsen flame until the whole mass is thoroughly melted.

The fusion after cooling is digested with hot water. The salts which contain all the sulphur as sulphate, are filtered from the oxide residue, the filtrate is acidulated with hydrochloric acid and boiled to remove all carbonic acid. The solution is then neutralized with ammonia and made slightly acid by carefully adding hydrochloric acid until an acid reaction appears, and then 2 or 3 drops in excess are added. The solution is then brought to boiling, and a boiling solution of barium chloride is added.

Letting the solution stand for one-half hour in a warm place, but not boiling it further, all the sulphur will be precipitated as barium sulphate, which can then be readily filtered and washed.

The weight of the barium sulphate times 0.13734 is equivalent to the weight of sulphur in the sample.

Using an iron crucible does not appreciably increase the figures obtained, as the sulphur taken up from the iron amounts, at the outside, to $^1/_{100}$ to $^2/_{100}$ of 1 per cent.

If great accuracy, however, is required, a silver crucible can be used, or a nickel crucible.

It is self understood of course, that all the reagents must be tested for a possible presence of sulphur before they are used in this method.

GUSTAV THURNAUER.

LABORATORY OF THE
AURORA METAL CO.,
AURORA, ILL.

THE WATER OF THE COLUMBIA AND WILLAMETTE RIVERS.

In the course of some soil investigations which are being carried out at this Station we have had occasion to collect

for analysis monthly samples throughout the year from the Columbia and Willamette rivers. As the composition of these waters has not been recorded so far as known by us, the following analyses made by Mr. B. Pilkington of this department may be of interest.

The Willamette sample was collected at Corvallis July 18, 1909; the Columbia water was taken August 6, 1909, at Mayger, Oregon, a point about fifty miles above the river's mouth. The Willamette at the time of sampling stood 1.7 feet, and the Columbia 9.1 feet above low water.

	Columbia.		Willamette.	
	Parts per million.	Per cent. of total solids.	Parts per million.	Per cent. of total solids.
CO_3	16.4	31.66	1.1	3.08
SO_4	5.5	10.62	4.7	13.13
Cl	5.5	10.62	4.4	12.29
PO_4	0.08	0.15	0.08	0.22
Ca	8.7	16.80	3.8	10.61
Mg	2.5	4.83	1.0	2.79
Na	4.0	7.72	4.9	13.69
K	4.1	7.91	2.8	7.82
NH_4	0.42	0.81	0.52	1.45
SiO_2	2.4	4.63	12.1	33.80
Al_2O_3 Fe_2O_3	2.2	4.25	0.4	1.12
Total	51.8	100.00	35.8	100.00

The Columbia water is seen to be relatively rich in carbonate of lime obtained no doubt from its upper course where lime formations are found. The soil of the Willamette Valley, on the other hand, contains only traces of carbonates, which is reflected in the low content of carbonates in the Willamette water. The tributaries of the Willamette are generally high in silica. The ammonium in the samples was calculated from the value for total nitrogen.

C. E. BRADLEY.

AGRICULTURAL EXPERIMENT STATION,
CORVALLIS, OREGON.

BOOK REVIEWS AND NOTICES.

Reports of the Chemical Laboratory of the American Medical Association. Vol. 1. From its establishment to Jan. 1, 1909. Vol. 2, Jan. to Dec. 1909.

Reprint of the Reports of the Council on Pharmacy and Chemistry of the American Medical Association with the comments that appeared in THE JOURNAL during 1905–8, Vol. 1, and 1909, Vol. 2. Published by THE AMERICAN MEDICAL ASSOCIATION.

In no other country are there more drugs and medicines consumed per capita than this. Also nowhere else has the sale of patent medicines and proprietaries assumed such tremendous proportions, resulting largely from the extravagant claims. In order to protect the public as well as the medical practitioner from this avalanche of medicines, the American Medical Association appointed in 1906 a committee known as the Council of Medicine and Pharmacy, aided by its chemical laboratory of which Prof. Puckner is the director. The duty of this committee is to examine all remedies applying for recognition before the medical profession, rejecting such as make fraudulent claims as to origin, unwarranted or misleading therapeutic claims, secrecy as to composition, or objectionable advertising, etc.

The Reports of the Chemical Laboratory, serve to give in concise form, the various methods employed in the analysis of the preparations submitted. These afford much valuable information to the general analyst not obtainable elsewhere. The Reports of the Council represent the results of the scientific investigations including all clinical and pharmacologic data as well as comments. Among these, the reports on Medicinal Foods, Diastase Ferments, Formaldehyd Derivatives (Vol. I), Isopral and Bromural, show an immense amount of painstaking labor on the part of the chemist and pharmacologist. In this connection attention is called to the "New and Non-Official Remedies," a volume of 256 p. which gives descriptions and tests of all remedies recognized up to June 1, '10.

To give the reader an insight into the kind and variety of work accomplished, a few instances may be cited. An example of a misleading label is "Tyree's Antiseptic Powder" which states it to contain, borax, alum, phenol, glycerol, thymol, eucalyptol, gaultheria and mentha (?), was found to consist essentially of zinc sulfate and boric acid with traces of phenol. Thialion a "sodio-trilithic anhydrosulphate" of formula $3Li_2O.NaO.SO_3.7HO$ was found to consist of a mixture of sodium sulphate and citrate with small quantity of lithium citrate. The need of an invasion into the field of galenicals, is illustrated by the results of an examination of unofficial non-alcoholic fluid extracts of Hydrastis (Golden Seal). Preparations of this drug are extensively used, and the selling price varies between $1.25 and $4.50 per pound, although all are claimed to be of same strength. Assays demonstrated the yield to be between 0.58 and 1.79 grams of hydrastin per 100 cc., while the Pharmacopoeia standard demands 2 grams alkaloid per 100 cc. Worth careful study are the methods recommended for assay of Phenol, Hexamethylene Tetramine, Castor Oil in Powder form, Croton in Castor Oil, Mercury and Iodin in Mayer's Reagent, Pepsin and Bismuth Preparations, etc. (Lab. Reports).

We note the melting point of urotropin is given at 194.200°. On page 35, Vol. 2, Laboratory Reports, we note that the presence of bismuth sulphid is based on the conclusion that hydrogen sulphid is given off upon the addition of hydrochloric acid to a mixture containing bismuth sulphonate, zinc oxid, etc., the operator not having noted the presence of ultramarine blue added as color corrigent. Under Medicinal Foods (Peptonoids, Predigested Beefs, Panopeptone, etc.), none are approved that contain less nutritive value than milk, and at least 1/4 of the value shall reside in the nitrogenous matter. Such legitimate pharmaceuticals as Taka-Diastase, Maltzyme, Holadin, etc., come in for their share of criticism in that grossly exaggerated claims are made, further that "to be of value, statements regarding the digestive power of diastase should be based on standard and uniform methods of testing." The Council has adopted methods of its own against the vigorous protests of some of our largest manufacturers in this line. In adopting standard methods, it would be no more than just and reasonable, that manufacturers who have devoted their entire time to the study of such products be consulted and their methods given a fair trial. It is through such coöperation and study, that a uniformity of methods is secured in conjunction with the good will of firms whose integrity and experience is beyond question.

We must realize that errors of judgment and experiment are possible under all conditions, and where a policy of "control" is to be exercised by a body of analysts and clinicians, the greatest care should be exercised in formulating standards. Analysts may differ and clinicians usually differ, since therapeutics is not as yet an exact science. The judgment of those whose field lies within a special line should never be ignored.

Nothing is gained by a "hammer and tongs" policy (perhaps necessary in patent medicine line), when applied towards legitimate manufacturers, they are amenable to reason, but once antagonized, their united opposition may sometime overthrow all the good that has been and will be accomplished by the Council.

V. COBLENTZ.

Fungus Diseases of Plants. By BENJAMIN MINGE DUGGAR. Cloth. 8vo. XII + 508 pp. Ill. Boston, Ginn & Co. 1909.

This book is based principally upon the investigations of the

past thirty years on the fungus diseases of plants and it is the only work of American origin available to the student on the subject. In plan and execution the work is excellent. The contribution of chemists to the subject lies principally in the methods of disease control by the use of fungicides. It would appear that there is an immense field here for the investigator. At present the use of fungicides is based entirely upon empirical knowledge, and it is probably true that it is based largely upon information accidently acquired. Systematic investigation on the many possible fungicides is but beginning. It goes without saying that the work will be found of value to mycologists and it would also prove of value to the chemist working in this field. The book is well bound, printed and illustrated and typographical errors are few.

The University, of Illinois, Engineering Experiment Station, has just issued three bulletins of great interest to students and users of fuel. *Bull.* 37, Unit Coal and the Composition of Coal Ash, by S. W. Parr and W. F. Wheeler; *Bull.* 38, The Weathering of Coal (series of 1909) S. W. Parr and W. F. Wheeler; *Bull.* 39, Tests of Washed Grades of Illinois Coal, by C. S. McGovney. The titles of these bulletins indicate the ground covered and the reputations of the authors will speak for the quality of the contents.

From the University of Wisconsin comes *Bull.* 346, on the subject of Alloys of Nickel and Copper with Electrolytic Iron, by Chas. F. Burgess and Jas. Ashton. This is a valuable contribution to the literature on binary alloys of iron with the common metals—a fruitful field for the student, which has not received as much attention as it deserves.

Dust Preventives and Road Binders. By Prevost Hubbard, New York, Wiley & Sons, Octavo vi + 416 pps. illustr. $3.00 net.

Although at first thought it would seem to one who has been connected with the construction of highways for many years that the present is hardly the time to write a book on the subject which Mr. Hubbard has selected, in view of the fact that it is still in a highly experimental and transitional state, the author has assembled in a very satisfactory way many data, some original with him and more taken from the publications of others, in regard to various materials employed at the present time as dust preventives and road binders and as to their preparation and use, all of which will prove of great value for reference to many engineers and public officials who are constructing and endeavoring to improve the character of our highways. He has also presented some of the conclusions bearing on the application of these materials, which have been arrived at in the Office of Public Roads of the United States Department of Agriculture during recent years which, although many of them available in the bulletins of that office, are justifiably republished for general use. Mr. Hubbard's chapter on "The Examination of Bituminous Road Materials and Interpretation of Results" will be acceptable to the numerous chemists who are taking up such work for the first time, as is now frequently the case, and will prove of interest to the more expert operators.

Where the author advances opinions as to the merits of various materials, he hardly seems justified in all his statements in view of the fact that service tests, from which the only satisfactory conclusions can be drawn, have not extended over a sufficiently long period to lead to anything definite. Undoubtedly many of the statements involving mere opinion, which the book contains, will necessarily require modification in the future, but as a whole the book has a present usefulness which commends it.

Mr. Hubbard has wisely avoided the use of trade names and in most respects, has handled his subject impartially and with a scientific spirit. The style in which the book is written is excellent and it will undoubtedly have the large circulation which it deserves. Clifford Richardson.

RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building 908 G St., N. W., Washington, D. C.

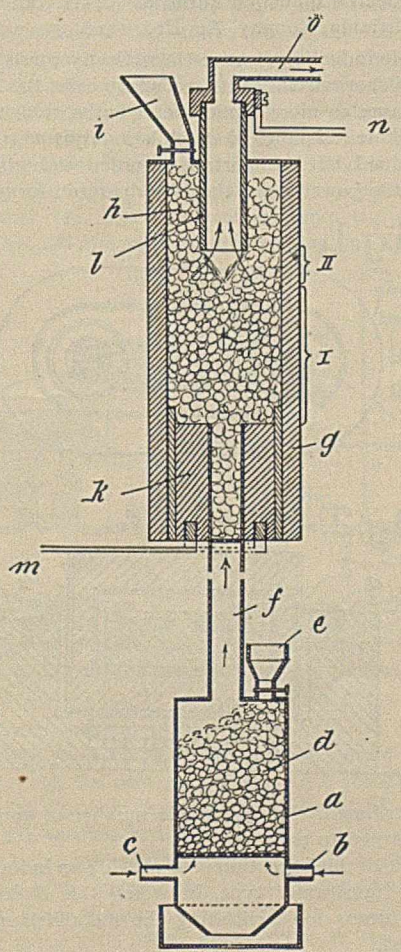
Only a few patents which are deemed of greatest importance are abstracted in this department.

Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

954,080. Process of Producing Hydrocyanic Acid. O. Diefenbach and W. Moldenhauer, Darmstadt, Germany, April 5, 1910.

It is well known that hydrocyanic acid can be produced by passing a mixture of nitrogen and hydrogen over highly heated carbon, and recent experiments have, moreover, demonstrated that a proportional yield as high as 35 per cent. can be obtained at temperatures of about 35000° C.

For the industrial application of this process a cheap and simple method of producing the necessary nitrogen-hydrogen mixture is of importance. Since the production of pure nitrogen and hydrogen, by whatever method attained, involves considerable expense, the question arises whether the mixtures of the same with carbon monoxide or carbon dioxide, which can be cheaply and easily produced commercially, are suitable for the purpose in view. From the theoretical standpoint, it would appear that the possibility of so applying these mixtures



is very small, for since hydrocyanic acid at high temperatures is capable of reacting with carbon monoxide, according to the equation:

$$2HCN + CO = H_2O + N_2 + 3C,$$

it might certainly be expected that it would not be formed at all in the presence of carbon monoxide or that it would be destroyed by the latter immediately upon its formation. When it is found that this view is contradicted by experiment, the only explanation possible is that the rapidity of the above reaction is not sufficiently great when, under suitable experimental conditions, the gas-mixture is subjected to rapid cooling, as to permit of the decomposition of large quantities of the hydrocyanic acid newly produced. If, for instance, the mixture known as Dowson gas, which consists chiefly of hydrogen, carbon monoxide, nitrogen and a little carbon dioxide, is led over carbon which—by any suitable means—is maintained at a very high temperature, more or less considerable quantities of hydrocyanic acid can be detected in the gases rapidly aspirated from the furnace, according to the degree of temperature at which the process is conducted.

The hydrocyanic acid thus produced can be employed for the production of other cyanogen compounds, or may be transformed into ammonium sulphate by passing it through concentrated sulphuric acid. The hydrogen and nitrogen which have not undergone transformation into hydrocyanic acid together with the carbon monoxide mixed therewith may, after the removal of the acid, be again passed over incandescent carbon for the purpose of obtaining a further yield of hydrocyanic acid, or they may be applied to heating purposes.

The accompanying illustration shows an apparatus used by the patentees in practicing their process.

954,827. Electric Induction Furnace. C. W. Soderberg, Ski, near Christiania, Norway, April 12, 1910.

An electric induction furnace theoretically consists of a transformer with short circuit in its secondary coils, the latter mostly consists of one or more liquid metal baths, which replace the coils, the ohmic resistance of which is so adjusted, that a middle load is obtained. It is important, in order to obtain a minimum leakage of the power lines, that the disc transformers have the

Fig.1.

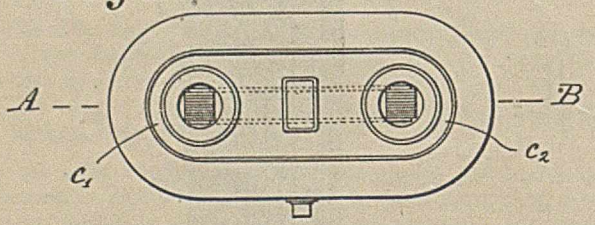
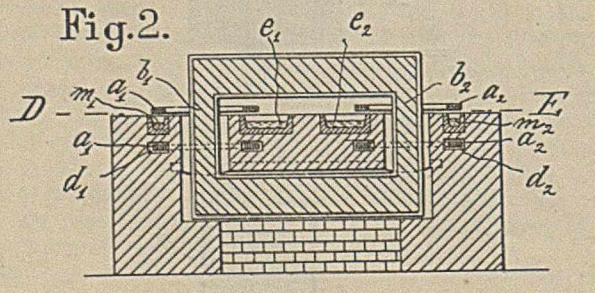


Fig.2.



coils so distributed, that the whole number of ampere-turns is not concentrated to one coil.

The object of this invention is to provide an induction furnace of the disc-transformer type, in which this electrical feature as well as means for facilitating the metallurgical operations are embodied.

In this furnace the primary windings are distributed on four coils as a^1, a^2 enclosing both of the vertical parts b^1, b^2 of the iron core. The secondary armature consists of a metal bath, m^1, m^2 contained in a hearth m arranged between the primary coils and formed with an intermediate portion, and two semi-annular channels e^1, e^2, which together with the intermediate portion enclose both of the vertical pieces of the iron core. By arrangement of four coils the leakage of the power lines is cut down to about one-fourth of what it would otherwise have been under similar circumstances.

The lower primary coils are cooled by currents of air which pass through channels d^1, d^2 in the foundation of the furnace which may be of masonry or any suitable material as the effect of the intensity of the current is proportional to its square; the above-mentioned cooling diminishes the resistance and the intensity of current is increased. The efficiency of the furnace per unit of time thus increases, an advantage which is the more important in this construction, because the coils enclose both of the vertical legs of the transformers.

In order to facilitate the metallurgical operations, which are rendered difficult on account of the primary coil covering part of the metal bath, the extended parts of the baths are situated outside of the current carrying parts of the bath and not covered by primary coils. Such channels have been used in some prior constructions, but never in furnaces of the disc-transformer type for the above-mentioned purposes of providing working space, the metallurgical operations, the feed, and the treatment of the slag are facilitated and repairs may be easily made without removing any part of the primary coils of the furnace.

956,381. Process for Treating Ores. A. A. Lockwood and M. R. A. Samuel, London, England, April 26, 1910.

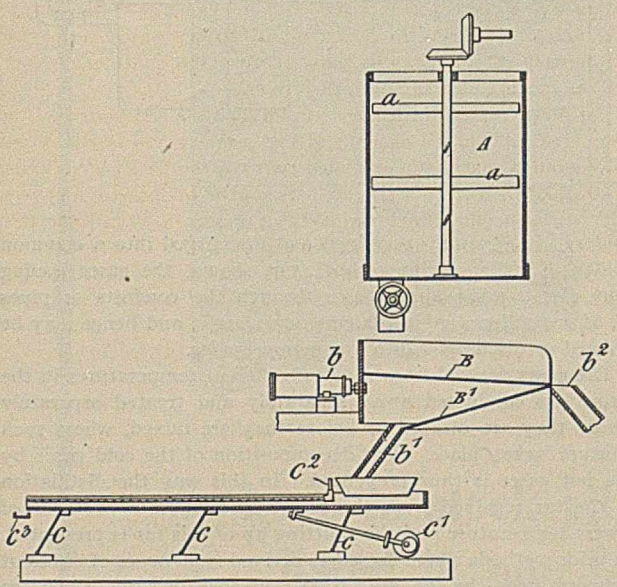
This invention relates to the treatment of such sulphide ores, tailings, middlings, or concentrates, as are difficult to separate into their constituents owing to their physical formation. This difficulty is usually caused by the pseudomorph formation of the ore; this is the case for example in complex lead and zinc ores such as Broken Hill ores.

According to this invention crushed ores, under which term it is intended to include tailings, middlings or concentrates, are subjected to a preliminary treatment of agitation with a reagent or reagents in such a manner that the incrustations are sufficiently attacked to free the metallic particles so that they can be classified by any known means. In some cases improved results may be obtained by first heating the ore or the like to a temperature preferably just below that of desulphurization. As reagents there are employed solutions of substances such as caustic alkali or sodium or potassium silicate which may be used either separately or in succession or in combination according to the ore to be treated. The quantity of the reagent and water necessary and the length of time required for the treatment will differ more or less according to the ore to be treated, it should be such that the incrustations are loosened while the metals remain undissolved.

As a comparative example of the treatment, a parcel of two tons of Broken Hill proprietary ore of a very complex formation was taken and crushed to about 40 mesh to the linear inch. 2,240 lbs. of this was treated with a solution containing about 5 per cent. of caustic soda and 1 per cent. of silicate of soda in the proportion of 25 lbs. of the solution to each 100 lbs. of ore. After agitating for about 30 minutes the pulp was fed onto sizing screens and thence passed to a vanning table. The result of this treatment was as follows, the scale of the mesh to the linear inch being 60 and 80—103¼ lbs. of coarse (plus 60) galena (dried), 172 lbs. of fine (plus 80 and minus 80) galena and 43¼ lbs. of zinc lead middlings from the coarse and 36½ lbs. middlings from fine. The assay value of the galena was 76.8 per cent. lead with 3.9 per cent. zinc and the middlings

contained free galena and free blende. The remaining 2240 lbs. of the ore was treated in the same manner including the agitation for 30 minutes with water but without the addition of caustic or silicate. The result was 88 lbs. of coarse (plus 60) galena, 134 lbs. of fine (plus 80 and minus 80) galena and 130 lbs. of zinc lead middlings from the coarse and 68 lbs. middling from the fine. The assay value of the galena was 72 per cent. lead with 6.5 per cent. zinc, while the middlings appeared to be quite inseparable and further crushing would have been required to free the metallic particles from one another.

It is quite obvious that the treatment may be applied as in the example to the ore in bulk or the metallic particles may be concentrated by an oil or similar selective process and then treated and classified or of course the crushed ore may be taken and passed over the table before treatment getting as much



free galena as possible, then taking off the table for treatment a large line of middlings containing the incrusted particles. The middlings are then treated as before described and passed over a table or otherwise classified. The particular method of treatment to be adopted will easily be found by the aid of a few experiments, which will show whether it is more profitable to treat the whole first, or to treat the middlings or the concentrates or tailings, together or separately.

In dealing with ores for treatment, a few tests will be necessary to ascertain the degree of fineness to which they should be crushed before treatment and this will vary with the formation of the ore and may also be varied to suit the particular method of concentration to be employed, but speaking generally the ore should be left as coarsely crushed as possible and this for two reasons, *viz.*: in order to reduce the amount of slimes formed and because of the decreasing advantage of such a treatment, for it will be obvious that with a pulverized ore the incrustations will no longer be present and the more finely the ore is crushed the more the incrustations will be broken down and the less need there will be for the treatment except when overcoming or preventing the acquired tendency of particles to adhere together when the ore is treated with oils or the like.

The accompanying illustration shows the apparatus employed in practicing the process in this illustration.

In the drawing A is a vessel provided with an agitator *a*.

B is a sizing screen, B′ a second and finer screen inclined in opposite direction to the first. The combined screens are directly connected to the piston of a reciprocating engine *b*.

b′, *b*² are delivery spouts.

The coarse and the finer ore is treated on a vanning table at different times. As shown the finer ore is delivered onto a vanning table.

C is a vanning table supported on springs *c* and reciprocated by means of an eccentric *c*′.

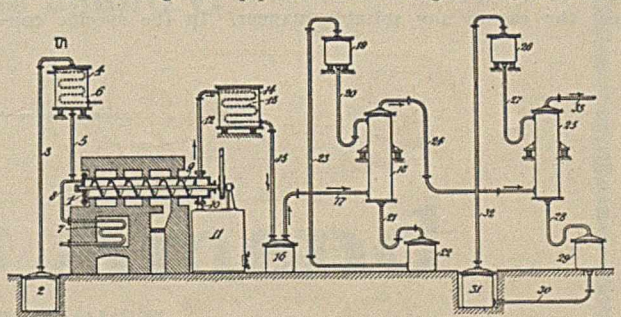
*c*² indicates means for supplying water to the table and *c*³ indicates a chute into which the heavier parts fall.

956,184. Process for Obtaining Sulfrous Acid from Acid Sludge. G. SCHILDHAUS AND CONDREA, Capina, Roumania, April 26, 1910.

It has now been found that acid tar may be distilled with good results by introducing heated air into the retort during distillation and thereby oxidizing the sulphur and its compounds. In this manner three products are obtained from the tar: (1) A mixture of gases mainly consisting of sulphurous acid, nitrogen and air and containing small quantities of carbonic acid and gaseous hydrocarbons. (2) Liquid hydrocarbons. (3) Coke. The tar is preferably vaporized at a comparatively low temperature of between 250 and 350° C. and the air introduced into the retort is preferably heated to the same temperature. The acid tar is run into the retort in a thin stream. The coke remaining in the retort is porous and brittle and is continuously evacuated by a mechanical device and transported to a closed chamber. The gases that issue from the retort are conducted through a cooler to condense the liquid hydrocarbons, and are then washed first by means of heavy hydrocarbon oil and finally by means of concentrated sulfric acid to remove the gaseous hydrocarbons and the last traces of the vapors of liquid hydrocarbons.

The illustration shows a diagrammatic side-view of the apparatus for carrying out the process.

The process is as follows: The tar is introduced in a thin stream into the retort 1 from the montejus 2 through the pipe 3, vessel 4 by means of the heating coil 6. In the retort 1 the tar is vaporized, preferably at a comparatively low temperature of between 250 and 350° C. The air is preferably heated to the same temperature by means of the heating coil 7 and is introduced into the retort 1 through pipe 8. The coke remaining in the retort is porous and brittle, and is continuously evacuated by the feeding screw 9 through the pipe 10 into the closed chamber 11. The gases issuing from the retort 1 are conducted through the pipe 12 and cooling coil 13 which lies



within the condenser 14. The larger part of the liquid hydrocarbons is condensed in the cooler and fed through pipe 15 into the vessel 16. The gases escaping from the vessel 16 are fed through pipe 17 into the scrubber 18 in which they are washed by means of heavy hydrocarbon oil which is run continuously from the vessel 19, through the pipe 20, through the scrubber 18 and the pipe 21 into the vessel 22 and back to the vessel 19, through the pipe 23. The washed gases escape from the scrubber 18 through the pipe 24 and enter the scrubber 25, where they are washed with sulphuric acid which is contained in the vessel 26 and flows through the pipe 27 into the scrubber 25, pipe 28 to vessel 29 and pipe 30 to the montejus 31 wherefrom it is fed back through the pipe 32 into the vessel 26. By washing the gases with heavy hydrocarbon in the scrubber 18

and afterward with sulphuric acid in the scrubber 25 they are freed from the last traces of the gaseous hydrocarbons. The purified gases consist in their essential part of sulphurous acid which escapes through the pipe 33, and they are then collected and may be utilized for known purposes, particularly for the production of sulphuric acid.

956,019. Process of Manufacturing Gas. ADOLPH ZINDLER, New York, N. Y., April 26, 1910.

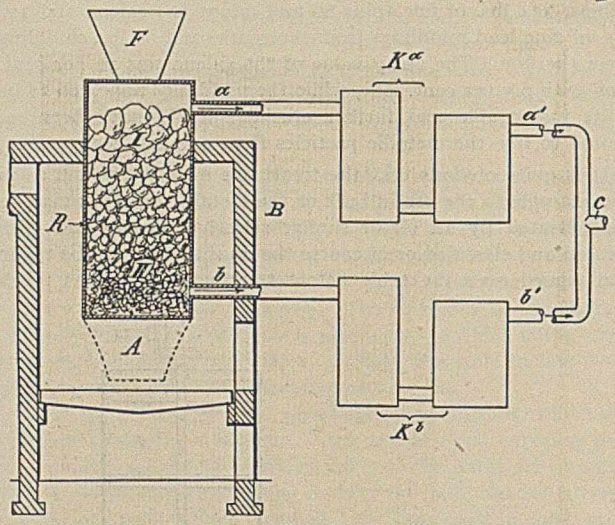
In the dry distillation of shales, peat, wood and all bituminous matter by the continuous process, it is usual to take the gases, by suction, from the different parts of the furnaces or retorts, but to conduct them collectively through one main to the cooling and purifying apparatus. In the gas-main the hot gases are mixed with comparatively cold gases, and it is well known that the latter are decomposed and deteriorated by the former.

It is the object of this invention to prevent this deterioration.

The invention will be described in connection with the accompanying drawings.

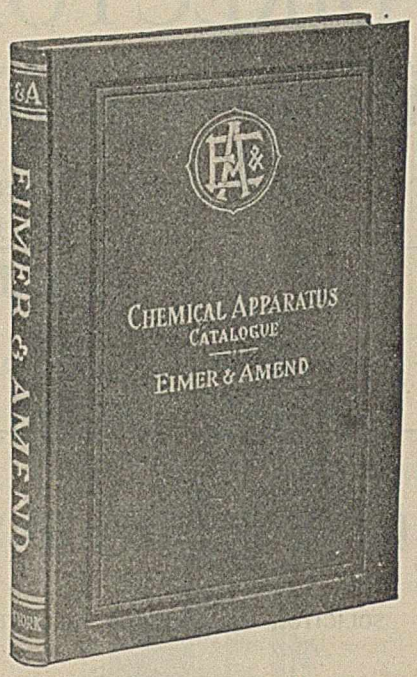
The apparatus consists of a retort R provided with a filling hopper F and a discharge chute A. The retort R may be of any suitable construction, and may be a device of any suitable type other than that shown. This retort is heated externally by means of a furnace B. The fuel placed in the retort will as the gas is distilled pass downwardly and through the discharge chute A. This discharge chute is shown in dotted lines and may extend laterally and downwardly outside of the furnace so that the distilled fuel may be raked out. The gas as generated is drawn from the retort by means of a plurality of conduits or pipes *a*, *b*. These conduits connect with the retort at the upper and lower zones of different temperatures, that is, the lower zone is at a higher temperature than the upper zone. In the specific embodiment shown these zones of different temperatures are shown as upper and lower zones respectively. It is to be understood, however, that this invention is not limited to this specific embodiment, since any construction in which conduits connect with zones of different temperatures comes within the scope of this invention.

The gases derived from the different zones are independently passed through apparatuses K^a K^b, which separately treat the gases. These apparatuses may be of any suitable form and may treat the gas in any suitable manner. In the specific construction shown these apparatuses are each composed of coolers and scrubbers. The gases as they issue from these treating apparatuses may be utilized in any suitable manner. They may be kept apart and discharged into separate reservoirs or



holders, or they may be mixed and discharged into a common holder. In the specific embodiment shown, the gases issuing from the treating apparatuses through the conduits or pipes *a'*, *b'*, may discharge into a common main *c*, and hence may be utilized or discharged into a common holder.

The gases derived from zones of different temperatures in the retort are conducted away separately and treated separately before they are utilized or before they are mixed, where such mixture takes place. The decomposition of the cold gases by the hot gases is thus prevented. In this way the distillation of the tar regained from the colder derived from the zone of lowest temperature and the splitting up of this tar is prevented. In prior methods where the gases derived from zones of different temperatures—the tar, etc., from the separate gases which are of different qualities are mixed, thus necessitating fractional distillation to separate these different qualities. By separately treating the gases derived from the different zones, it is possible to obtain tar, etc., of different qualities, and therefore special and fractional distillation of the tar, etc., is obviated.



Our large and most comprehensive stock of Industrial and Educational Laboratory Supplies of the first quality, enables us to offer Chemists Unequalled Service and Satisfaction.

We keep in stock all the Laboratory Supplies, listed in our Catalogue—the largest and Standard work of its kind in this country.

Eimer & Amend

NEW YORK CITY

Headquarters for Laboratory Supplies, Apparatus for the Analysis of Steel, Iron, Cement, Foods, Fuels, Oils, etc., etc.

12-10

PROFESSIONAL DIRECTORY

Charles C. Kawin Co.

CHEMISTS AND METALLURGISTS

LABORATORIES:
CHICAGO, ILL.; DAYTON, OHIO
TORONTO, CAN. 12-10

Mariner & Hoskins

CHEMISTS AND ASSAYERS
81 SOUTH CLARK STREET 12-10
CHICAGO

Fred N. Arnold, Jr.

Chemical Engineer
Many years' experience in
OILS, FATS AND SOAPS.
at your service
61 Ringold Street, Dayton, O. 4-11

The Columbus Laboratories

Chicago, Illinois

Departments

Medical Food Commercial

Milling and Baking

Expert Staff of Consultants

Court and Medico-Legal Work

3-11

C. L. Parker, M.S.

SOLICITOR OF CHEMICAL PATENTS

SUITE 6 MCGILL BUILDING

WASHINGTON, D. C.

12-11

Edward Gudeman, Ph.D.

Consulting Chemist and Industrial Engineer

Food and Technical Expert before Commissions and Courts. Advice on Rules, Regulations, Labeling and Requirements under Federal and State Food Laws. General Chemical Analyses, Investigations and Researches.

Chicago, Illinois 12-10

Samuel P. Sadtler & Son

Consulting and Analytical Chemists

Analyses and reports made in all branches of Industrial Chemistry.

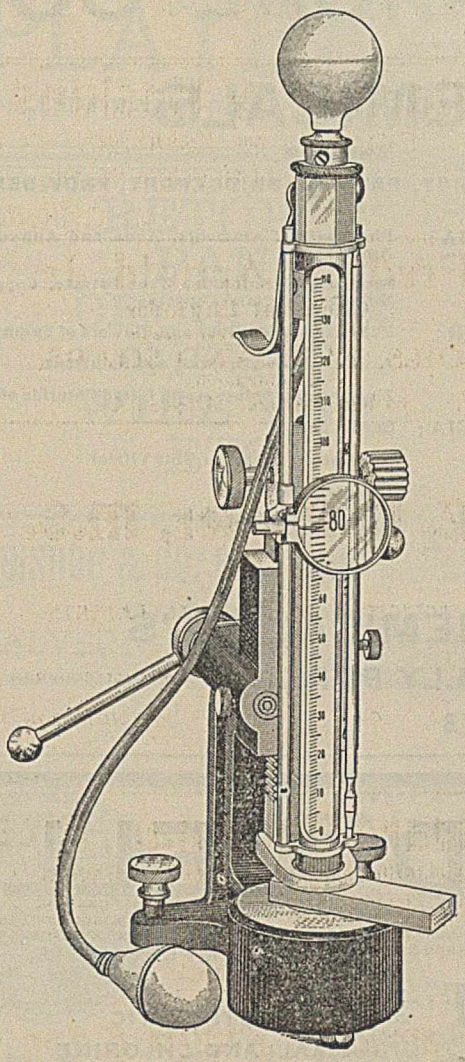
Expert assistance in the Development of Chemical Processes and Patents, and Preparation of Testimony in Chemical Patent Suits.

2-11 Philadelphia, Pa.

WANTED—To get into communication with a man capable of designing, constructing and operating a thoroughly up-to-date Acetone Plant. Address "Acetone," care of The Journal of Industrial and Engineering Chemistry, Easton, Penna. 6-10

"The first object of the industrial chemist should be that of increasing industrial efficiency. They have allowed the mechanical engineer to usurp many things, which properly come much more directly within their own province."—ARTHUR D. LITTLE.

Read Arthur D. Little's article "The Chemist's Place in Industry" in the February Number of this Journal.



THE SCLEROSCOPE

The only scientific instrument for **measuring the hardness** of metals, etc.

WHAT THE SCLEROSCOPE HAS DONE FOR UP-TO-DATE MANUFACTURERS

Cut down cost by increasing the life of tools, dies, rolls, etc.

Increased production by reducing time lost in making changes.

Improved the quality of product by making it just the correct hardness to give the best service for the purpose intended.

This instrument is now recognized as the International standard, and at least one is to be found in almost every University in the United States.

WRITE FOR BOOKLET

SCIENTIFIC MATERIALS COMPANY,

PITTSBURGH, PENNA.

Manufacturers and Importers { EVERYTHING FOR THE LABORATORY

Our catalogue of CHEMICAL and METALLURGICAL laboratory supplies is the most complete and best arranged of its kind ever issued in the United States. We send it **free of charge** to **Chief Chemists** and **College Professors.**

12-10

CABLE ADDRESS, LYCURGIS, NEW YORK

GENERAL CHEMICAL CO.

MAKERS OF

STANDARD CHEMICALS

PHILADELPHIA NEW YORK CHICAGO

ST. LOUIS, CLEVELAND, PITTSBURG, BUFFALO, SYRACUSE, TROY, PASSAIC, BRIDGEPORT, PROVIDENCE

ACIDS:	Sulphuric, Fuming Sulphuric, Muriatic, Nitric, Mixed, Acetic, Hydrofluoric, Battery and Phosphoric Acids, and Battery Solutions
SODAS:	Sulphate, Calcined Sulphate, Bichromate, Bisulphate, Liquid Bisulphite, Sulphite, Sulphide Crystals, Concentrated Sulphide, Acetate, Silicate, Caustic, and Sal Sodas; and Trisodium Phosphate, Glassmakers' Salt Cake, Glauber's Salt, and Nitre Cake
ALUM:	Lump, Burnt, Ground and Filter Alums
ALUMINA:	Sulphate and Chloride of Alumina
TIN:	Muriate of Tin Crystals and Muriate of Tin Solution, Bichloride and Oxy Muriate of Tin
AMMONIA:	Phosphate of Ammonia, Aqua and Anhydrous Ammonia
IRON:	Perchloride, Sulphide, True Nitrate, Copperas Nitrate of Iron and Copperas
SULPHUR:	Roll Brimstone, Flour and Flowers of Sulphur
LEAD:	Acetate of Lead Crystals and Solutions
ZINC:	Zinc Chloride Solution and Fused Chloride of Zinc
MAGNESIA:	Epsom Salt
COPPER:	Sulphate of Copper or Blue Vitriol
LIME:	Bleaching Powder
POTASH:	Bichromate of Potash

DISTRIBUTORS OF

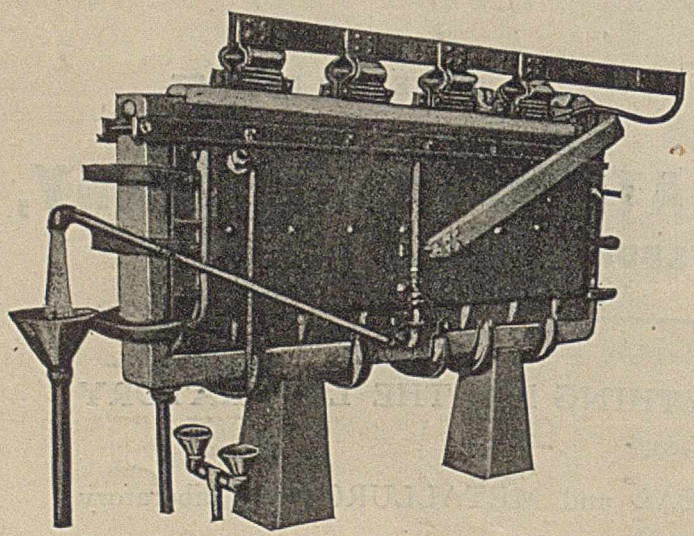
BAKER & ADAMSON CHEMICAL CO.'S

STANDARD CHEMICALLY PURE

ACIDS AND SALTS

12-10

TOWNSEND CELL



2500-5000 AMPERE UNITS

ELECTROLYTIC
ALKALI AND CHLORINE

CHLORINE

FOR METALLURGY

CAUSTIC SODA
BLEACHING POWDER

4 YEARS' OPERATION
NIAGARA FALLS, N. Y.

HOOKER ELECTROCHEMICAL COMPANY

40 WALL STREET, NEW YORK

I-11

PLATINUM

IN ANY FORM FOR ANY PURPOSE

RETORTS
PANS
CRUCIBLES
DISHES
WIRE FOIL
ETC.

J. BISHOP & CO. PLATINUM WORKS

ESTABLISHED 1842 12-10

MALVERN, PENNA., U. S. A.

Dearborn Drug and Chemical Works

Makers of Treatment for Boiler Waters

AS PER ANALYSIS

Operators of Analytical Laboratories

Physical Testing and Analysis of Lubricating Oils

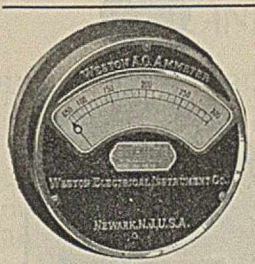
Main Offices and Laboratories
McCormick Building

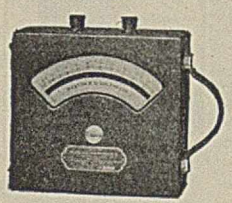
CHICAGO

ROBERT F. CARR, *President.*

W. A. CONVERSE, *Chemical Director.*

12-10





The New Weston Alternating Current Switchboard Ammeters and Voltmeters will be found vastly superior in accuracy, durability, workmanship and finish to any other instrument intended for the same service.

They are **ABSOLUTELY DEAD BEAT and EXTREMELY SENSITIVE.**

Their indications are **PRACTICALLY INDEPENDENT OF FREQUENCY** and also of **WAVE FORM.**

They are **PRACTICALLY FREE FROM TEMPERATURE ERROR.**

They require **EXTREMELY LITTLE POWER TO OPERATE, AND THEY ARE VERY LOW IN PRICE.**

The New Weston Portable Alternating-Current Ammeters, Milli-Ammeters and Voltmeters possess the same excellent characteristics.

The performance of all these instruments will be a revelation to users of alternating-current apparatus.

New Weston Eclipse Direct Current Switchboard Ammeters, Milli-Ammeters and Voltmeters are of the "Soft Iron" or Electro-magnetic type; but they possess so many novel and valuable characteristics as to practically constitute a new type of instrument.

12-9

They are *exceedingly cheap*, but are remarkably accurate and well made and nicely finished instruments, and are admirably adapted for general use in small plants, where cost is frequently an important consideration.

Correspondence concerning these new Weston instruments is solicited by

Weston Electrical Instrument Co.

New York Office, 114 Liberty St. **Waverly Park, Newark, N. J.**

C. O. BAKER, Pres. C. W. BAKER, Vice-Pres.

PLATINUM

CRUCIBLES and DISHES
ANODES and CATHODES
WIRE SHEET and FOIL

PLATINUM IN SPECIAL FORMS MADE TO DRAWING

Scrap purchased or exchanged
Write for Catalogue.

BAKER & CO., Inc.

408-414 N. J. R. R. Ave.,
NEWARK, N. J.

N. Y. OFFICE - - 30 CHURCH ST.

2-10

Let MERCK Make the "Blank" Test For You

To that end, buy

MERCK'S BLUE LABEL REAGENTS

MERCK & CO.
NEW YORK
ST. LOUIS
RAHWAY, N. J.

12-10

"Baker's Analyzed" C.P. Acids and Ammonia

on account of their uniform strength and high degree of purity, exactly meet the careful chemist's need of high quality acids and ammonia.

If you are not satisfied with the acid you are now using SPECIFY "BAKER'S ANALYZED" on your next order—it's bound to please you. Our careful analyses guarantee the purity.

IN CARBOYS

AND BOTTLES

J. T. Baker Chemical Company,

PHILLIPSBURG, N. J.

12-10