ORIGINAL PAPERS.

LABORATORY TESTS OF LUBRICANTS—INTERPRETATION OF ANALYSES.

By P. H. CONRADSON.[1]

Received March 14, 1910.

To make complete tests of lubricants, oils and greases requires a great deal of expert knowledge and experience to enable the chemist or engineer to interpret correctly the results obtained. This point will be clearer perhaps, if one considers the various classes of machinery to be lubricated, from the light spindles in cotton mills to the heavy rolls in the iron and steel mills; the fast running shaft or journals in a dynamo, to the slow heavy shaft in an ocean steamer or war ship, and the numerous classes of machinery in shops, the electric motors on street cars, the steam locomotives, the railroad cars, the steam turbine, automobiles, air compressors, steam cylinders, and so on, too long a list to enumerate, and if we consider that these machines are to be lubricated under all kinds of conditions as to weather changes, high and low temperatures, and service requirements, we readily will appreciate the wide scope "Lubricants and Lubrication" involves.

The method or methods of applying the oil to the parts to be lubricated plays a very important part

in connection with the proper interpretation of lubricating oil analyses; the conditions of the bearing surface, composition of the journal and bearings, etc.

An oil that would give satisfaction when applied direct to the journal by means of soaked waste, might fail altogether if the wick method of feeding the oil was used, likewise a sight-feed cup with wide enough orifice might give satisfaction, while a gravity feed through a long small bored pipe, might give very unsatisfactory results; or in other words the chemist or oil expert to interpret the results from laboratory tests of lubricating oils must be familiar with the particular kind of machines to be lubricated, the service conditions and requirements, and method of applying the oil, before he can give a qualified opinion as to the real adaptability of the lubricant, or comparative merits of two oils intended for the same service.

The value of physical and chemical tests of iron and steel used in construction work of all kinds and how to interpret the results obtained in laboratories is well known, likewise we must consider the laboratory tests of lubricants from a technical and practical point of view somewhat in the same light.

In making a complete investigation of the real or comparative value of a lubricating oil with another oil, we have then to consider the kind of machine to be lubricated, the service requirements and conditions, and the methods of applying the lubricant to the machine, and make the chemical and physical laboratory tests accordingly.

Generally speaking, the chemical tests, as made, are very inadequate, as are also the physical tests, especially frictional tests on oil-testing machines, unless the machines are constructed in such a way that the actual conditions can be approximately reproduced. For instance, in testing a spindle oil, the testing machine should be run practically at the same load and speed as the spindles are in actual service. In testing railway car and coach oils, the machine should have approximately the same size journal and bearing as would be found in actual railway car journals. The same is also true as regards speed, load and the application of the lubricant.

While many valuable conclusions may be drawn from properly conducted laboratory tests, those of the greatest practical value come from a close observation of the lubricant in actual service, and we can base our laboratory investigations on the results obtained, especially in comparing different oils intended for the same work. To bring out the point more

---

[1] Chief Chemist, Galena-Signal Oil Company, Franklin, Pa.

clearly, let us consider an air compressor, such as is used on street cars and electric locomotives. As is well known, these compressors are not water-cooled or even air-cooled. It is not difficult to get an oil that will lubricate the compressor cylinder, but it is difficult to find an oil that will not carbonize at the high temperature, often 450 to 460° F. in the street-car compressor, and 550° to 560° F. in the electric locomotive air compressor.

of a suitable oil for such service, and to make a proper laboratory investigation and test of an air-compressor oil, it would be necessary to have an air compressor and test the oil as near as possible under actual service conditions.

Again, we may consider a steam turbine and suitable oils for its lubrication. Ordinary laboratory tests, both chemical and physical, such as are generally used in this country, do not bring out the essential
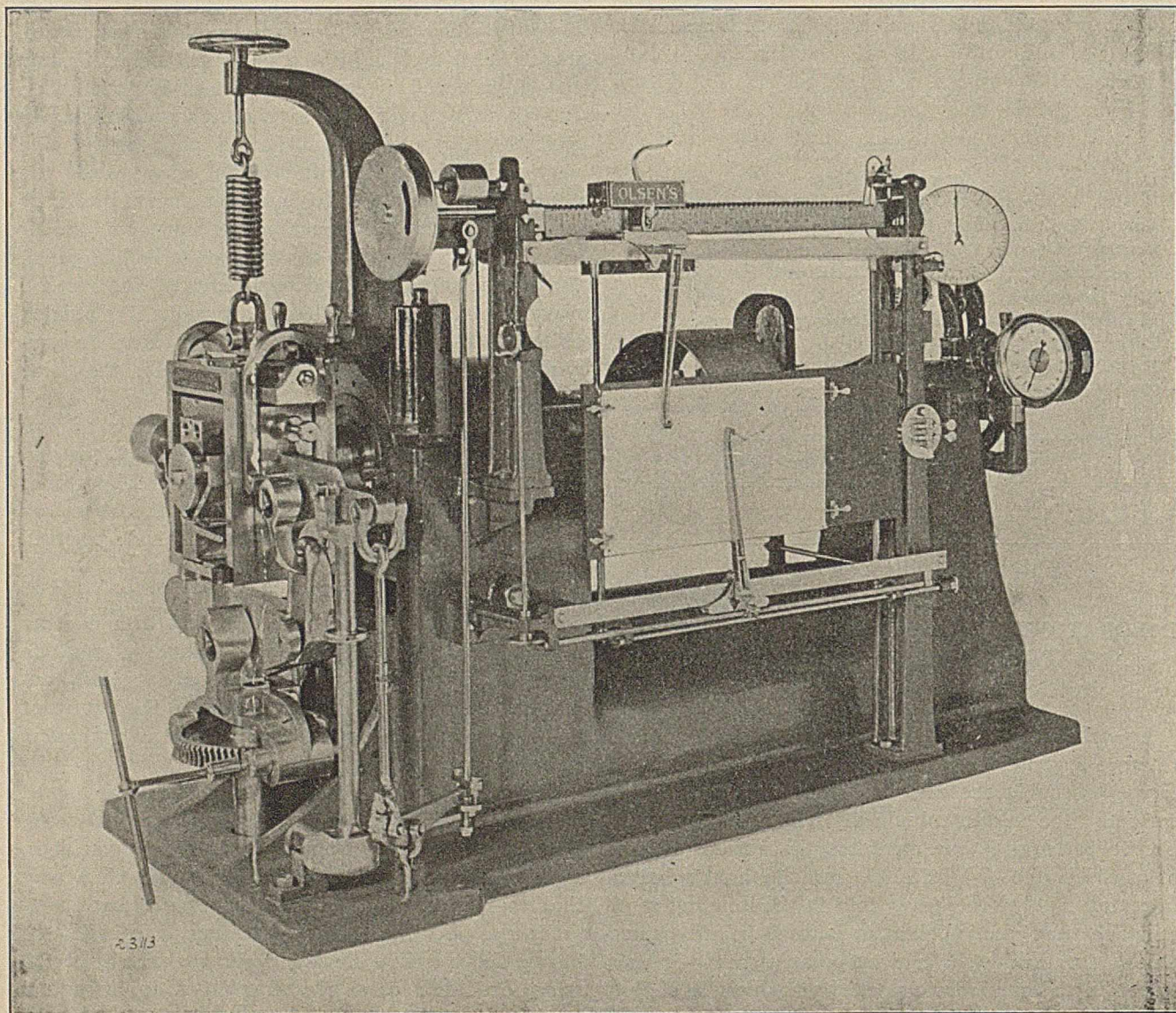

Fig. 1.

The difficulty lies in the fact that as the compressed air passes through the outlet ports and check valves in the compressor heads, there is a very rapid increase in the temperature. The small amount of oil that goes with the compressed air, if not of the best or suitable quality, will then begin to carbonize and cause trouble by forming heavy carbonaceous deposits on the check valves. Now, an ordinary oil-testing machine cannot bring out the essential requirements

qualities of a suitable turbine oil, because the service requirements and conditions are so entirely different from the general run of machinery, that special tests must be made. Therefore, from a practical point of view, to develop the essential qualities of turbine oils, it is necessary that the service conditions and requirements should be studied first, laboratory tests then being made in accordance therewith as far as practicable.

To illustrate, we consider a steam turbine of the Curtis type, where the oil is forced under high pressure to the step-bearing and then returned to the oil tank. At first this might to be a very small matter, but in actual practice and experience it is not, for the following reasons: In the first place, leakage of steam occurs in most of these steam turbines as now constructed; this steam condenses, becomes mixed or churned in with the oil, and if the oil is not of the proper kind, it becomes emulsified. The emulsified oil gradually becomes thicker, and as the same circulating system is used for the rest of the machine, the emulsified oil often causes considerable trouble. Then again, we often find that the amount of oil used in the oil-circulating system is entirely too small in quantity, so the oil has to pass through the turbine many times during the hour, in the twenty-four hours, and from week to week. This imposes a severe service requirement on the oil, which gradually becomes polymerized and oxidized, developing petroleum acids. If sulphur compounds are present to any extent, they become gradually oxidized and besides causing corrosion may also cause a great deal of trouble from formation of asphaltic and tarry matter, which would clog the filters and orifices through which the oil has to pass. From a practical point of view, therefore, the laboratory tests of turbine oils should be considered along these lines. The same may be said of all lubricating oils intended for use in oil-circulating systems, which are now so largely used in stationary power plants, shops, and mills, war vessels, steamships, etc.

It is a generally accepted idea that if the oil is adapted to the load and speed, the lower the viscosity the better lubricant it will be. This, to my mind, holds good only where the service conditions are uniform, and where the method of applying the oil to the bearing and journal is a positive one, such as in gravity or pressure-pump systems. Where the climatic changes are great, as on railroads, this will not hold good.

The load and speed of the railroad trains are the same during the summer and winter, and as is well known, the practice in this country is to convey the oil to the journals by means of oil-soaked waste. A satisfactory thin winter oil with a low cold test and low viscosity, containing sufficient lubricating capacity to keep the journal and bearing apart, would not be suitable during the hot season, not because it has not the adequate sustaining power, but because of the method of applying it to the surfaces to be lubricated, making it necessary to use a much thicker oil than is theoretically required.

Therefore, to make laboratory tests of the relative lubricating values of oils considered from a practical standpoint and to draw correct conclusions from the results obtained, we must consider the kind of machine or machines to be lubricated; the speed and the load;

the composition of the metal bearing; whether the journals are iron or hard steel; the method of applying the lubricant, either with wick feed, soaked waste, sight-feed cups, flooded bearing or continuous oil-circulating system; the actual service requirements and climatic conditions. We must make complete chemical and physical tests as near as possible in accordance with these conditions. I might with propriety state that one oil cannot be considered a better lubricant than another oil unless the service conditions and requirements are specified and fully understood and the laboratory tests made in accordance therewith.

I have spoken of the importance of adequate chemical tests in connection with physical and frictional tests. The following tests are therefore useful. While in some cases it is not necessary to subject the oil to all these tests, they are of great importance in connection with special or unusual service requirements and conditions.

CHEMICAL TESTS.

Flash point.
Burning point.
Gravity.
Color.
Odor.
Purity.
Gasolene tests, before and after flash.
Cloud test.
Cold test.
Viscosity.
Microscopic test for carbonaceous matter in suspension.
Saponifiable fats.
Free fatty acids.
Petroleum acids.
Sulphuric acids.
Chemicals from imperfect refining.
Sulphur-lamp tests and in wick.
Maumené test.
Iodine test.

Evaporating tests, a given time at 200° to 300° F. to study percentage of volatile and behavior of residues in 88° gasoline tests and acidity.
Heat tests, in air bath blowing air over the oil at 425° F. and 540° F. Examination of residue.
Emulsifying tests, to determine adaptability of the oil, say in turbine service.
Tar and coke-forming substances present before and after heat test. Oxidation or gumming tests.
Superheated steam tests.
Carbonizing test in connection with air compressor (not water-cooled) automobile gas-engine lubrication.
Capillarity or wick tests.

I will now consider the various tests and their importance.

First and Second, Flash Point and Burning Point.— This test indicates the temperature at which the more volatile elements present in the oil begin to go off to such an extent as to give a flash when a small flame is moved over and near the surface of the heated oil; the so-called open-cup method is generally used, and in connection with this test, the heat is continued till the oil begins to burn, when the flame test is made.

A too low flash and fire test may be objectionable on account of danger from fire; besides, too large a loss from evaporation, under given service conditions, in connection with the viscosity, congealing point or cold test and gravity, the flash and fire test also enables the analyst to form an idea of the source of the petroleum.

Third, Specific Gravity.—The gravity enables the analyst in many cases to form an idea whether the oil is a Pennsylvania, Virginia or western oil, the latter generally having a much higher gravity.

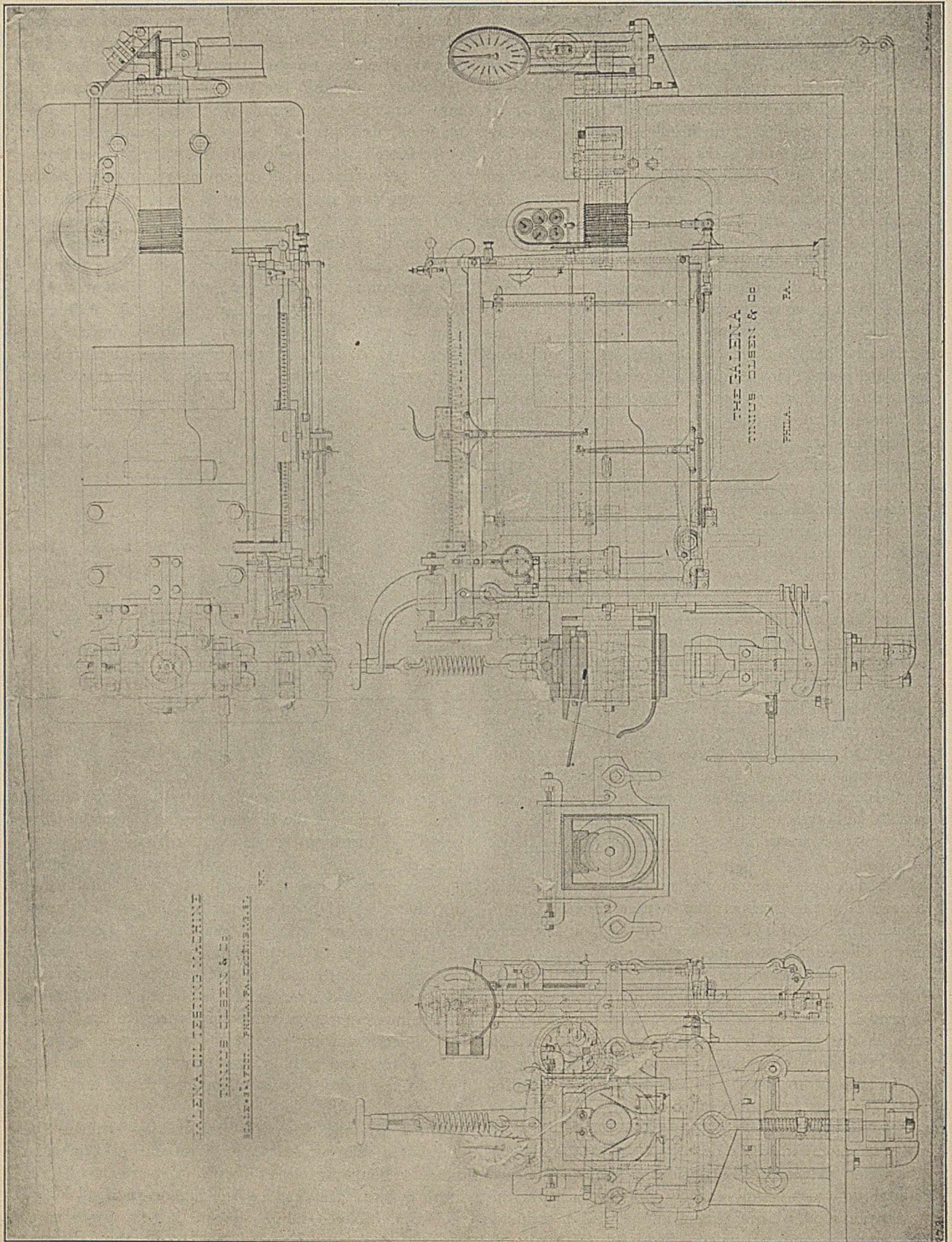*Fourth, Color.*—While not of much importance, other things being equal, an oil with a lighter color

Fig. 2.—Galena signal oil testing machine.

or pleasing appearance is oftentimes preferred to a very dark or black colored oil.

Fifth, Odor.—At times aids in detecting the kind and quality of fat oils in compounded oils.

Sixth, Purity.—Freedom from water, matters in suspension, whether clear or turbid, etc.

Seventh, Gasoline Tests.—This test tells you if water or other foreign matters are present, tar and asphaltic matter, and if the oil gives a clear solution with 88° gasoline before it is heated to take the burning point, but gives a precipitate with 88° gasoline after said test, this indicates petroleum compounds which are readily acted upon by heat, and such an oil in comparison with another oil, other things being equal, would not have the same lubricating value.

Eighth, Cloud Test of a lubricating oil is sometimes of value in determining the amount of paraffines present and the behavior of the oil in chilling down to a temperature above congealing point.

Ninth, Cold Test (Congealing point, Melting point).— This test together with the viscosity of the oil in comparative tests is of much importance in connection with the service utility of the oil and should be given careful consideration.

The method used in determining the cold test and melting point, as well as getting at the comparative fluidity or sluggishness at temperatures lower than 70° F., is generally not considered as it should be. To illustrate: A valve or cylinder oil, if the cold test was taken by the so-called P. R. R. method (that is, the oil was frozen direct in ice mixture, and then stirred by the thermometer till it began to flow when the bottle is inverted), might show a cold test of 40° F., and if no further observation was taken one would have no idea of the fluidity of 60° to 70 F.; that is, the cold test in the report would give 40° F., but in reality the oil at 60° F. would be so sluggish that it would hardly feed through the narrow-bore feed-pipe to the steam chest and cylinders, and unless the analyst knows for a fact that the engineer has his pipe covered or warmed in some way, trouble may arise, the oil be condemned, and still the oil might be of the best and purest quality.

Again if the congealing point is taken by the S. O. Co's. method (that is, the oil in the bottle with its thermometer inserted is put into a cooling box, gradually cooled till the oil just ceases to flow when the bottle is inverted, or still better, lifting up the thermometer stem from time to time and noting when the oil hardly flows from the stem), but without further observations this method like the P. R. R. does not tell all.

The rate of cooling or chilling, the time the oil remains in the chilling or cold test box, plays an important part in proper interpretation of the comparative value of the oil in actual service. Much more

could be said on this point, but the above allusion may be sufficient.

Tenth, Viscosity.—This test is the bugbear of the oil tester: it may mean so much and it may mean so little. Certainly in my line of work in connection with the cold test and flash point, we might have a good idea of the quality and adaptability of the oil with the aid of a good viscosimeter.

As an adjunct to other tests, and a careful study and knowledge of the service requirements, I have found the viscosity tests of the utmost value; in fact, from my knowledge of all the analytical data, with the aid of the viscosimeter, I can pretty near foretell the comparative friction under given conditions between two oils.

Eleventh, Microscopic Tests.—In testing dark-colored oils, heavy machine oils, and cylinder oils, it is well to put a few drops on a slide and examine under the microscope—one may find carbonaceous matter in suspension; and paraffine crystals if present at ordinary temperatures will disappear on warming the oil, and other foreign matters held in suspension will be brought out.

Certainly an oil, other things being equal, that is free or practically so from carbonaceous specks or flakes is superior to an oil containing these in some quantity.

Twelfth, Saponifiable Fats.—I will not enter into a discussion of the methods to determine these, but merely point out that two cylinder oils, one containing 30 per cent. of fat oil and the other only say 5 to 10 per cent. of fat oil, other things being equal, while not of the same intrinsic commercial value, may have equally good and economical practical lubricating value.

Again a cylinder oil containing 25 to 30 per cent. of good fat oil might give excellent and economical results in a steam engine of 100 to 150 pounds pressure per sq. in. and where the exhaust steam is not condensed or used over again in the boiler, and be very objectionable in connection with superheated steam and where surface condensers are used. The reason, of course, is obvious.

Thirteenth, Fourteenth, Fifteenth and Sixteenth.—Other things being equal, the less free fatty acids present the better.

The presence of petroleum acids, sulphuric acid, sulphonates and chemicals from imperfectly refined petroleum oils should always be carefully investigated, as the presence of these foreign materials in a lubricating oil, at least for certain important services, might lead to serious trouble and complications. A first-class lubricating oil should be free from, or at least only contain traces of, these impurities.

Seventeenth, Sulphur.—In general very little attention is paid to the sulphur and organic sulphur compounds that may be present in a lubricating oil.

In the future the sulphur in lubricating oils will have to be reckoned with when these oils are intended for turbine service, or in services where the oil is used over and over again as in a continued oil-circulating system, where the oil, due to continuous exposure to heat, air, moisture, metal wearings, gradually becomes oxidized and polymerized, forming acid petroleum products, changing it both chemically and physically. The sulphur compounds present in the oil largely augment the corrosive or pitting action on the bearings and journals under these conditions.

In the examination of lubricating oils for sulphur content, it is important to make a distinction ot how the same occurs in the oil. I have often found that in making sulphur tests by burning a given amount of oil in lamps and taking up the products of combustion in carbonate of soda solution, it is necessary to consume all the oil in the test lamps, and to make a determination of the sulphur compounds left in the wick; in some poorly chemically refined lubricating oils, the sulphur compounds found in the wick oftentimes amount to from 20 to 40 per cent. of the sulphur present.

Eighteenth, Maumené Test.—The sulphuric acid thermal test is of value in connection with tests of compounded lubricating oils.

Nineteenth, Iodine Test.—Omitted. Refer to standard text-books.

Twentieth, Evaporating Tests.—At temperatures of of 212 to 300° F., by exposing the oil in shallow flat-bottomed dishes in an air bath at 212 to 300° F. for six hours, noting the percentage of loss and condition of residue and its behavior when mixed with 88° gasoline, we obtain valuable information as to the amount of volatile matter at low temperatures.

Twenty-First, Heat Tests.—For certain service, such as for air compressors not water-cooled, turbines, etc., valuable data may be obtained by exposing the oils in shallow flat-bottomed dishes in a covered air bath through which air is blown for six hours at temperatures of 425 to 540° F.; and study the residue in the dish by dissolving the same in 88° gasoline, noting whether the gasoline solution is clear or turbid and the amount of precipitate, if any, on standing.

Twenty-Second, Emulsifying Tests.—To determine the adaptability of an oil for lubrication in turbines of the Curtis type (step-bearing) it is of the utmost importance to ascertain the behavior of the oil when coming in contact with steam through the step-bearing, whether it forms a thick, creamy emulsion or separates from the steam and condensed water.

FRICTIONAL TESTS.

To make frictional tests of oils and greases of practical value requires, as indicated, testing machines so constructed that various loads, speeds, size of journal and bearings, and methods of applying the lubricant, comparable to those in actual service as well as devices to keep journal and bearing at any desired constant temperature during the tests.

The constant temperature tests are of importance not only for the purpose of standardizing the machine for each test so as to get all conditions, bearing, journal, and feed, etc., properly regulated before the actual tests begin, but equally so in making comparative frictional tests of two oils, which have practically the same viscosity.

The two oils may show practically the same friction at a given temperature, but to keep the journal and bearing at such temperature, one oil may require a great deal more water or steam to pass through the journal and bearing; again the two oils may give practically the same friction at a temperature of say 150° or at 125° F., but great difference at 90° or at 70° F.; therefore, the constant temperature frictional tests are ot great value in conducting comparative tests.

As a rule the reports of frictional tests are very incomplete; the report should give all the constants and data taken during the frictional tests, such as area of contact, projected area, total pressure on journal in pounds, pressure by square inch in pounds, total, maximum, minimum and average friction in pounds, and coefficient of friction, temperature of journal and bearing number of revolutions and feet traveled by rubbing surface per minute, duration of tests, constant or freely increasing temperature, method and amount of lubricant fed besides complete chemical, analytical data.

If two oils or greases are submitted for comparative tests where the service conditions are uniform or fairly constant, such as in mills or power-houses, the comparative viscosity and congealing or fluidity points and friction, other things being equal, would establish the most economical or suitable oil or grease for the service. But in making comparative tests, chemical, physical and frictional, of lubricants where the service conditions vary much, especially as to climatic conditions, it should be borne in mind that while the two oils submitted may show considerable difference in viscosity, congealing or fluidity point and friction, one oil may be equally good for the service requirements as the other; that is, supposing a consumer requests two oil manufacturers to submit samples for comparative tests. They may submit one sample intended to do the service for the whole year, or they may submit samples for the different seasons which latter would be the proper thing, then the samples for each season could properly be submitted to comparative frictional and other tests, otherwise not.

GALENA OIL TESTING MACHINE.

This machine was specially constructed and built for the Galena-Signal Oil Company, by Tinius Olsen &

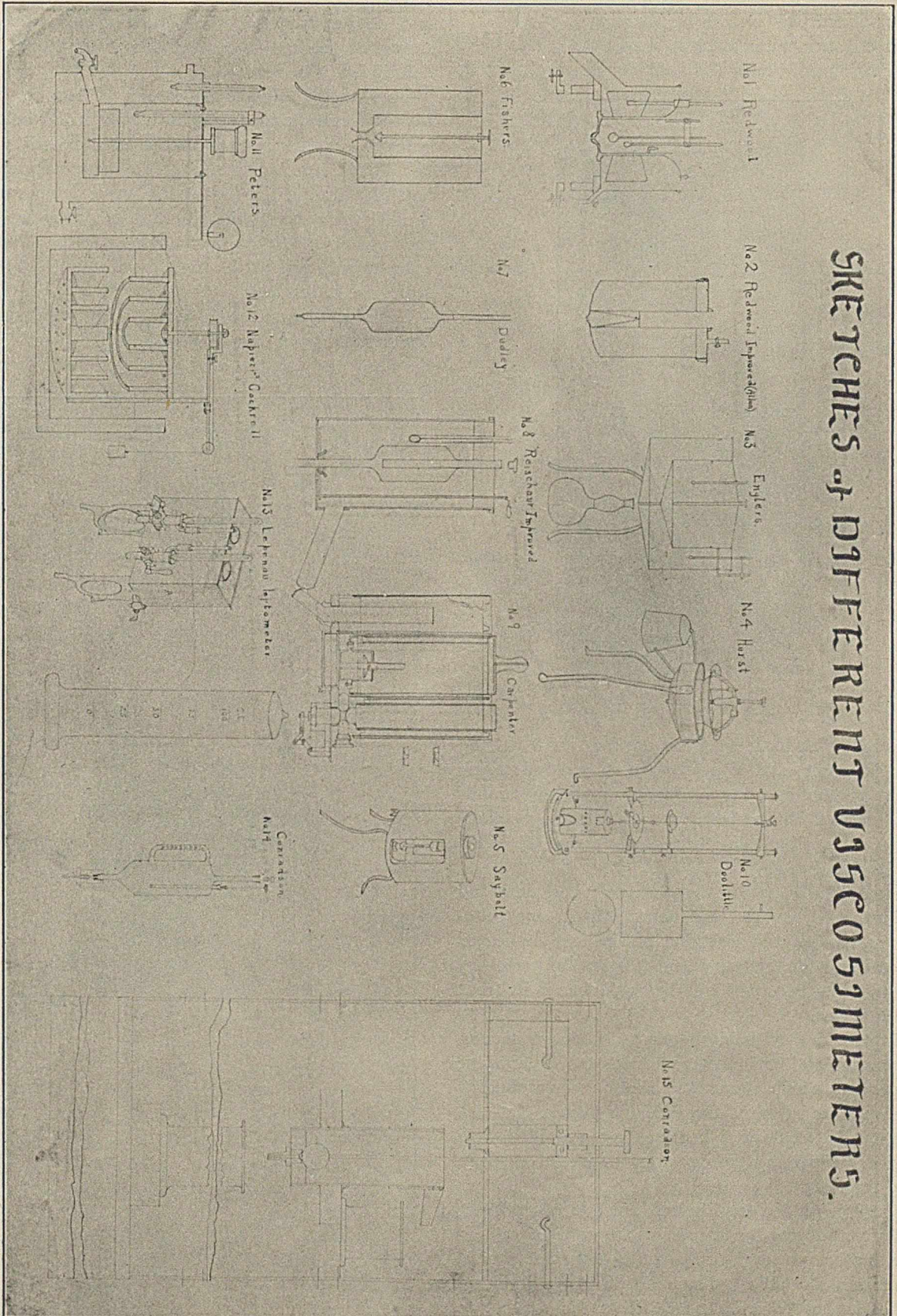SKETCHES of DIFFERENT VISCOSIMETERS.

Fig. 3.

Co., Philadelphia, and is the largest and most complete ever made in this country, having a capacity up to 20,000 pounds load on the test-bearing.

It is constructed in such a way that full-size M. C. B. car journal boxes and bearings can be inserted;
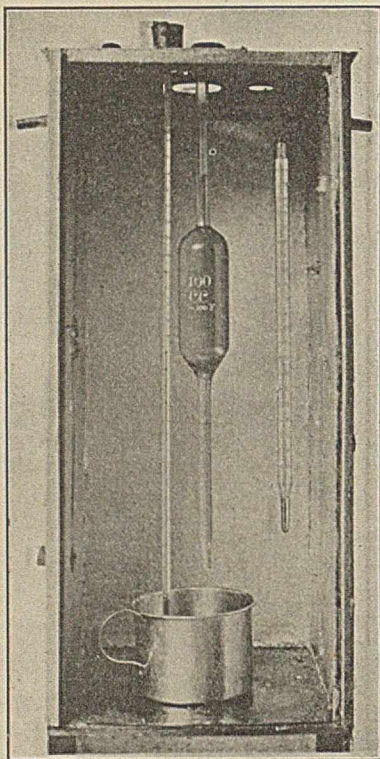

Fig. 4.—Dr. Chas. B. Dudley viscosity pipette.

the test journals to the machine are 4 1/4 x 8 in. and 5 x 9 in.; by means of a leverage, screw and spring balance system, varying loads up to 20,000 pounds can be applied on the test journal while the machine is running in either direction, at any desired speed up to its maximum.

The machine is provided with a very complete and ingenious leverage and balancing system for automatic measuring and weighing of the load indicated on a dial and the friction in pounds on the periphery of the journal recorded on the scale beam in front of the machine.

It is provided with temperature indicator, revolution counter and tachometer, besides an autographic arrangement which shows the friction corresponding to the number of turns the machine makes.

The test journals and bearings are provided with a device for passing either water or steam through during the tests.

Arrangements for any desired method of applying the lubricant during the test are also provided.

The motive power is an electric motor of special construction so that the machine can be run in either direction at any desired speed, from the slowest to the fastest or *vice versa* during the test, without having to stop the same.

VISCOSIMETERS.

The cuts show two viscosimeters, the Redwood and Dudley pipette; the Redwood viscosimeter as shown in the cut is so well known that no further description is necessary.

The Dudley pipette as seen is a 100 cc. pipette with a mark on the stem both above and below the bulb; the viscosimeter is placed in a closed box provided with a glass door, and the temperature in the box kept during the test at the same temperature as the oil; this is of the greatest importance, taking the viscosity with an instrument of this kind.

In connection with the foregoing the following tables are of interest.

Table 1.—Nos. 1, 2, 3, 4 and 5 are the same oil fractionated by means of Florida fuller's earth. While the flash and fire test and gravity remain practically
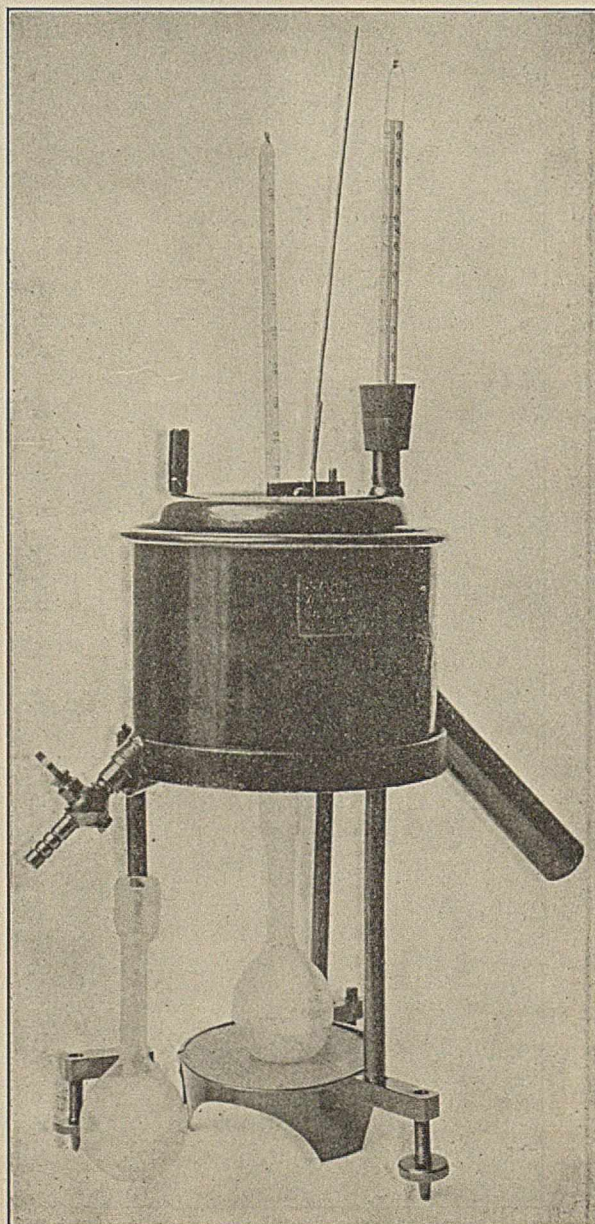

Fig. 5.—Redwood viscosimeter.

the same, with changes in color and some in viscosity, the congealing or fluidity point has as seen during the successive stages materially changed from the original No. 1. Nos. 6 and 7 represent an oil before and after being in continuous service in an oil-circulating system about ten months. Here again the flash, fire and gravity tests remain practically the same, but the congealing point and body or viscosity have greatly

congealing points or degrees of fluidity at different temperatures.

Table 4 gives results of frictional tests on the Carpenter frictional machine at Cornell University of a Galena railway summer oil, with increasing load on the journal from 135 pounds to 878 pounds per square inch—a sort of endurance test to determine the load capacity of the oil. From the results obtained

TABLE 1.—LUBRICATING OILS.

	1.	2.	3.	4.	5.	6.	7.
Flash point	365° F.	370° F.	370° F.	370° F.	370° F.	410° F.	415° F.
Burning point	440° F.	440° F.	440° F.	440° F.	440° F.	470° F.	480° F.
Grav. at 60° F.	30° B.	30.7° B.	30.5° B.	30.3° B.	30.2° B.	23.0° B.	22.8° B.
Color	Very dark	Yellowish	Orange	Red	Deep red	Red	Dark red
Cold test	Zero	+18° F.	+25° F.	+25° F.	+25° F.	+5° F.	+20° F.
Viscosity (P. R. R.) pipette:							
At 125° F.	98	92	94	94	93	85	162
" 100°	160	149	148	153	151	143	309
" 90°	205	184	192	195	195	188	410
" 80°	271	238	249	254	254	253	Drops

changed during continuous service. Petroleum acids and polymerized products have formed to a considerable extent; the adaptability or durability of an oil like this is seriously questioned for the service in which it is used. Have we any laboratory test (frictional, physical, or chemical) that would reveal the unstableness of this oil? This is a practical question that practical men want to know, and to make laboratory tests of real practical value, problems of this nature must be satisfactorily worked out and answered.

some interesting curves as to friction and temperatures could be plotted. The main point, however, is to show that the oil after the pressure on the journal gets above 400 pounds per square inch, and to the maximum load used in the test, the coefficient of friction remains practically stationary, and would give a nearly horizontal curve. From a practical standpoint this information is of great value.

Table 5.—We find first three series of tests at constant but different temperatures; second, two

TABLE 2.—GALENA CAR, COACH AND ENGINE OILS, SHOWING WIDE RANGE OF VISCOSITY AND COLD TEST.

Dudley viscosity pipette, 100 cc. water at 60° F. (15.5° C.) 32 sec.
Redwood viscosimeter, 50 cc. rape-seed oil at 60° F. (15.5° C.) 535 sec.

Viscosity taken at 100° F. (37.7° C.).

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.
							Time in seconds.								
Dudley	104	125	140	162	177	195	220	252	276	300	320	348	375	401	426
Redwood	151	183	204	240	260	283	335	378	392	444	480	510	556	595	650

Viscosity taken with Dr. Dudley viscosimeter, 100 cc. water at 60° F. (15.5° C.) 32 sec.

Instrument kept in air bath at same temp. of the oils.

						Time in seconds.			
125° F. (51.6° C.)	67	71	86	109	125	138	150	171	197
100° F. (37.7° C.)	96	99	132	185	214	247	277	318	370
90° F. (32.2° C.)	115	124	170	243	291	321	362	422	509
80° F. (26.6° C.)	141	156	216	318	380	439	501	...	...

	Flash point open cup.	Burning point.	Grav. at 60° F. Baumé.	Cold test.
Summer:				
Car	350–380° F.	425–450° F.	26.1–27.7°	+20– +40° F.
Engine	350–380° F.	425–450° F.	25.4–26.4°	+20– +40° F.
Coach	350–380° F.	425–450° F.	24.3–24.6°	+20– +40° F.
Winter:				
Car	210–300° F.	260–380° F.	27.4–29.0°	—5– +10° F.
Engine	210–300° F.	260–380° F.	26.6–27.9°	—5– +10° F.
Coach	210–300° F.	260–380° F.	25.5–26.4°	—5– +10° F.

Table 2 gives comparison between two viscosimeters, and illustrates the wide variation in congealing points or cold tests and viscosities possessed by first-class railroad car lubricating oils; a close study of this table is of great assistance to the practical user of lubricants.

Table 3 is of great interest in connection with viscosity and cold test or fluidity of cylinder oils both compounded and straight petroleum oils, indicating the necessity of additional data in taking the

series of great difference in speed (300 and 600 r. p. m.), all other things being the same; third, comparative tests of a purely vegetable oil (rape-seed) with a compounded petroleum oil (Galena lead-oxide process) with viscosities not far apart, as measured with the pipette viscosimeter; fourth, the difference in friction of the two oils at the slower speed (300 r. p. m.) is very small, while the difference at the greater speed (600 r. p. m.) is considerable, the Galena oil having a much lower friction. This is very instructive when

we consider the nature of these two oils, as well as the great load and speed.

Table 6 gives an interesting comparison between a winter and summer Galena car oil. Both have sufficient body to carry the heaviest load and speed in railroad service, but owing to the present method of conveying the oil to the car journals, a thick and sluggish oil with an unnecessary high viscosity is or has to be used during the warm or hot weather, naturally increasing the total train journal resistance, which, of course, means excessive coal consumption. Note the great difference in the fric-

Second, the necessary requisites or qualities that a first-class lubricating oil should possess in a high degree may be enumerated as follows: Necessary body to withstand the severest pressure in the service for which the oil is intended, so as to keep the rubbing surfaces apart, forming a continuous film between the same, filling up the inequalities in the surfaces; the quality of spreading itself rapidly over the rubbing surfaces, with the requisite degree of adhesive power to remain between the rubbing surfaces without creating undue friction and heating; requisite mobility or fluidity at all seasons of the year, and all climates

TABLE 3.—CYLINDER OILS.

	1.	2.	3.	4.	5.	6.	7.	8.
Flashing point	560° F.	595° F.	525° F.	525° F.	520° F.	515° F.	545° F.	550° F.
Burning point	....	....	600° F.	....	....·	....	....	600° F.
Color	Very dark	Very dark	Light filter	Light filter	Light filter	Light filter	Reddish	Dark
Viscosity (Saybolt) at								
212° F.	196	212	126	146	112	83	136	145
Cold test	+30° F.	+48° F.	+55° F.	+60° F.	+50° F.	+55° F.	+40° F.	+32° F.
Barely flows from								
thermometer at	+30° F.	+50° F.	55° F.	+60° F.	+50° F.	+55° F.	....	+32° F.
Fair at	+40° F.	+60ᵈ F.	+60° F.	+65° F.	+60° F.	+60° F.	....	+40° F.
Fair to good at	+50° F.	+70° F.	+70° F.	+70° F.	+70° F.	+70° F.	....	+45–50° F.
Quite thick at	+60–65° F.	+70–80° F.	+70–75° F.	+70–80° F.	+70–80° F.	+70–80° F.	....	+60° F.
Saponifiable fat					10%	33%		

tional resistance between these oils. Practical railroaders should ponder a little more on these facts and utilize such knowledge.

In conclusion, what function should a lubricant perform? What are the necessary requisites or qualities that should be inherent in a first-class lubricating oil? These are trite questions, and will be answered briefly:

First, the function of a lubricant is to keep the rubbing surfaces (journal and bearing) apart to prevent undue abrasion, friction and heating.

from the coldest to the hottest, without impairment of the necessary intrinsic lubricating body for the required service; durability, freedom from mineral and organic impurities, tarry and asphaltic matter, unaffected by atmospheric conditions, non-drying, non-gumming; these are the essential qualities that a first-class lubricating oil should and must possess in a high degree.

Yet no matter how excellent and suitable a material or machine may be if it is not properly applied or used, the best and most economical results are not obtained.

TABLE 4.—FRICTIONAL TESTS OF GALENA SUMMER OIL, CARPENTER MACHINE.

Bearing metal, brass; journal, steel; bearing surface; length, 3.9 in.; diameter, 3.75 in.; width, 1.9 in.; area, 7.4 in.

Number of test.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Pres. on jour., lbs. total	1000	2000	3000	3500	4000	5000	5500	6000	6500
Pres. on jour., lbs. per sq. in.	135	270	405	475	540	675	743	810	878
Method of lubrication				Flooding bearing.					
Min. coef of friction	0.020	0.019	0.0163	0.016	0.0156	0.0158	0.0153	0.0152	0.0151
Max. temp. of journal F	109	114	115	118	122	134	136	140	144
Temperature of room F	68	68	68	69	68	70	71	71	71
Elev. temp. jour. ab. room	41	46	47	49	54	64	65	69	73
Rev. of journal per min.	215	220	220	220	223	220	220	220	185
Ft. trav. by rubbing surf per min.	211	216	216	216	219	216	216	216	182

Time.	Rev. per min.	Temp. journal, F.	Tot. fric. lbs.	Coef. fric.		Time.	Rev. per min.	Temp. journal, F.	Total fric. lbs.	Coef. fric.
1: 8.40	210	106	20	0.020		6: 10.50	220	133	79.1	0.0458
45	218	107	20	0.020		55	220	134	79.1	0.0158
50	216	109	20	0.020		11.00	220	134	79.1	0.0158
2: 9.00	220	112	38	0.019		7: 11.10	220	135	84.0	0.0153
05	222	114	38	0.019		15	219	136	84.0	0.0153
10	218	114	38	0.019		20	221	136	84.0	0.0153
3: 9.20	220	114	49	0.0163		8: 11.30	220	138	92.0	0.0153
25	220	114	49	0.0163		35	218	140	92.0	0.0153
30	220	117	49	0.0163		40	221	140	92.0	0.0153
4: 9.40	220	117	56	0.016		9: 11.50	214	142	104.0	0.0160
45	220	117	56	0.016		55	180	144	104.0	0.0160
50	220	118	56	0.016		58	160	145	104.0	0.0160
5: 10.00	216	120	63	0.0157		10:[1]				
05	218	121	63	0.0157						
10	234	122	63	0.0157						

[1] Journal stopped at 11.58; pressure 6500 lbs.

This has brought about the idea of oil manufacturers employing practical and experienced men educated in actual service to follow up and watch the proper application and economic use of the various lubricating oils and greases. These men have demonstrated, not only to their employers, but also to the consumer, the practical and economic value of their educational work.

TABLE 5.—CONSTANT-TEMPERATURE TESTS, GALENA OIL TESTING MACHINE.

Comparative frictional tests between pure rape-seed oil and winter Galena railroad car oil (zero cold test oil).

Steel journal, size 5″ × 9″; bearing, genuine babbitt; total load on bearing, 10,000 lbs.; projected area, 15.5 sq. in.

Area of contact, 16.40 sq. in.

Pressure per sq. in. projected area, 645 lbs.

Manner of lubrication, oil-bath.

300 revolutions per min. = 392.5 ft. surface speed, average friction of four tests for each temperature.

Rape-seed oil.		Winter Galena car oil.	
Total fric. in lbs.	Coef. of friction.	Total fric. in lbs.	Coef. of friction.
50° F.....21.06	0.00211	50° F....20.37	0.00205
70° F.....15.375	0.00154	70° F....14.54	0.00146
90° F.....13.875	0.00139	90° F....12.75	0.00128

600 revolutions per min. = 785 ft. surface speed, average friction of four tests for each temperature.

Rape-seed oil.		Winter Galena car oil.	
Total fric. in lbs.	Coef. of friction.	Total fric. in lbs.	Coef. of friction.
56° F.....26.25	0.00263	60° F....19.94	0.00199
70° F.....25.375	0.00254	70° F....18.31	0.00183
90° F.....19.75	0.00198	90° F....15.31	0.00153

Viscosity (P. R. R.):

	Rape-seed oil.	Winter Galena car oil.
At 125° F.	80 units	72 units
100° F.	125 "	104 "
90° F.	141 "	125 "
80° F.	186 "	160 "
Cold test	+15° F.	—5° F.

By constant temperature is meant that the oil-bath and bearing is kept at uniform constant temperature during the whole time of test, which lasts not less than one hour after the desired constant temperature of oil and bearing is reached.

The importance of this "following up" is far-reaching. It has gradually brought about much more systematic and uniform method or methods in lubrication, it has brought about greater economy in the consumption of lubricating oils, and at the same time demonstrated better lubrication; in fact, in many instances brought down the consumption of oil from 50 to 100 per cent., without impairment of the best and most economic lubrication. This, of course, means a saving of large sums of money by the consumers, and satisfaction to the company in the knowledge of giving its patrons the best possible service.

From these remarks, you will readily appreciate that to make laboratory tests of lubricants of real practical value, not only to the consumer but also to the manufacturer, involves considerable technical and practical knowledge and experience, besides full and complete laboratory equipment, and the chemist or engineer who is called upon to give a qualified opinion as to the relative, comparative lubricating values of two oils or greases for a given service, considered from a practical and economical service standpoint, has indeed a difficult and oftentimes thankless task to perform.

TABLE 6.—CONSTANT-TEMPERATURE TESTS, GALENA OIL TESTING MACHINE.

Steel journal, 5″ × 9″; bronze bearing; 7800 lbs. total load on bearing; 300 lbs. pressure per sq. in.; 27.7 sq. in. area of contact; 363 rev. per min. =475 feet surface speed; manner of lubrication, oil-bath; average friction of four tests for each temperature.

Temp. 65° F.	Galena winter car oil, lbs.		Galena summer car oil, lbs.	
Friction, right	18.50	18.50	41.00	41.00
Friction, left	18.50	18.50	41.50	41.50
Friction, average	18.50		41.25	
Coef. of fric.	0.00237		0.00529	
Mean resistance per sq. in. of surface	0.665 lb.		1.489 lbs.	
Temp. 80° F.				
Friction, right	15.50	15.00	29.50	28.50
Friction, left	15.00	15.00	30.25	29.50
Friction, average	15.125		29.44	
Coef. of fric.	0.00196		0.00377	
Mean resistance per sq. in of surface	0.546 lb.		1.063 lbs.	
Temp. 100° F.				
Friction, right	11.25	11.00	20.00	20.00
Friction, left	10.00	10.00	20.00	20.00
Friction, average	10.563		20.063	
Coef. of fric.	0.00135		0.00257	
Mean resistance per sq. in of surface	0.382 lb.		0.724 lb.	

The mean resistance per square inch of surface obtained by dividing the average total friction by the number of square inches (27.7) area of contact.

	Galena winter car.	Galena summer car.
Flashing point	315° F.	395° F.
Burning point	370° F.	455° F.
Gravity at 60° F.	27.3° Bé.	24.3° Bé.
Cold test	+2° F.	+36° F.
Viscosity (P. R. R.):		
Pipette, at 125° F.	83 units	189 units
100° F.	124 "	343 "
90° F.	156 "	473 "
80° F.	201 "	... "

METHODS OF ASPHALT EXAMINATION.

By ALBERT SOMMER.

The present chemical knowledge of bituminous substances is undoubtedly most limited, and their practical chemistry is confined to the most rudimentary tests, basing on "rule of thumb" methods rather than on an exact system of chemical analysis. The lack of such scientific analytical methods has always been felt more or less keenly, but never more than at present.

The commercial importance of bituminous products has been vastly increased by the application of those materials to country roads, and the following discourse deals largely with asphaltic materials applicable for that purpose.

Bitumen available to-day for this purpose originates largely from the following sources:

A. *Residuals.*

1. So-called "native" bitumen, such as deposits of Trinidad, Bermudez and similar ones.
2. Residues from crude petroleum oil. These may be divided into:
   (a) Residue from pure asphaltic oils.
   (b) Those from semi-asphaltic oils.
   (c) And, also sometimes those from straight paraffine oils.

B. *Distillates or Pyro Products*
3. Coal gas tar.
4. Water gas tar.

Inasmuch as all "natural" asphalts in class 1 undoubtedly represent residuum of petroleum, evaporated by natural causes, there is no strict dividing line between those products and the ones originating from asphaltic petroleum, reduced artificially in stills; and there being no essential, chemically differentiating features, any qualitative discrimination is unwarranted.

Furthermore, in order to become applicable, these natural products have to be softened by "fluxing," or the addition of oil residuum (especially in the case of softer road asphalts) which latter then more and more predominates and transfers into the compound its own characteristics.

Tar, however, and its derivatives are distillates or pyro-bitumen and naturally totally different from the previous two divisions.

The following is confined to a short description of methods either entirely new, or recently applied to asphaltic materials.

1. *Specific Gravity.*—It is remarkable how little attention has been paid to this part of bituminous research, whereas specific gravity is always one of the first means of identification of oils and other liquids.

Naturally the difficulties in determining the gravity of asphalts were considerable, inasmuch as by means of the hydrometer the gravity has to be taken at a temperature far above the ordinary one, and again, to take the gravity in a common pycnometer is also connected with the greatest difficulties on account of the shrinkage of bituminous materials when solidifying. An apparatus by which it is possible to determine the specific gravity of bitumen, in a quick and accurate way, in its normal consistency, was described by the author in a paper read before the American Society for Testing Materials, in July, this year. The principle of the method consists in letting the asphalt chill in a vessel consisting of two parts, the upper part of which takes up the shrinkage and is removed after the asphalt is chilled to a normal temperature. The lower part contains exactly 10 cc. and the gravity can be ascertained either by weighing out directly or by suspending the lower cup from a special hydrometer in water of $15.5°$ C.

2. *Determination of Asphalt.*—To one not familiar with commercial conditions it may appear peculiar upon first sight to hear of "percentage of asphalt" where asphalt has not as yet been chemically defined, and cannot, therefore, be determined like other chemical individuals. Nevertheless, in many instances it is essential to give a determination which is commercially satisfactory; hence a number of methods have been devised which are necessarily more or less arbitrary. The importance of determining asphaltic contents has become more appreciated since the introduction of semi-liquid asphaltic substances in the building of roads, for making so-called "bituminous macadam." It may be stated that the only reason for applying bitumen of such consistency is the necessity of incorporating it with cold stone under ordinary conditions; hard asphalt (such as is used in sheet asphalt pavement) would chill in contact with cold stone, and is therefore excluded, though it would otherwise be chosen, inasmuch as a certain hardness is required to make a satisfactory and permanent binder. For this reason such "cold" macadam binders must combine the highest percentage of hard asphalt with the highest possible fluidity, in order to be applicable; therefore the determination of asphaltic content in the same is of utmost importance to the purchaser of such materials. Unfortunately the difficulties are great and it can by no means be stated that they have at this date been solved. The present means of ascertaining the percentage of asphalt in such compounds are the following:

(a) Precipitation with petroleum ether.
(b) Precipitation with alcohol-ether.
(c) In case of soft materials, evaporation until a certain consistency is reached.

It might be said that methods "a" and "b" tend to determine the percentage of asphalt by a chemical

— SLEEVE —   — CUP —

— FLANGE —   — COVER —
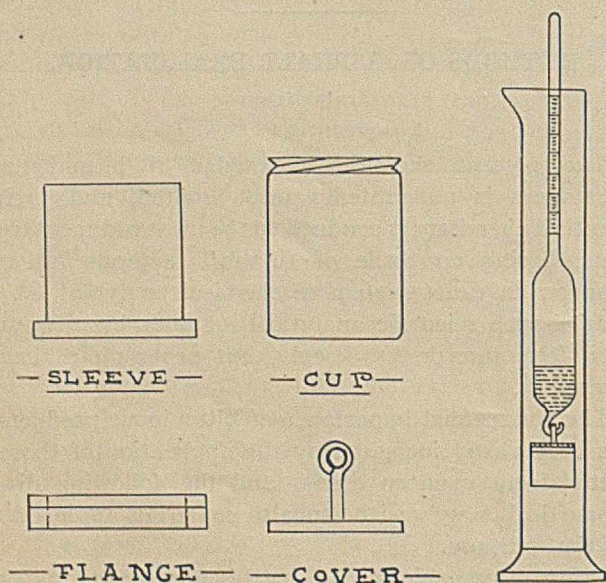
Apparatus for determination of specific gravity.

reaction, precipitating a part of the same, while method "*c*" would define this percentage by reducing the bitumen to a certain, fixed, physical consistency, pronouncing anything "asphalt" which has that consistency or is harder. As to the first method with petroleum ether, it is known that petroleum ether precipitates the so-called "asphaltenes," whereas it dissolves the so-called "petrolenes." The difference between the two, however, is not sharp, as they are by no means defined chemical individuals, and their ratio is largely dependent on the solvent power of the petroleum ether used. Usually this ether is specified by gravity alone; for instance 86° Beaumé (= 0.6480 specific gravity) but it has been shown by numerous investigations by Holde, and also in the writer's laboratory, that petroleum ethers distilled from different crudes have different solvent power and that, therefore, beside the gravity, a distillation test should also be specified as lately recommended by Holde, the combination of both insuring absolute uniformity. Holde calls a petroleum ether of definite specific gravity and distillation "normal benzine."[1] In our laboratory we apply a distillate of 86° Beaumé gravity, distilling between 100 and 240° F. This combination of gravity and distillation tests insures a Pennsylvania product and therefore absolute uniformity in the results of precipitation. The precipitation by petroleum ether is of course not a direct measure for the real contents of asphalt, as it permits only of an approximate estimation of the same by the percentage of asphaltenes, provided that the nature of the bitumen is previously known; and furthermore, if the asphaltic material contains some light distillates, these very frequently act as a solvent and hence the precipitation with 86° naphtha shows less asphaltenes than it would if those light oils were not present. In the writer's laboratory this precipitation is performed by the following method:

Two grams of asphalt are weighed into a 100 cc. Jena glass flask, covered with 75 cc. of the normal petroleum ether mentioned above, and shaken until the entire asphalt is disintegrated. The flask is then allowed to stand over night, after which the solution is decanted and the precipitate poured into a small filter. An additional quantity of petroleum ether is then poured into the flask, rinsed and also poured through the filter, this being repeated with additional quantities of petroleum ether until the same runs off from the filter clear in color. After this a quantity of benzene is poured into the flask, which will dissolve all precipitate which may stick to the glass; then a weighted china dish is placed under the filter and the same benzene poured through the filter, the solution being received in the china dish. Benzene is applied in small quantities until all the asphalt precipitated in the bottle, as well as on the filter, is dissolved and contained in the china dish. The benzene is then evaporated on the water bath until the dish has attained constant weight.

Should the asphalt contain anything non-soluble in CS_2, this of course will have to be deducted from the asphaltenes before figuring their percentage.

Precipitation by Ether-alcohol.—This method is not much in use in this country, although it combines a good many advantages, as will be shown further below by experimental data. Ether-alcohol precipitates not only asphaltenes but also the softer components of asphalt, and is therefore used especially to determine the total amount of asphaltic matter in crude oils, etc. The tables below will indicate that the method can also be well adopted for the determination in fluxes and harder bitumen.

The procedure for such grades is as follows:

Two grams of the asphalt are weighed into a 100 cc. graduated cylinder with a well-fitting glass stopper, and 40 cc. of a mixture of alcohol-ether, consisting of four parts alcohol and three parts ether, poured in the same cylinder. The same should then be attached to a shaking device and shaken well for about twenty minutes. After this time it should be left to stand over night, and should be filtered in the same manner as described with petroleum ether, only the same mixture of alcohol-ether should be used until all the soluble parts are removed from the precipitate. Benzene is then used in the same manner as above described, and the weighing and calculation made in the same manner as with the asphaltenes.[1]

Determination of Asphaltic Contents by Evaporation.—This is the one most generally used in this country, especially on softer bituminous products. A certain quantity of asphalt is evaporated in a dish of certain dimensions, at a certain temperature. The loss is taken and consistency of the residuum determined by the usual methods such as penetration, *i. e.*, the number of tenths of mm. which a needle, weighted with 100 grams, penetrates in the asphalt at 25° C. Ten mm. of "100 penetration" is usually the chosen standard, and the percentage of remainder of that consistency usually called "asphaltic contents." Unfortunately the percentage thus found is not always the real one, as will be shown in the following:

Regardless of origin, there are two classes of such binders on the market at present.

1. Semi-liquid oil residuum, which is drawn from the stills of a consistency which makes it applicable to cold stone because of its physical characteristics alone.

Natural and lake asphalts such as Trinidad and Bermudez, fluxed with oil residuum to consistency, would of course also belong to this class.

---

[1] Normal petroleum ether might be preferable to normal benzine on account of the similarity between "benzine and benzene."—Ed.

[1] In the case of oils which are very rich in paraffine this method sometimes precipitates part of the latter also. Therefore the precipitate of such oils should be repeatedly extracted with hot alcohol.

2. So-called "cut back" materials which are made from a hard but pliable asphalt by the addition of enough light distillate to render the compound applicable, with the view of having the liquid serve only as a thinner or vehicle, much the same in principle as thinning varnish.

TABLE 1.—PERCENTAGES OF ASPHALT BY VARIOUS METHODS.

	Compound "A" (asphalt base).	Residual flux "B" (asphalt base).	Residual flux "C" (semi-paraffine).	Residual flux "D" (semi-paraffine).
1. Gravity, specific........	0.986	0.980	0.963	0.980
Beaumé..............	12	12.9	15.4	12.9
2. Viscosity, Engler, at 100° C., 50 cc. run.....	195 sec.	150 sec.	62 sec.	165 sec.
3. Asphalt by 86° naphtha	14.72%	4.56%	2.30%	4.2%
4. Asphalt by alcohol ether	35.40%	17.20%	18.10%	41.3%
5. Asphalt by evaporation:				
(a) Per cent. of 100 penetration residue........	88%	80%	68%	88%
(b) Time of evaporation	1½ hrs.	10 hrs.	12⅔ hrs.	10 hrs.
6. Engler distillation:[1]				
16% distilled off, boil'g	170° C.	205° C.	295° C.	266° C.
5% off at..........	200° C.	325° C.	350° C.	350° C.
10% off at..........	260° C.	355° C.	360° C.	360° C.
16% off at..........	340° C.	361° C.	360° C.	370° C.
Gravity of distillate....	38.3° Bé.	29.1° Bé.	33.2° Bé.	34.1° Bé.
Viscosity in pipette....	11 sec.	21 sec.	18 sec.	17.0 sec.
7. Paraffine, Holde method	0.78%	0.29%	3.72%	3.35%
Melting point..........	138° F.	130° F.	121° F.	134° F.

From the standpoint of an oil refiner naturally the easiest way is to put out a product of class No. 1; whether, however, this is best from the standpoint of usefulness or efficiency is another question. This difference has been rather overlooked in the past and the results shown in Table 1 should serve as an illustration of the difference in various materials. Three types of fluxes were chosen for this investigation:

1. Compounded as above described (marked "A").

2. A residual flux (marked "B"), originated from an asphalt base petroleum as per Class No. 1, and

3. Residual fluxes (marked "C" and "D"), obtained from semi-paraffine base crude oils also per Class No. 1.

All semi-liquid asphalts used for these tests represent types of commercially available products,[2] such as used in actual work, and, all had nearly the same consistency, namely, semi-liquid. Table 1 shows percentages of asphalt of all these binders, as obtained by the various methods. The results of this table show that there are marked differences in true asphaltic content, which are to an extent illustrated by the results of precipitation with petroleum ether and also with alcohol-ether. The results of evaporation also show differences, but the mere percentages thus obtained do not illustrate the true nature of the various fluxes and, what is more important, do not show whether the asphalt which was thus found was already present in the flux or had been formed during the evaporation test itself. It cannot be emphasized too strongly that in all evaporation tests this will

[1] Note: Evaporation taken on 100 grams, in 5″ × 2 3/8″ box, at 500° F., in the open without stirring.

[2] And all marketed as "90 per cent. binder."

have to be reckoned with, although very few specifications at the present time take this into consideration. One glance at the table shows that the *time* required for the various evaporations indicates vast differences, and this already proves that percentages of asphalt obtained by the evaporation method in an unlimited time and high temperatures are often "pseudo percentages" which are of no practical value, inasmuch as such distilling or baking will never take place when those materials are in actual use. Practical experience has in the meantime confirmed these differences.

Precipitation and evaporation combined show that the hard asphalt obtained from residual fluxes was not originally present in the same, but has been produced by distilling or "cooking" heavy oils. In other words, their consistency is due to the presence of some asphaltogenous substances, which, while not being asphalts themselves, represent, as may be said, asphalt in an embryonic state which will form asphalt by the influence of great heat and oxygen; and combined with heavy, viscous, residual oils which can only be driven off at high temperatures; whereas the fluidity of "A" is caused by the admixing of a liquid vehicle to an already present base of hard asphalt, very much like the process of making varnish out of gum and turpentine.

The writer applies a method of distinguishing those products successfully by the determination of the consistency of the distillate obtained from such compounds. The distillation is performed in an ordinary Engler apparatus. We distil off a certain percentage of the compound, noting the temperature and if the same suddenly rises or jumps this in most cases indicates presence of a light thinner, whereas a residual oil will distil off more evenly; at any rate, to distil off about 20 per cent. will be sufficient in most cases. Distillates are then compared by gravity and viscosity and results shown in Table 1 exhibit the differences which may thus be obtained.

TABLE 2.—VARIOUS RESULTS OF EVAPORATIONS UNDER DIFFERENT CONDITIONS.

	Compound "A" (asphalt base).	Residual flux "B" (asphalt base).	Residual flux "C" (semi-paraffine).	Residual flux "D" (semi-paraffine).
Evaporations on 100 grams at 500° Fahrenheit:				
(a) Open, without stirring; loss............	16%	20%	33%	12%
Penetration of residue	82	95	98	92
Time..............	1⅚ hrs.	10 hrs.	12⅔ hrs.	10 hrs.
(b) Open, with stirring; loss	16%	20%	33%	12%
Penetration of residue	86	120	96	114
Time..............	1⅔ hrs.	5 hrs.	5⅔ hrs.	8½ hrs.
(c) In oven, without stirring; loss........	16%	20%	30.5%	12%
Penetration of residue	73	49	97	300
Time..............	5 hrs.	19 hrs.	17 hrs.	3 hrs.

In the second table there are exhibited results of

evaporations on the same materials as in Table 1, but under various conditions. All the evaporations in Table 1 were made on 100 grams of asphalt in a container 5 inches in diameter by $2^3/_8$ inches deep. That there are very marked differences, regardless of the quantity and other data, and depending only on the difference in the various methods of heating is shown in Table 2, from which it can readily be seen that the oils of various bases behave very differently under varying conditions.

Therefore, it is necessary when specifying asphaltic contents, to always state the following:

1. Quantity of asphalt applied (the evaporation being a surface function, is of course largely dependent on the ratio of the surface to the volume, and will vary with varying quantities).

2. Size of vessel.

3. Temperature, and *length of time* to be exposed to the same; the latter item is evidently the most important one.

4. Whether the evaporation takes place.
 (a) In a closed oven.
 (b) In the open.
 (c) With or without stirring.

2. *Paraffine.*—Next in importance to asphalt is paraffine as a distinguishing feature of petroleum. Without entering here into the question of merit or disadvantages of paraffine in asphalt, there has been a great deal of uncertainty regarding its determination. It should be remembered that paraffine is not a chemical individual, and that the percentage of crystallizing paraffine scale in a given distillate depends entirely on the solvent and also on the temperature at which this crystallizing takes place. It should also be remembered that paraffine is never contained in a crude oil or in a residual in its scaly modification, but always as amorphous, so-called "proto" paraffine. Therefore the first demand is to make the asphaltic material subject to destructive distillation to coke, and determine the scale in the distillate. In some asphalts there is no paraffine whatsoever and for this reason a qualitative test should be made first, as follows: The asphalt is distilled to coke, and a drop of the distillate is caught at intervals and put on ice. The temperature and percentage of distillate should be noted at the point when this drop chills.

Some asphalts furnish a distillate which chills at once, whereas others are practically free from paraffine scale; therefore a quantitative determination does not have to be made. The quantitative methods now in use are either the one by Zalociecki or that by Holde. Zalociecki dissolves the distillate in amyl alcohol and precipitates with ethyl alcohol at 0° to —5° F., whereas Holde precipitates with alcohol ether at—20° C.

Table 3 contains paraffine determinations of various asphalts and it will be seen at first sight that the results, although taken on one and the same material, differ vastly. This is for the reason that, as above stated, paraffine is not paraffine in every case, and that the amount of paraffine scale crystallizing out is entirely dependent on its consistency. The colder the "wax distillate," the softer is the crystallizing scale; this is in accordance with the commercial process of bringing out paraffine wax, which is marketed and designated from different "pressings" by melting point. The writer has therefore made it a practice
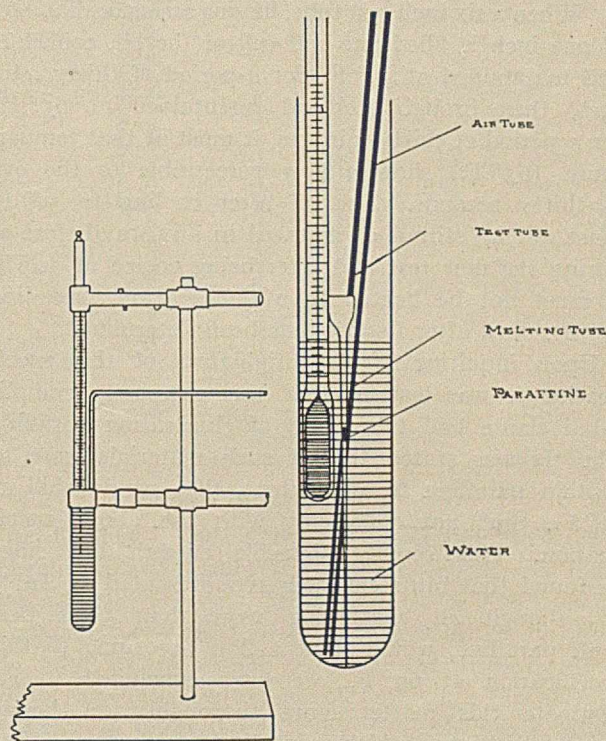
Apparatus for determining melting point of paraffine.

to invariably determine the melting point of paraffine, and it cannot be demanded urgently enough that in all such present specifications which set a limit to paraffine scale, its melting point should also be given, as otherwise there would be no end of discrepancy. There seems to be a certain ratio between melting point and percentage, and in most cases a difference of 2° F., melting point, seems to be equivalent to one per cent. scale.

TABLE 3.—RELATION BETWEEN CONSISTENCY AND PERCENTAGE OF PARAFFINE.

Determinations:	1. Zal.	2. Zal.	3. Holde.	4. Holde.	
No. 1 (65% binder; residual)	16.5	15.5	4.5	....	
Melting point...........	96° F.	104° F.	120° F.	....	Flows
No. 2 (90% binder; residual).................	10.0	9.0	5.0	....	
Melting point..........	108° F.	110° F.	118° F.	....	Flows
No. 3 (95% binder; residual).................	6.2	4.3	2.7	....	Semi-
Melting point..........	116° F.	122° F.	131° F.	....	fluid
Compound No. 3..........	13.4	7.5	7.3	10.0	
Melting point..........	105° F.	124° F.	126° F.	118° F.	Liquid

For the melting point we use the capillary method. The results as exhibited in Table 2 speak for

themselves. It should be remembered in this connection that even the originators of the methods of determination do not claim accuracy within one per cent., whereas there are a number of asphalt specifications stipulating percentages within one-quarter of one per cent. and even less of paraffine; this is totally objectionable especially when no melting point is given.

There are also a number of specifications having a so-called "cold test," as follows:

"When a six inch test tube, having an inside diameter of one inch is filled one-half full of the oil, cooled to and maintained at 50° F., for a period of thirty minutes, then brought to and maintained at 65° F., for a period of thirty minutes, it must at that temperature (65° F.) show a flow perceptible to the eye in thirty seconds. The oil after cooling to 50° F. must not be stirred or agitated in any way before or during the flow test and after being cooled at 50° F. it must not be heated to a temperature exceeding 65° F., until after its flow has been determined."

Upon inquiring of the originators of this specification it was learned that this extremely complicated clause had the object of eliminating paraffine oils. It was stated that if such materials were to contain paraffine to any extent, they would chill at 65° F., thus not complying with the above specification. This sounds plausible enough but since we found that bitumens such as represented on Table 3, although all containing more than three per cent. paraffine, would show a flow according to this specification at 65° F., we have concluded to investigate this matter more thoroughly. A heavy Texas distillate, which contained neither paraffine nor asphalt, was taken as a neutral base. At first we dissolved in it 8 per cent. of paraffine scale of a melting point of 125° F. This compound represented a solid mass at room temperatures. We then added 8 per cent. of a soft Texas asphalt, and the result was compound No. 3, which is a thorough liquid, and more liquid even than the asphalt dissolved in the oil alone. We have, therefore, the case of a lowering of the melting point produced by the combined action of paraffine plus asphalt. Therefore, the only reason that binders 1, 2 and 3 (Table 3) are liquid at 65° F. as specified, can be sought for in the fact that they contain asphalt *and* paraffine. If one or the other were removed, the remainder would become harder. This we have also shown on a residual cylinder oil, of semi-asphaltic basis which contained some asphaltic matter; alcohol ether precipitated 18.5 per cent. The oil was thoroughly liquid (cold test = 75° F.). It was filtered through porous matter, which retained the asphaltic substance, and the result was a light-colored product which is solid at ordinary temperatures, its cold test being 90° F. Attached is an analysis of the oil before and after filtering.

This case illustrates conclusively that the *consistency* of an asphaltic compound alone can never give an idea of its true contents, and that a specification like the above is utterly worthless.

3. *Determination of Tar.*—It has so far been impossible to ascertain the presence of tar except by more than very doubtful methods. The method which is herewith introduced will give, if not extremely accurate ones, results of satisfactory commercial value. The principle of the method consists in distilling the bitumen to coke, and applying dimethylsulfate to the same. Dimethylsulfate dissolves oil products of benzene character or pyro distillates, whereas it does not dissolve paraffine or olefine hydrocarbons, such as produced by the distillation of mineral oil. E. Graefe has applied this reaction to separate brown coal or shale distillate from coal tar products, and the writer found that it represents an ideal means of separating all distillates obtained from pyro-bitumen, or all benzene derivatives from petroleum distillates, which, of course, consist largely of paraffine chains or other saturated hydrocarbons.

TABLE 4.—PERCENTAGE COAL TAR BY SOLUBILITY OF THE DISTILLATE IN DIMETHYLSULPATE.

Description of product.	Solubility in per cent
E Grade petrol. asphalt	Not soluble
Bermudez asphalt	" "
Cuban asphalt	" "
Gilsonite	" "
Coal tar	100 "
20% tar + 80% asphalt	15 "
40% " + 60% "	30 "
50% " + 50% "	35 "
60% " + 40% "	40 "
80% " + 20% "	60 "

Table 4 containing results obtained by this method gives the solubilities in dimethylsulfate of straight coal tar distillate, straight asphalt distillate (both native and oil), and various mixtures. The results illustrate that there is a certain fixed proportion by which we can very well judge the relative proportion of each. It is also interesting to note that all native asphalts, including gilsonite, act exactly like oil asphalts with the dimethylsulfate, which is a further proof of the identity of their origin. The importance of this method is considerable, inasmuch as the market value of tar is of course far below that of asphalt, and the lack of a method of determination has been felt very keenly. The method as executed in the writer's laboratory is as follows:

Four cc. of the distillate obtained by destructive distillation of the asphalt (to coke) are put in a ten cc. graduated cylinder with ground glass stopper, and six cc. of dimethylsulfate are added and shaken thoroughly for one minute. If the distillate is not entirely soluble, separation takes place within a few minutes and a separating mark can be accurately read. The percentage of solubility is calculated from this reading.

The methods outlined above may well be char-

acterized as an attempt to characterize and eventually analyze bitumina by their destructive distillate, which principle is new and I believe highly promising.

APPENDIX.

In the following we briefly describe a method of determination of water and one for the determination of sulphur. Both of these methods were originated by Edmund Graefe for crude oils and coal; the following descibes their modification for asphaltic substances, for which they supply long-felt wants.

(a) *Water Determination.*—In distilling off water from heavy bodies such as bituminous matters or crude oil, foaming takes place which renders distillation entirely impossible. Graefe applies a light volatile oil, such as petroleum distillate or coal tar distillate, to the substance and distils both. In order to determine water in asphalt, 50 cc. of asphalt are mixed with 50 cc. of a petroleum distillate of volatile character. A product of this kind can be purchased in any quantities, it being a well-known turpentine substitute.[1] The total is then distilled and distillation proceeds easily and without any explosions. The same volume of the applied solvent is distilled off and thus made sure that all the water will be driven over, which, of course, settles after condensing. The combined distillates are caught in a flask having a
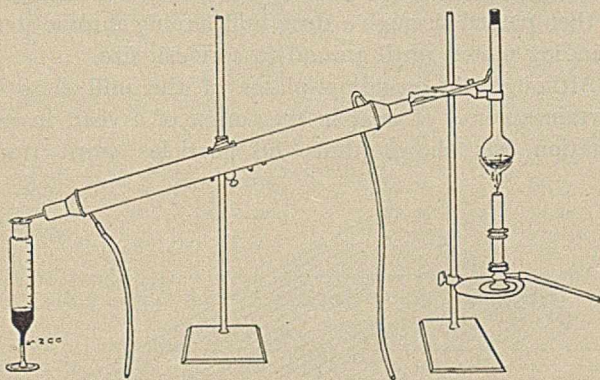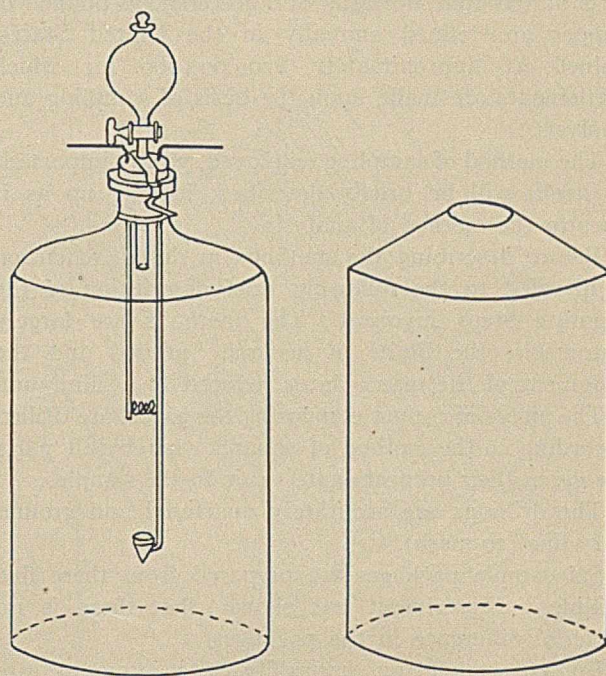

Apparatus for determination of water.

stem divided into 2 cc. This corresponds to one per cent. if 50 cc. of asphalt were applied, the water settling easily from the light distillate, and its percentage can be read at once, without any figuring.

(b) *Sulphur Determination.*—The principle of this method consists in the combusion of the bitumen in an atmosphere of oxygen. This was at first suggested by Hempel, and later modified by Graefe for coal products and was successfully applied in the author's laboratory on oils and asphalts. About 0.2 gram of bitumen are weighed and placed on a small lump of chemically pure cotton, which must be free from sulphur. This is then placed on a small platinum cone which, again, is suspended from a copper wire. The cotton containing the bitumen is connected to

[1] The commercial name of this product is *Texene.* Its gravity is 42° Beaumé and its limits of evaporation are between 270° and 450° F.

a thin platinum wire, forming a short-circuit between the suspending copper wire and another wire through which an electric current can be sent coming from

Apparatus for determination of sulphur.

a dry battery. The current will thus ignite the thread, the cotton and finally the asphalt, which will burn freely in the oxygen. After combustion is completed a solution of sodium peroxide is permitted to enter the flask. Care should be taken that this be done either after the bottle is cold, or that the surplus pressure is released gradually through the solution of sodium peroxide in which case it would retain all sulphurous gases. Determination of sulphur is finally accomplished by neutralization and precipitation of the solution with barium chloride. With a sufficient number of apparatus it is easy to execute two dozen sulphur analyses per day. They are accurate almost to the theoretical point which has been established by a number of experiments.

THE DETERMINATION OF COPPER IN BLISTER AND REFINING COPPER.

By WILLIAM C. FERGUSON.[1]

Received March 18, 1910.

Through the efforts of representatives of those interested in the commerce of copper, continual advances have been made in sampling and analysis with the object of securing its correct valuation.

Although the electrolytic method for the determination of copper is universally employed, marked differences exist in the detail of its performance.

A description of the method developed in the laboratory of the Nichols Copper Co. is, therefore, pre-

[1] Chief Chemist, Nichols Copper Co.

sented with the object of interesting chemists in a movement towards uniformity of practice.

The importance of this subject will be realized when it is stated that upwards of 1,400,000,000 pounds of copper are refined annually in the United States, valued at approximately $200,000,000 for which settlements are made upon the basis of sampling and analysis.

The method of sampling employed, vitally important in itself, will be briefly described, leading up as it does to the method of analysis.

Before describing the methods in detail, attention is directed to the following brief description of the separate steps involved. The methods are largely automatic, the limits of accuracy proved and the judgment of the manipulator reduced to a minimum.

The pieces of copper composing the parcel are drilled according to the method of squares whereby all parts are given their proportionate value in the sample.

The drillings are accurately quartered and ground very fine (20 mesh).

Six sample packages are prepared from these fine drillings. Experiment has shown that there is no material difference in the packages.

Eighty grams, an unusually large amount, are weighed out for analysis (almost one-quarter of the sample package).

The ground drillings are dissolved in a 2000 cc. flask accurately calibrated to the overflow pipette which is employed for dividing the solution for electrolysis.

The flask and pipette are surrounded by water to eliminate the influence of temperature upon the volume of the solution.

Two grams of copper are deposited on a foil much smaller than those used in laboratories with which the writer is familiar, where one gram is deposited.

A constant current is employed.

Strength of current and composition of electrolyte used have been demonstrated to give the purest deposit.

The minute quantity of impurities deposited with the copper are systematically determined and corrections applied to daily analyses.

Twice a week refined copper of known composition is put right through with the blister samples, being treated in the same way in every particular.

All of the statistical tables, illustrating the accuracy of the different steps in the method, have been compiled from consecutive results, involving *no selection* whatever, *i. e.*, all the results obtained are incorporated in the tables.

PREPARATION OF THE SAMPLE UP TO THE POINT OF
DELIVERY AT THE LABORATORY.

Blister copper, in lots averaging forty to fifty tons, is delivered at the refinery in the form of pigs, cakes or slabs weighing from fifty to three hundred pounds each.

The method of sampling depends upon the factors of size, value, shape, uniformity of grade and the number of pieces in the lot. But, the fundamental principles involved are the same in all cases and depend upon the fact that the average composition of individual pieces in a single lot may vary and, also, that different portions of the same piece differ, sometimes largely.

Briefly, the procedure is to drill a one-half inch hole of certain depth and position in each piece or in a percentage of the total number. The position of the hole is changed in successive pieces in such a manner that, if all the holes were drilled in a single piece, the face of which is divided into equal squares, a hole would be made in the centre of each square. The number of the squares corresponds to the number of the pieces in the lot or a ratio thereof.

By means of a funnel-shaped collar laid on the piece and around the drill, chips, other than those cut by it, are prevented from entering the sample.

Upon withdrawal of the drill the borings are brushed from the collar through the hole in the piece and a corresponding one in the table of the drill press into a receptacle underneath.

The borings from each lot, weighing from 18 to 27 pounds, are collected and ground in a sample grinder, to pass an 8-mesh sieve and then reduced to four and a half pounds by use of a trough sampler. This amount is then passed through a drug mill having chrome steel grinding plates, until ground to 20-mesh size.

Although the grinding plates of the mill show a certain amount of wear in the course of a year, investigation has shown that the particles worn from
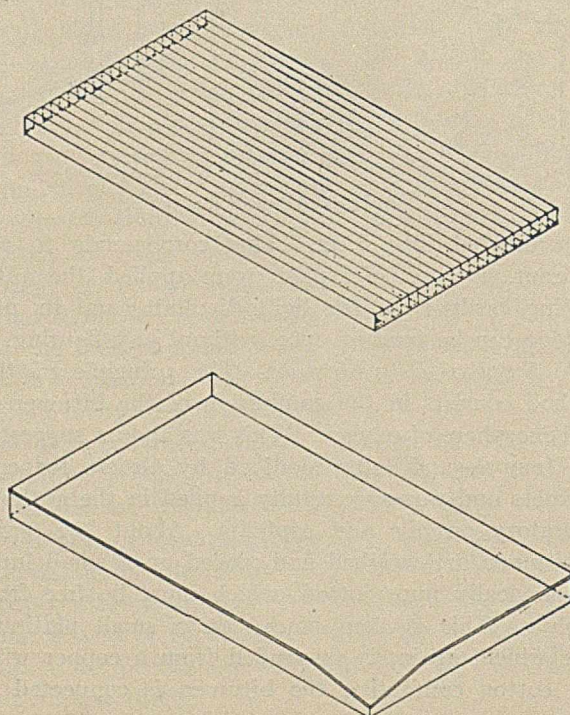

Fig. 1.

the mill are quite insufficient to affect the value of the sample.

After thus grinding the quartered portion to 20-mesh size, it is then thoroughly mixed and divided by the use of a trough sampler, into six parts averaging 320 grams each.

Since the coarse and fine portions of the sample have quite different copper, silver and gold values it is essential that their relative proportions should be maintained in the division of the sample. The trough sampler (see Fig. 1.) has been found, by repeated experiments, to be more accurate than "heap quartering" in this respect.

Experiments have shown that the six portions, into which the ground drillings are divided, contain practically the same amount of coarse and fine material.

Comparison of copper results from different packages of the same sample.

Brand.	Lot.	Package. No. 1.	Package. No. 2.
A...................	106	99.26	99.26
B...................	678	99.12	99.11
	683	98.98	98.90
	703	98.84	98.78
	734	98.93	98.93
	760	99.05	99.06
	805	99.11	99.06
C...................	198	99.34	99.33
	200	99.29	99.27
	202	99.23	99.22
D...................	396	98.74	98.70
	406	98.98	99.00
	424	99.06	99.07
	428	99.04	99.03
E...................	552	98.96	99.01
	555	99.08	99.10
	562	98.82	98.84
	577	98.97	98.97
F...................	293	99.38	99.39
G...................	190	98.96	98.93
Average..............		99.057	99.048

SIEVING TESTS TO SHOW WHAT DIFFERENCE IN PROPORTION OF COARSE AND FINE MAY EXIST IN PACKAGES OF THE SAME SAMPLE.

Sample.	No.	Per cent. of 40-mesh fines in							
		1.	2.	3.	4.	5.	6.	7.	8.
A....	...	18.27	18.19	18.11	18.23	18.34	18.19	18.15	18.09
B....	...	15.61	15.26	15.47	15.58	15.34	15.34	15.50	15.56
C....	...	16.93	16.62	16.76	16.96	16.78	16.77	16.98	16.91
D....	...	17.43	17.82	17.64	17.61	17.90	17.56	17.58	17.49
E....	703	18.12	18.36	....	....	....	....	....	....
F....	704	18.64	18.51	....	....	....	....	....	....
	705	17.98	18.26	....	....	....	....	....	....
	315	22.14	21.79	....	....	....	....	....	....
G....	312	15.93	16.07	....	....	....	....	....	....
	313	16.47	16.51	....	....	....	....	....	....
	314	16.11	16.48	....	....	....	....	....	....
H....	17	19.41	19.32	....	....	....	....	....	....
I.....	526	21.36	21.76	....	....	....	....	....	....
	527	20.86	21.07	....	....	....	....	....	....

Maximum difference is 0.40% which would affect the copper results 0.016% if a difference of 4% copper be assumed to exist between the assay of coarse and fine.

MANIPULATION OF THE SAMPLE FROM THE PACKAGE TO THE FLASK.

A trough sampler is used both in the sample room and in the laboratory. The one in the sample room has troughs and spaces half an inch wide and is used for dividing the whole sample of ground drillings

into six parts as described above. The other (Fig. 2), in the laboratory, has troughs and spaces quarter of an inch wide and is used to obtain the portion for analysis from one of the six sample packages.
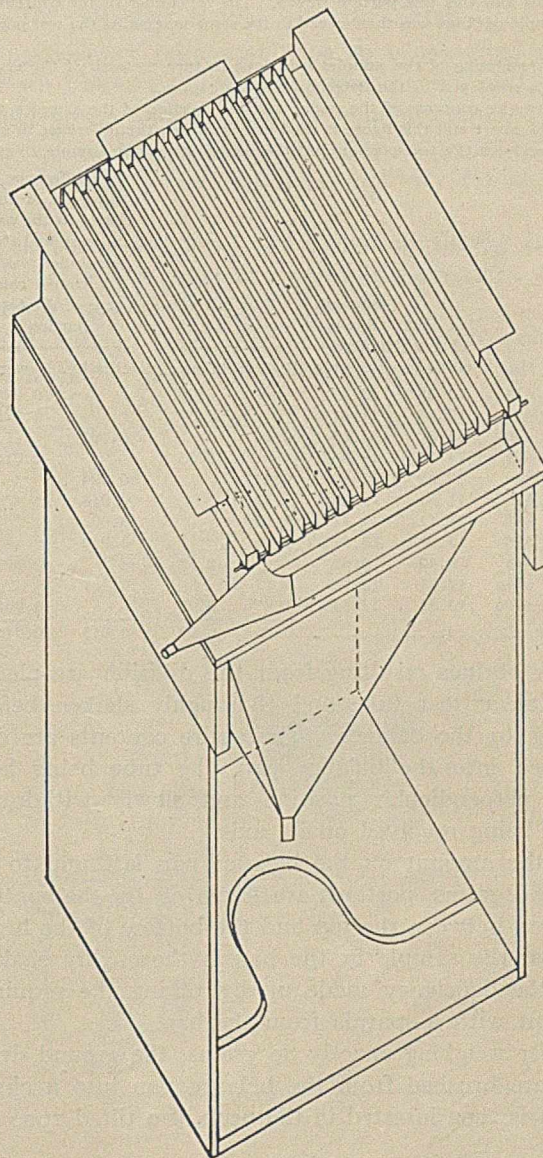

Fig. 2.

In the use of both, the sample should be scattered with a motion that will allow the particles to fall in an even stream upon the troughs. A full arm, side to side, movement of the bag or pan accomplishes a very accurate division. A rotary or axial motion should be avoided.

The amount for analysis used in this laboratory is 80 grams, approximately one-quarter of the contents of the sample bag. It is an easy matter to divide the sample to within a few grams of the mathematical quarter.

Experiments by sieving have shown that the maximum difference in composition between the 80-gram portion and the remainder of the package is no more

than 0.025 per cent. in copper and that the average difference is inappreciable.

TABLE COMPARING THE TEST PORTION WITH THE REMAINDER OF THE SAMPLE BAG.

The sample packages were quartered by trough sampler to approximate 80 grams and this test portion sieved. The remainder of the contents of the sample package was then sieved in the same manner as the test portion in turn.

The quartering of the samples was done in turn by each of the several chemists employed in the determination of copper.

The copper contents of the coarse and fine portion of the samples averaged 5% apart and this figure is used in calculating the difference in assay value between the test portion and the remainder of the sample.

Brand.	Lot.	Per cent. fine of test portion.	60-mesh fine remainder of sample.	Fine in test portion. Higher.	Fine in test portion. Lower.	The difference of per cent. of fine between the test portion and the remainder makes the copper content of the test portion. Higher by.	... Lower by.
A....	74	13.38	13.77		0.39		0.020
	77	12.10	12.61		0.51		0.025
B....	449	11.32	11.23	0.09		0.005	
C....	51	14.53	14.86		0.33		0.016
D....	444	12.59	12.12	0.47		0.024	
E....	120	11.83	12.15	0.32		0.016	
F....	818	11.51	11.41	0.10		0.005	
G....	588	13.92	13.52	0.40		0.020	
H....	678	9.40	9.58		0.18		0.009
	679a	12.91	12.74	0.17		0.009	
	679b	12.51	12.54		0.03		0.002
Average......				0.26	0.29	0.013	0.015

The borings resulting from the division are placed in a clean test tube and thoroughly shaken before taking to the balance. The entire contents are discharged into the balance pan, the tube being held in a perpendicular position and slowly withdrawn while being revolved on its axis.

If the amount on the balance pan is found to be over 80 grams, portions are taken off by the spatula midway between the top and the bottom of the heap. If less, the sample in the bag is thoroughly shaken and the deficiency made up by taking the required amount with a spatula from the bag.

After weighing exactly 80 grams, the ground drillings are brushed from the balance pan into a chute which is then inserted in the neck of a tilted 2000 cc. flask.

The chute (Fig. 3) is made by folding a smooth piece of writing paper, nine inches long and 3¼ inches wide, once over on the double fold and then unfolding. This chute completely envelops the ground drillings during insertion and prevents loss of fines.
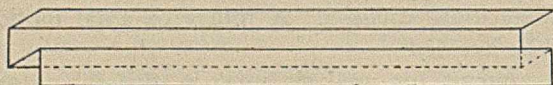

Fig. 3.

By bringing the flask to an upright position, the drillings will fall to the bottom without allowing fine particles to adhere to the neck. The chute is brushed downwards while being withdrawn from the flask.

The "coarse and fine" as well as the "catch weight" methods have been compared, on numerous samples, with the practice of weighing out exactly 80 grams. As will be observed from Tables D and E, the results by the several methods average practically the same in the long run.

D.

The "coarse and fine" method consists of sieving the entire contents of the sample package through a 40-mesh screen. The siftings and portion left on the screen are each weighed in order to ascertain their percentage to the entire sample. The coarse is then quartered by use of the trough sampler to about 80 grams. Exactly 80 grams are weighed out and assayed according to the regular procedure. The whole of the fine, which varies from 40 to 90 grams, is taken for assay according to the regular procedure. From the data thus obtained the per cent. copper in the sample is calculated.

This method eliminates completely the question of proportion of coarse and fine in the test portion.

Brand.	Lot.	Regular 80-gram method.	"Coarse and fine" method.
A..................	1	99.46	99.42
B..................	47	98.47	98.44
C..................	46	98.33	98.38
D..................	1	98.98	98.91
E..................	61	98.81	98.86
F..................	187	98.88	98.91
G..................	748	98.55	98.59
H..................	21	99.09	99.12
	36	99.05	98.96
	40	99.02	99.01
	41	98.96	98.97
	43	99.15	99.13
	854	99.29	99.26
	855	99.26	99.31
I..................	184	98.94	99.12
	218	99.14	99.15
	269	99.08	99.05
J..................	131	99.29	99.21
	135	99.43	99.35
	138	99.40	99.47
	147	99.36	99.38
	544	99.28	99.21
K..................	166	99.22	99.22
	168	99.20	99.16
	171	99.21	99.17
	444	99.05	98.99
Average............		99.073	99.067

E.

COMPARISON OF DIFFERENT METHODS OF WEIGHING-OUT PORTIONS FOR ANALYSIS.

The method of "catch" or "struck" weights consists of quartering the contents of the sample package by the trough sampler, but, instead of weighing out exactly 80 grams, the whole product of the quartering which may vary several grams more or less than the required amount, is used for analysis.

The following table shows how results by the two methods compare:

Brand.	Lot.	80 grams weighed out.	"Catch weight" approximately 80 grams weighed out.
A..................	127	99.04	99.02
B..................	138	99.04	99.04
	140	99.01	99.00
	150	98.92	98.92
C..................	313	99.28	99.31
	315	99.37	99.35
D..................	91	99.30	99.26
	106	99.28	99.27
	113	99.30	99.30
E..................	493	99.32	99.34
	497	99.27	99.20
	500	99.15	99.16
F..................	428	99.04	98.97
	449	98.98	99.05
	543	98.82	98.80
	552	98.94	98.97
G..................	32	97.64	97.65
H..................	250	99.25	99.29
I..................	28	98.52	98.50
J..................	92	99.37	99.36
Average............		99.042	99.038

CALIBRATION OF THE FLASKS.

Calibration of the flasks, to the automatic dividing pipette, by the method of repeated delivery, is done by two men working independently and employing for the purpose the regular type of solution used in daily copper determinations.

A difference of one-tenth cc., the equivalent of 0.005 per cent. copper, is easily discernible on the narrow necks of the 2000-cc. flasks and the analysts check each other within that limit.

It has been determined that, throughout the range of normal room temperature, a difference of 1° F. causes a change of volume of 0.46 cc. in 2000, and, since this amount will affect the copper result to the extent of 0.023 per cent., extreme precaution is taken to keep the temperature of the solution constant during the process of calibration.

The flask, during the operation of standardizing, is placed in a small tank through which water, of the same temperature, is flowing from a larger tank. The water in the larger tank surrounds the reservoir of copper solution which is to be siphoned to the pipette (Fig. 4).

Immediately after the requisite number of the deliveries have been made, the flask is placed on a fixed level table while the volume mark is scratched on the neck with a diamond pencil.

The system of water-jacketing obviates entirely all temperature corrections, the maximum variation in temperature of the solution during standardizing being 0.2° F.

The temperature observations are made with long-stemmed thermometers graduated into tenth degrees F.

It has been demonstrated that, in the solution of the ordinary brands of blister and refined copper, the viscosity is the same, and therefore, the rate of flow from the pipette is not affected.

During the process of calibration the evaporation of the copper solution running into the flask has been found to be insufficient to cause appreciable error.

Dividing Pipette.—The 50 cc. dividing pipette (Fig. 4) has a capillary overflow and three-way stop-cock and is water-jacketed for a purpose which will later be explained. This pipette, when constructed in the proper manner, delivers with great accuracy and speed.

The stop-cock and delivery bore should be along the axis of the body of the pipette. For ease in handling, the stop-cock should be rather large.

The delivery bore should be so constructed as to give an unbroken stream for four inches, and there should be no tendency for the retained liquor in the delivery end to spread and draw up on the outside of the tube, nor to run out after delivery for at least a minute.

The manipulation of the stop-cock should always be uniform in manner and speed, the knack of which is readily acquired.

The supply tube, which is also water-jacketed, is connected with a removable siphon which dips
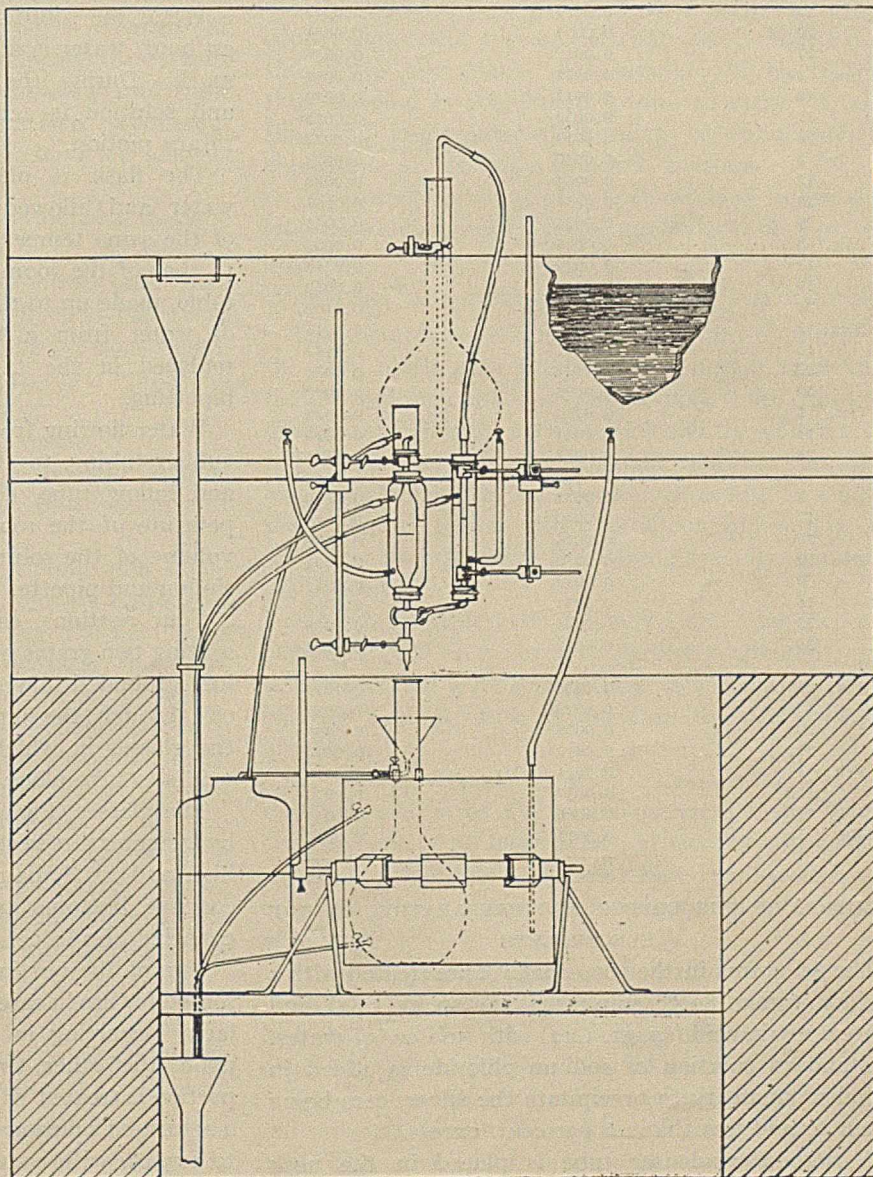

Fig. 4.

into the body of the flask containing the copper solution. On the end of the siphon is a filter of fine bolting-cloth. Suction applied to the pipette starts the action of the siphon.

The delivery of the pipette and the skill of the operator are tested weekly by running off four deliveries from the pipette into 50-cc. glass-stoppered tared flasks.

From our record of the weight of deliveries during the last nine months, the largest average variation in a trial set of four draughts is equivalent to 0.014 per cent. of copper while the average variation in all the trials during this period is equivalent to 0.004 per cent. copper.

VARIATIONS OF DELIVERIES.

Record of variations of deliveries of draughts from pipette in 1909–'10 in copper per cent.

Date. 1909.	Average difference in grams.	Copper per cent.
May 6	0.0010	0.0017
13	0.0027	0.0047
20	0.0031	0.0054
27	0.0017	0.0030
Jun. 3	0.0025	0.0044
10	0.0017	0.0030
17	0.0032	0.0055
24	0.0012	0.0022
July 8	0.0040	0.0078
15	0.0044	0.0080
22	0.0036	0.0063
29	0.0026	0.0043
Aug. 5	0.0004	0.0007
12	0.0029	0.0046
19	0.0017	0.0030
26	0.0060	0.0100
Sep. 2	0.0008	0.0014
16	0.0081	0.0142
23	0.0018	0.0031
30	0.0005	0.0009
Oct. 5	0.0016	0.0028
14	0.0011	0.0020
28	0.0077	0.0135
Nov. 4	0.0023	0.0040
8	0.0022	0.0039
17	0.0040	0.0075
25	0.0074	0.0130
Dec. 2	0.0052	0.0091
9	0.0022	0.0039
16	0.0034	0.0060
23	0.0005	0.0009
30	0.0019	0.0035
1910.		
Jan. 6	0.0008	0.0015
13	0.0029	0.0055
20	0.0005	0.0009
27	0.0012	0.0020
Feb. 3	0.0011	0.0019
17	0.0017	0.0030
24	0.0006	0.0011
Mar. 3	0.0011	0.0019
Average,	0.0026	0.0044

SOLUTION OF THE COPPER AND PREPARATION OF THE ELECTROLYTE.

The 80 grams in the 2000-cc. flask are treated with a cold mixture of 80 cc. sulphuric acid (sp. gr. 1.84), and 200 cc. nitric acid (sp. gr. 1.42) with 500 cc. of water. A standard solution of sodium chloride is added in sufficient quantity to precipitate the silver, care being taken to add less than 20 per cent. excess.

A bulbed condenser tube is placed in the neck before putting the flask on a plate which gradually heats the solution to boiling.

When but little of the ground drillings remain undissolved the solution is boiled gently for one hour.

Systematic examination of the residue left undissolved, by this treatment, has shown that the amount of copper retained in the residue rarely exceeds 0.001 per cent. in the case of normal brands of blister copper.

In the analysis of abnormal samples, bulky insoluble residues containing lead, tin or silica are separated at this point by filtration. The residues or precipitates are completely freed from copper by repeated fusions and precipitations.

When silver chloride is present in quantity sufficient to appreciably affect the volume of the solution, correction is applied to the copper result in accordance with a calculation based on the amount of silver as determined by the silver assay and the specific gravity of silver chloride.

When the solution in the flask has cooled for half an hour, water is added to a little above the 2000 cc. mark. During the addition, mixture of the water and solution is accomplished by giving the flask a rotary motion.

The flask is placed in a large tank containing water and allowed to remain until it becomes of the same temperature as the water and very close to that of the room. It is then removed to the level table, made up to the 2000 cc. mark by the addition of water from a burette, very thoroughly shaken, replaced in the tank and allowed to settle before pipetting.

Water flowing from the tank, through heavy walled rubber tubing, to the jacketed portion of the pipette and inflow tube, corrects the influence of the temperature of the room on the volume of the solution in the siphon and pipette.

Four portions, each representing two grams of the original ground drillings, are run off through the pipette into the glasses in which electrolysis is to take place.

The glasses (Fig. 5) are like hydrometer jars in shape, $6^1/_2''$ high and $2^1/_6''$ diameter with concave bottoms and have a capacity of 180 cc.

Two of the portions are reserved for use in case of irregularity occurring in the work upon the other two. Each portion is treated with 5 cc. of

Fig. 5.

a saturated solution of ammonium nitrate and diluted to 125 cc. with water.

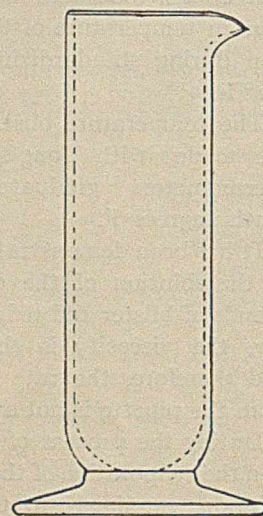Ammonium nitrate, in the quantity added, has proved quite efficient in delaying the deposition of

arsenic and antimony until the electrolyte is completely freed from copper. The electrolyte, at this stage, contains about 3.7 cc. of nitric acid.

ELECTROLYSIS.

The positive electrode is a straight platinum wire extending to the bottom of the jar. The negative electrode is a cylinder $1^3/_4''$ long, $1''$ in diameter, of $0.004''$ irido-platinum foil, all joints gold soldered, having a weight of about 12 grams and depositing surface of $11^1/_2$ square inches. During electrolysis the jar is covered with split watch glasses.

Electrolysis is usually commenced at 5 P.M. with a current of 0.33 ampere per 100 sq. cm. which is kept constant until deposition is completed. In the morning the inside of the jar, the rods of the electrodes and the split watch glasses which cover the jar are rinsed with a spray from a wash bottle.

When deposition is completed, about 20 hours after the commencement of electrolysis, each electrode is quickly detached from the binding posts, the cathode plunged into cold water, then successively into three jars of 95 per cent. alcohol, shaken free of adherent drops and dried over a Bunsen flame for a few seconds after ignition of the film of alcohol.

The weighing of the foil plus the deposit is made with as little delay as possible.

Duplicate results rarely differ more than 0.02 per cent. The practice is to weigh each foil every two weeks and the difference from the previous weighing is rarely more than two-tenths of a milligram, the equivalent of 0.01 per cent. copper.

The foils are burnished when necessary.

The weights used are checked periodically against a set standardized by the Bureau of Standards at Washington.

For the weighing of the foils, a four-inch beam button balance fitted with wide bows is employed. With the full load of about 14 grams the balance is sensitive and accurate to one-twentieth milligram and will make one swing in eight seconds.

The six electrolytic circuits are connected with a conveniently arranged switch and rheostat board. By switch connection an ammeter can be thrown into circuit with any one of the systems.

At night, storage batteries supply the current which is kept constant by the factory watchman. During the day, while the batteries are being charged, the current is from the factory generator plant and its constancy is maintained by the analysts.

A uniform current is essential.

DETERMINATION OF THE AMOUNT OF COPPER LEFT IN SOLUTION AFTER ELECTROLYSIS.

After the electrodes have been removed, hydrogen sulphide is passed into one electrolyte of each sample in order to discover by the color of the precipitate whether an abnormal amount of copper remains in solution.

The electrolytes, duplicates to those subjected to the above treatment, are combined, according to brand, evaporated to small bulk if necessary, neutralized and then slightly acidified with HCl. The retained copper is precipitated as sulphide and filtered off. The filter paper and contents are placed in a porcelain crucible, dried, ignited and the residue dissolved with little hot nitric acid.

Without removal from the crucible, the copper is determined by comparison of the shade of the ammoniacal solution with that of a similar solution containing a known amount of copper. Care is taken that similar conditions prevail when making the comparison. Correction is made for the small amount of copper so determined.

Those electrolytes from which the duplicates do not agree within 0.02 per cent. and such that retain copper equivalent to 0.02 per cent. are excluded from the above operations. The number of electrolytes thus rejected is very small, owing to active circulation and consequent uniformity of completion of deposition in jars with concave bottoms.

The average amount of copper retained in the electrolytes seldom exceeds the equivalent of 0.01 per cent.

CHARACTER AND PURITY OF THE DEPOSITED COPPER.

The ideal deposit, which can only be obtained by the electrolysis of a pure copper solution under the right conditions, is of a salmon-pink color, silky in texture and luster, smooth and tightly adherent.

The presence of even a small quantity of other metallic elements in the electrolyte is apt to modify these characteristics, either as a contaminant or by influencing the shape of the minute crystals that form the deposit.

A slightly spongy or coarsely crystalline deposit, although good in color and perfectly adherent, will invariably give a high result and is a condition to be guarded against quite as much as the deposition of impurity.

A loosely adherent deposit, caused either by too rapid deposition at the commencement or too low a current density at some period of electrolysis, usually shows a red tint and may give a high result on account of oxidation or a low result because of detachment of particles.

A darkly shaded deposit indicates the presence of impurity in greater or less quantity. If it is impossible to complete the deposition without this appearance the electrolyte must be purified.

Very impure copper is so exceptional in our practice that we will merely state, without going into detail, that, from such material bismuth, arsenic, antimony, selenium and tellurium are separated from the pipetted

portion by the addition of ferric nitrate and precipitation with ammonia.

Inasmuch as the deposited copper is never absolutely pure it is necessary that its appreciable impurity should be deducted from its weight. It is, therefore, a part of the general method to make a periodical complete analysis of the deposited copper from each brand of blister. The very small percentage of the impurities found becomes a correction to be applied to the analyses of samples of the corresponding brands.

IMPURITIES IN COPPER DEPOSIT IN DAILY WORK.

150–200 grams of the deposited copper used in the case of each analysis·

Brand.	Per cent. AgCl.	Per cent. Ag.	Per cent. As.	Per cent. Sb.	Per cent. Se and Te.	Per cent. Bi.	Per cent. Pb.	Total Per cent.
A.	0.0046	0.0040	0.0018	0.0029	0.0029	None	....	0.0162
		0.0100	Trace	0.0007	0.0270	"	....	0.0377
	0.0085	0.0015	0.0003	0.0002	0.0017	....	None	0.0122
	0.0130	0.0009	0.0011	None	0.0034	....	"	0.0184
B.	0.0057	None	0.0005	0.0016	0.0064	None	....	0.0107
	....	0.0090	None	0.0014	0.0050	"	....	0.0154
	....	0.0090	"	0.0013	0.0004	"	....	0.0107
	0.0073	0.0006	"	0.0002	0.0022	....	None	0.0103
C.	0.0123	0.0004	0.0022	0.0040	0.0028	Trace	....	0.0217
	0.0210	0.0012	0.0019	0.0027	0.0012	....	....	0.0280
	0.0120	0.0010	0.0013	0.0013	0.0060	....	....	0.0216
	0.0096	0.0041	0.0012	0.0022	0.0017	....	....	0.0188
D.	....	0.0120	None	0.0017	0.0048	0.0003	None	0.0188
E.	....	0.0074	"	0.0011	0.0021	None	"	0.0106
F.	....	0.0115	0.0010	0.0020	....	"	"	0.0045
*.	....	0.0175	0.0030	0.0022	0.0034	"	....	0.0261
*.	0.0123	0.0010	None	0.0016	0.0016	"	None	0.0165
*.	0.0262	0.0044	0.0014	0.0028	0.0010	"	"	0.0358

METHOD FOR DETERMINING COPPER IN REFINED COPPER.

A "catch weight," approximately 5 grams of drillings, is placed in a beaker-shaped dissolving apparatus designed to hold a series of watch glasses. 10.5 cc. of nitric acid, 4.5 cc. of sulphuric acid and 35 cc. of distilled water are added and solution effected on a steam plate.
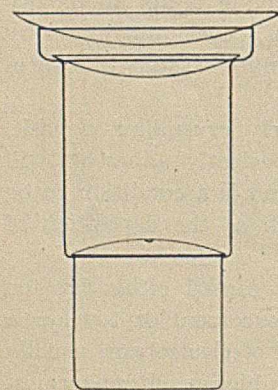
All possibility of loss is prevented by means of the watch glass traps (see Fig. 6).

After the dissolving glass is free from red fumes the watch glasses are rinsed, the electrolyte is made up to 200 cc. with distilled water, five grams of ammonium nitrate added and electrolysis carried on for 21 or 22 hours with a current of 0.47 ampere per 100 sq. cm.

Fig. 6.

The negative electrode is a platinum cylinder of 25 square inches surface. The anode is a spiral platinum wire.

The split watch glasses which cover the flask are rinsed with a spray from a wash-bottle four or five hours before the completion of electrolysis.

After electrolysis the exhausted electrolytes are combined and the amount of copper in solution, always

* Impurities in combined deposits.

less than 0.01 per cent., estimated by the method previously described.

For the purpose of systematically checking the blister copper method of analysis, a standard sample is prepared from the borings of a single bar of furnace refined electrolytic copper.

The shavings from the surface of the casting are separated by hand-picking and rejected together with the fines passing through a 6-mesh screen.

The coarse, clean shavings are subjected to an analysis for copper according to the method just described, using 6 lots of 5 grams each, and also for oxygen and other impurities.

The following table gives the complete analysis of four separate samples of such standard copper:

	A.	B.	C.	D.
Cu + Ag	99.916	99.973	99.9600	99.97400
O	0.068	0.029	0.0400	0.03200
As			0.0002	0.00015
Sb			0.0004	0.00090
Se and Te			0.0002	0.00100
	99.984	100.002	100.0014	100.00805

These analyses are proof of the purity of the deposited copper.

Twice a week, in routine with the regular work, this standard is assayed by the same method which is employed for blister copper. The results are made items of permanent record and indicate, at once, any tendency to error on account of faulty manipulation or apparatus.

CONCLUSION.

In concluding this paper, it is to be noted that one proof of the accuracy of the method lies in the fact that, in the case of the standard copper, results by it agree exactly with those by the exceedingly accurate "five-gram method."

Up to the point of depositing the copper, the accuracy of each step of this method has been verified by experiment, but our experience, and what we have observed of the experience of others, shows that the tendency is to obtain results higher than truth in the process of electrolysis.

Too low a current density or excessive oxidizing power of the electrolyte may produce high results due to oxidation of the deposited copper, while too high a current density or deficiency of oxidizing power in the electrolyte, by causing the deposition of impurities, will have the same effect.

The conditions governing electrolysis must be fixed by rigid investigation.

The salient features of the method are summarized as follows:

The unusually large amount of 80 grams is taken for the purpose of reducing to a very low limit the error pertaining to the use of a sample composed of particles very dissimilar in size and value.

An automatic dividing pipette is employed for the sake of expedition and accuracy.

Constancy of the volume of the assay solution is maintained during the operation of aliquoting by means of water of the same temperature as the solution running through the jacketed portion of the pipette from the tank in which the flask is immersed.

Error in weighing is minimized by the deposition of two grams of copper on an electrode of small area and weight.

With the object of preventing oxidation of the copper by the electrolyte, as high a current density is employed as is consistent with the formation of a smooth deposit.

Active circulation throughout the electrolyte is procured by electrolyzing in a glass having a concave bottom.

Account is taken of deposited impurities and correction is applied appropriate to the brands undergoing assay.

By the weekly testing of the accuracy of the delivery of the pipette and the twice-a-week assay of standard copper, the accuracy of the work is checked.

In developing the method to its present standard of excellence, I wish to acknowledge the assistance of all the laboratory staff who have contributed, but, more especially to Mr. William O'Gorman who has charge of copper determinations and Mr. F. A. Holbrook, formerly first assistant chemist.

I wish, also, to express appreciation to Mr. W. G. Derby, present first assistant chemist, for doing most of the work of preparing this paper and for reading it before the New York Section of the American Chemical Society.

A RAPID METHOD FOR THE ELECTROLYTIC DETERMINATION OF COPPER IN ORES.

By R. C. BENNER.

When the greatest possible accuracy is desired in the determination of copper, recourse is had to the electrolytic method. The great disadvantages in this have been either the length of time it took to make the determination in case of the ordinary method; or (when the deposition is to be quickly made), the necessity of a special piece of complex apparatus, the rotating electrode, or a solenoid. Quite recently it has been found that it is possible, by means of the gauze electrode,[1] to deposit certain metals nearly as rapidly as with either of the pieces of apparatus mentioned. This gives an apparatus which is as simple and costs no more than that in ordinary use; and yet will give results with a rapidity nearly equal to those obtained with the more complicated and costly pieces.

The platinum electrode used in these determinations was corrugated and sand-blasted, cylindrical in shape,

[1] Stoddard, *J. Am. Chem. Soc.*, **31**, 385 (1909); *Chem. News*, **99**, 292.

and about one inch in diameter by one and one-half inches long, made from fifty-two mesh wire gauze.

The accuracy was checked against C. P. copper foil, which had been proven to contain 100 per cent. copper by the ordinary electrolytic method. The copper foil was dissolved in three cc. of nitric acid (sp. gr. 1.4), diluted to seventy-five cc. with water and electrolyzed in from ten to fifteen minutes with a current of about ten amperes and four volts.

Cu taken.	Cu found.	Volume of solution.	Amperes.	Nitric acid.	Time.
0.1181	0.1181	75 cc.	10–15	1 cc.	10
0.3586	0.3584	75 cc.	10	3 cc.	12
0.2330	0.2332	75 cc.	8–10	3 cc.	12
0.2142	0.2142	75 cc.	8–10	3 cc.	15
0.2374	0.2375	75 cc.	8–10	3 cc.	15

The preceding results show that the accuracy is equal to that of the older method. The character of the deposit is all that could be asked for.

The rate of deposition under these conditions will be readily seen from the following results and a glance at the curve.
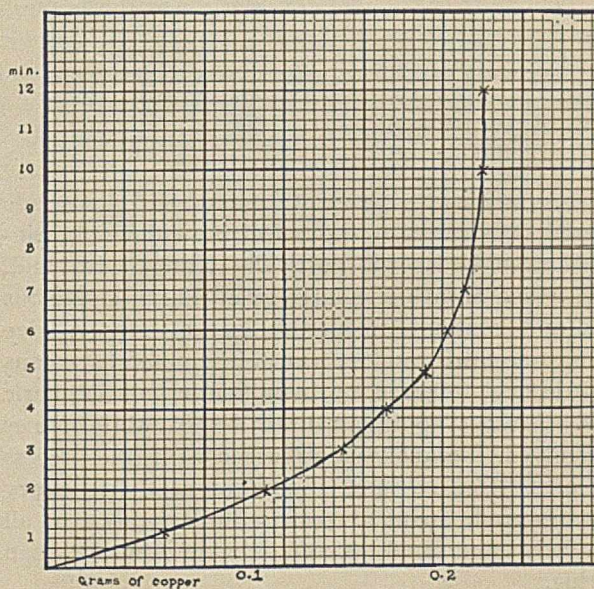
Cu taken.	Cu found.	Volume of solution .cc.	Amperes.	Nitric acid cc.	Time.
0.2203	0.0625	75	10	3	1
0.2203	0.1129	75	10	3	2
0.2203	0.1518	75	10	3	3
0.2203	0.1706	75	10	3	4
0.2203	0.1901	75	10	3	5
0.2203	0.2039	75	10	3	6
0.2203	0.2100	75	10	5	7
0.2203	0.2205	75	10	3	10
0.2203	0.2206	75	10	3	12

All but about seven and five-tenths per cent. is precipitated in the first five minutes, while it takes another five to complete the precipitation. This point is frequently overlooked, especially in technical work, and therefore gives rise to error.

Process for Ores.—From 0.5 to 1.0 gram of the ore, which contains none of the interfering elements, is dissolved in nitric or nitric and hydrochloric acids. When

aqua regia is used, or if lead is present, sulphuric acid is added and evaporation continued until the heavy white fumes of sulphuric anhydride are evolved. The excess of sulphuric acid is neutralized with ammonia and three cc. of concentrated nitric acid added.

Providing sulphuric acid is not added it is only necessary to concentrate to three cubic centimeters. In either case the solution is diluted to 75 cc., transferred to a tall battery beaker, without being filtered (if the residue does not settle it is better to filter) and the copper deposited by means of a current of 8 to 10 amperes and 3 to 4 volts. If the deposit is black or dark colored it is dissolved in nitric acid and redeposited in the same way. This redeposition is, as a rule, easier and quicker than filtering. The following results show the accuracy of this method on ores, as compared with those obtained by the older method.

RESULTS OBTAINED WITH THE GAUZE ELECTRODE.

No. of sample.	Amount of ore taken.	Per cent. Cu in ore.	Copper found.
4	0.5003	0.0825	16.49
4	0.5003	0.0824	16.47
6	0.5003	0.0770	15.39
6	0.5003	0.0769	15.37

RESULTS OBTAINED BY THE ORDINARY METHOD.

4	0.5000	0.0825	16.50
4	0.5000	0.0825	16.50
6	0.5000	0.0770	15.38
6	0.5000	0.0769	15.38

Process for Slags.—In case of slags and other low-grade material it is necessary to select a method of disintegration suited to the particular material in hand. Slags, which always give large quantities of gelatinous silica and contain low percentages of copper, give the most accurate results when disintegrated by means of nitric acid followed by hydrofluoric and sulphuric acids. After evaporation until heavy white fumes are evolved, the analysis is finished as in the process with ores. Redeposition is more frequently necessary with low-grade material than with high-, but in all cases it is more rapid, as well as more accurate, than filtering.

The following will illustrate the accuracy of the procedure:

DETERMINATIONS MADE WITH THE GAUZE ELECTRODE.

No. of ore.	Amount of ore taken	Copper found.	Per cent. Cu in ore.
13	1.0000	0.0060	0.60
13	1.0000	0.0059	0.59
13	2.0000	0.0123	0.61
11	2.0000	0.0103	0.51
11	2.0000	0.0101	0.50

DETERMINATIONS MADE BY THE ORDINARY METHOD.

13	2.0000	0.0121	0.60
13	2.0000	0.0121	0.60
11	1.0000	0.0051	0.51
11	1.0000	0.0050	0.50

Elements which interfere, and at the same time are likely to occur in copper ores, are arsenic, antimony, lead and bismuth. The separation of antimony and bismuth from copper was tried under the preceding conditions but without success. Lead, in such quan-

tities that it will deposit with the copper, is best removed as the sulphate. Arsenic, in small quantities, will not deposit with the copper, but in amounts about equivalent to the copper present begins to be deposited with the last of this. The following series of experiments, in which copper was deposited in the presence of varying amounts of arsenic, illustrates this point.

Arsenic taken.	Copper taken.	Copper found.
0.0605	0.2652	0.2648
0.1210	0.2751	0.2747
0.1815	0.2183	0.2183
0.1210	0.3038	0.3035
0.2420	0.2686	0.3106
....	0.2028	0.2026

All these depositions were made under the usual conditions. From these results it is seen that arsenic, when present in amounts large enough to contaminate the copper deposited, can easily be removed by dissolving the deposited copper and reprecipitating under the same conditions as before. The removal of the interfering elements by chemical means can be accomplished by the following method:

The ore is disintegrated with nitric and hydrochloric acids, five or six cubic centimeters of sulphuric acid added and then it is evaporated until heavy white fumes of sulphuric anhydride are given off. It is now diluted to one hundred and fifty cubic centimeters with water, boiling to insure complete solution of the basic sulphate of iron (a few drops of hydrochloric acid are added if silver is present), filtered and washed with water containing a little sulphuric acid. The lead and silver remain on the filter paper. The filtrate is now heated to boiling and saturated with hydrogen sulphide, allowing the solution to cool during the process. The precipitated copper sulphide is filtered off and washed with water containing hydrogen sulphide. The precipitated sulphides are rinsed from the filter paper into a beaker using as little water as possible, warmed with a little colorless sodium sulphide to remove the antimony and arsenic and again passed through the same filter, being washed with water containing some sodium sulphide. Bismuth is now removed from copper by warming the mixed sulphides with a solution of potassium cyanide alkaline with ammonia. This dissolves the sulphide of copper leaving that of bismuth insoluble. The solution of the copper is boiled with nitric acid to destroy the potassium cyanide and electrolyzed in the usual manner.

UNIV. OF ARIZONA,
    TUCSON.

THE EXACT DETERMINATION OF SULPHUR IN PYRITE AND MARCASITE.

By E. T. ALLEN AND JOHN JOHNSTON.

Technical chemists have regarded the determination of sulphur in pyrite, which serves as the starting point in the manufacture of vast quantities of sul-

phuric acid, of very high importance. The fact is abundantly attested by the great body of literature which has been devoted to the subject. This has been well summarized by Lunge, who has himself made valuable contributions to it.[1] Lunge's well-known method, as formerly carried out, with a slow precipitation of the barium sulphate, gave results which were considerably too low. As since modified by the rapid precipitation suggested by Hintz and Weber,[2] it is more accurate, but, as we have elsewhere shown,[3] the results of the improved method involve a number of variable errors which compensate one another only partially. In the method which we have to propose, the results obtained under carefully regulated conditions are corrected for actual errors by methods which have been fully studied, and though it is less convenient in some respects than Lunge's method and lays no claim to rapidity, it should be of value as an umpire method.

Although the errors in the determination of pyrite and marcasite are chiefly the errors involved in the precipitation of barium sulphate from a solution of sodium sulphate and sodium chloride, very considerable errors may be involved in the grinding of the material.

Oxidation of the Sulphides of Iron in Dry Grinding.— It is well known that the sulphides of iron, especially marcasite, gradually oxidize when exposed to the atmosphere. We have frequently noticed a strong odor of sulphur dioxide on opening a bottle containing any of them, more particularly when finely ground. During the operation of grinding, oxidation appears to be accelerated, probably by the local heating in the disruption of particles.[4] The evolution of sulphur dioxide is not sufficiently rapid to be noticed in the grinding but, as shown below, ferrous sulphate is always found in the ground material. The data follow:

*Pyrite.—*A sample of pure pyrite from Elba was ground for an hour in the agate mortar of a McKenna ore-grinder. The product was washed on a filter paper and the iron and sulphur were determined in the soluble portion.

$$Fe = 0.0117 \text{ g.}^5 \text{ equiv. to } SO_4 \ 0.0200 \text{ g.}$$
$$SO_4 \text{ found } 0.0202 \text{ g.}$$

Another portion of the same sample, ground 6 hours, yielded a water extract which contained:

$$Fe = 0.0253 \text{ g. equiv. to } SO_4 \ 0.0434 \text{ g.}$$
$$SO_4 \text{ found } 0.0435 \text{ g.}$$

*Marcasite.—*A sample of marcasite from Joplin, Mo., also ground six hours and extracted with water, gave:

[1] Report Int. Com. on Analysis, Subcommittee 9, 5th Int. Cong. Applied Chemistry, Rome, 1906, p. 399.

[2] *Z. anal. Chem.*, **45**, 31 (1906).

[3] *J. Am. Chem. Soc.*, **32**, 602.

[4] The ferrous silicates behave in a similar way. See *Mauzelius, Arsbok Sveriges Geologiska Undersökning*, **1907**, No. 3. Hillebrand, *J. Am. Chem. Soc.*, **30**, 1120 (1908).

[5] On the assumption that the soluble iron exists wholly as ferrous sulphate.

$$Fe = 0.0079 \text{ g. equiv. to } SO_4 \ 0.0136 \text{ g.}$$
$$SO_4 \text{ found } 0.0139 \text{ g.}$$

*Pyrrhotite.—*A sample of artificial pyrrhotite containing only a little sulphur in excess of the ratio $Fe : S = 1 : 1$, gave on the same treatment:

$$Fe = 0.0057 \text{ g. equiv. to } SO_4 \ 0.0098 \text{ g.}$$
$$SO_4 \text{ found } 0.0092 \text{ g.}$$

These figures show plainly that ferrous sulphate is formed in grinding the sulphides of iron. The ground material yielded no oxide of iron when digested with 20 per cent. hydrochloric acid (conc. HCl diluted with an equal volume of water); ferrous sulphate and sulphur dioxide are therefore the only products of oxidation and the reaction may be represented by the equation

$$FeS_2 + 3O_2 = FeSO_4 + SO_2.$$
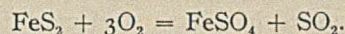
The weights of sulphide taken are not included in the above data, because it was found that a part of the oxidation in these experiments occurred during the washing. To eliminate this error, in the following experiments the ground material was washed in an atmosphere of carbon dioxide. The apparatus, enclosing a funnel with dry filter to which the ground material was transferred, was first exhausted by an ordinary water pump, and filled with carbon dioxide which had been freed from oxygen by heated copper. To remove oxygen more completely from the apparatus the process of exhaustion and filling with carbon dioxide was repeated. The sulphide was now washed with boiled water which had been cooled in carbon dioxide.

OXIDATION IN GRINDING PYRITE.

Time 1 h.

Taken. Gram.	Fe in filtrate. Gram.	Equiv. to FeS₂. Gram.	Per cent. FeS₂ oxidized.
4.11	0.0042	0.0090	0.22
5.77	0.0059	0.0126	0.22

Time 6 h.

4.21	0.0211	0.0451	1.07
6.13	0.0317	0.0679	1.11

A mixture of 99 pts. FeS₂ plus 1.3 pts. FeSO₄ would be formed by the oxidation of 1 per cent. of the pyrite. Such a mixture contains only 53.02 per cent. instead of 53.45 per cent. sulphur. Thus when 1 per cent. of the pyrite is oxidized, the sulphur found in analysis should be 0.43 per cent. too low. This corresponds to a loss of $0.43/0.53 = 0.8$ per cent. of the sulphur originally present. A six-hour grinding may perhaps be regarded as excessive, but it is probable that the time is not so important as the degree of fineness to which the material is reduced. The operation is manifestly one which is likely to vary considerably, differences of pressure on the pestle especially influencing the rate of oxidation. The above figures are not intended as an accurate measure of this rate, but are quoted merely to show that grinding causes oxidation, the errors from which must be considered

in exact work, especially when, as Treadwell directs, the material is ground as fine as possible.[1]

As a matter of fact fine grinding is not necessary in the method given below, except as it enables one to mix inhomogeneous material thoroughly. If the material is not sufficiently homogeneous, the extent of oxidation in the finely-ground sample should be determined in the way just indicated. As far as the analysis is concerned, one can use, perfectly well, material which will pass through a 20-mesh screen. When the sulphides are gently crushed to this size there is scarcely any oxidation as the following experiments serve to prove.

Perfectly bright pyrite from the interior of a solid lump, and therefore presumably free from oxidation, was gently crushed in a hard steel mortar and passed through a 20-mesh screen. 3.75 g. of the screenings were treated with boiled water in an atmosphere of carbon dioxide as above.

Fe in the filtrate = 0.0009 g. equiv. to 0.0019 g. FeS$_2$ or 0.05% oxidized.

In a duplicate experiment, 4.61 g. gave:

Fe in the filtrate = 0.0010 g. equiv. to 0.0021 g. FeS$_2$ = 0.05% oxidized.

Preparation of Material for Analysis.—The samples of the minerals which were used in the subsequent analyses were as pure as could be found. The marcasite was from Joplin, Mo., and the pyrite from Elba. They were further purified from oxidation products in order to obtain uniform samples, as well as to increase the certainty of the analytical determinations. It will of course be understood that such a procedure is not applicable to commercial work. To remove the oxidation products both samples were boiled with 20 per cent. hydrochloric acid until fresh portions of the reagent were no longer colored. They were then washed very carefully in an atmosphere of carbon dioxide. The washing was done first with 20 per cent. hydrochloric acid, then with boiled water cooled in carbon dioxide. The filters and their contents were now transferred to vacuum desiccators which had previously been filled with carbon dioxide. The desiccators were then rapidly exhausted, first by the water pump, then by the mercury pump to a pressure of 1 mm. of mercury or less. These samples were not absolutely homogeneous; each contained a little quartz, but so little that it was believed that any error occasioned by the lack of uniformity was less than the errors of analysis. The samples thus prepared were used for all the subsequent work. They were kept in vacuum desiccators and only exposed to the air long enough to take out portions for analysis.

Determination of the Sulphur. a. Oxidation.—To insure the complete oxidation of the sulphur with absolutely no loss, we employed the method of Carius. About 4 cc. fuming nitric acid entirely free from sulphur were used for the oxidation of half a gram of

sulphide. The sealed tube, containing the sulphide and reagent prepared in the ordinary way, was heated to 125° (maximum) over night.[1] The excess of nitric acid was removed after transferring to a beaker by evaporation to dryness on the steam-bath, the operation being several times repeated with concentrated hydrochloric acid. The beaker was covered with a watch glass so long as there was any danger of loss from spattering.

b. Separation of the Iron.—The sulphate of iron was cooled and brought into solution with water (no acid is necessary), diluted to about 300 cc. and precipitated with sodium carbonate solution (5 per cent. solution of Na$_2$CO$_3$ is suitable) with constant stirring. *Only a slight excess* should be used. The addition of a few drops of ammonia makes the precipitation complete. The precipitate settles well after warming on the steam-bath. Sodium carbonate was used instead of ammonia, because, as will be explained farther on, the losses of sulphur are much increased when barium sulphate is precipitated from ammonium sulphate. The precipitate of ferric hydroxide was now filtered and washed; to insure the complete separation of sulphur it was redissolved in the least possible quantity of 20 per cent. hydrochloric acid, and the iron reprecipitated. The second filtrate and washings were kept separate from the first.

c. Precipitation of the Sodium Sulphate by Barium Chloride.—Each of the above filtrates was now brought to a volume of about 350 cc., either by dilution or evaporation as the case may require. The solutions were just acidified by hydrochloric acid, with the aid of a drop or two of methyl orange, then 2 cc. 2 per cent. hydrochloric acid (1 vol. conc. HCl diluted to 20 vol.) were added to each. In the precipitation of the barium sulphate, as will be explained farther on, the rate at which the reagent (22.5 cc. in quantity)[2] is added is all important. This is best regulated by attaching a capillary tip to the burette. The right diameter may be found by a few trials. The sulphate solutions were heated boiling hot and vigorously stirred while the reagent was allowed to flow down the side of the beaker. The precipitates were then left[3] to stand for about 18 hours, when they were filtered on paper and washed with hot water, till 25 cc. washings showed only the faintest opalescence with silver nitrate. Filtering and washing thus requires usually 1–1¼ hours. The wet paper and precipitate were then heated *very slowly and carefully* in a platinum crucible, and finally, when the combustion was complete, ignited to constant weight.

---

[1] "Quant. Anal.," trans. by Hall, p. 281.

[1] The glass tubes were heated in long steel bombs containing water, which served to compensate the pressure inside. This apparatus was at hand for other work and was used as a matter of convenience, but it was doubtless unnecessary.

[2] 0.5 g. pure FeS$_2$ requires about 21 cc. of 10 per cent. BaCl$_2$ solution, i. e., 10 g. BaCl$_2$ 2H$_2$O in 100 cc. H$_2$O.

[3] A Gooch crucible may be used, but precipitates formed in solutions containing very little acid are voluminous and inclined to clog the asbestos filter.

d. Errors in the Determination of Sulphur and their Corrections.[1]—When a precipitation of barium sulphate is thus made from a solution of sodium sulphate, the weight of the precipitate is always too low. The authors have made a detailed study of the errors in the above case and of the methods of correcting them; these will here be briefly summarized:

1. The removal of nitrates is necessary, as has long been recognized; barium sulphate carries down nitrates and consequently the results are too high.

2. The solubility of the barium sulphate, of course, occasions a small loss, which is, however, much increased by free acid. With the quantity recommended, 2 cc. 2 per cent. HCl in a volume of 350 cc., and an added volume of 350 cc. washings, it amounts to 1–2 mg. only. It is not increased by the presence of sodium chloride. The solubility is determined in the usual way by evaporation of the filtrate and washings to dryness in a platinum basin, taking up with a little water and washing on a small filter, burning and weighing the precipitate.

3. All barium sulphate precipitates which have formed from alkali sulphates contain a number of impurities: barium chloride, alkali sulphate and *"free" sulphuric acid*, probably in the form of acid sulphate of the alkali metal. The quantity of alkali sulphate carried down by barium sulphate depends on many conditions, the most important of which are the quantities of free acid and alkali chloride present in the original solution. Barium sulphate from pure sodium sulphate carries down about 0.5 per cent. of the latter. This is more than doubled in the presence of much sodium chloride. The quantity may be determined by dissolving the weighed precipitate in 15 cc. concentrated sulphuric acid and pouring the cooled solution into about 300 cc. water with constant stirring. The precipitate and solution are heated some time and then filtered. The filtrate is carried to dryness in platinum under a hood with good draft and finally heated to redness. The residue is dissolved in a little water, filtered into a small tared dish, evaporated again to dryness, heated to redness, and weighed. This process does not extract all the sodium sulphate. Experiment has shown that the addition of 10 per cent. more to the quantity thus extracted will give the total amount with sufficient accuracy. If the analysis is made according to the directions in this paper, the quantity of sodium sulphate obtained by a single extraction in the precipitate should be close to 8.3 mgs. and the correction for it found by multiplying this quantity plus 10 per cent. by the factor $(BaSO_4-Na_2SO_4)/Na_2SO_4$, 5.8 mgs. If the iron is precipitated by ammonia the solution will, of course, contain ammonium sulphate and the barium sulphate precipitated from it will contain a considerable quantity of ammonium sulphate, which volatil-

izes when the barium sulphate is heated, thereby occasioning a loss considerably larger than that caused by the non-volatile sodium sulphate. Naturally, if corrections are to be made, they should, in the interests of accuracy, be kept as low as possible.

4. *The Loss of Sulphuric Acid by Volatilization.*—Barium sulphate which has been precipitated from solutions of any of the alkali sulphates contains some "free" sulphuric acid, or presumably, acid sulphate of the alkali metal. This acid is lost on heating, though the precipitate remains quite neutral. This remarkable fact has been fully substantiated by many experiments. The losses are much increased by two conditions—the presence of free acid and of alkali chloride, and will easily surpass one per cent. of the total sulphur if the quantity of both these substances is not carefully limited. There is another condition also that exercises an important influence on it, *viz.*, the speed of precipitation. If this be rapid (ca. 10 secs.), the quantity of "free" sulphuric acid is lowered and under certain conditions practically vanishes. The determination of the volatility loss is best made by heating in a platinum boat, inside a platinum combustion tube, a precipitate formed under the same conditions as the one which is weighed. With the outlet of the combustion tube is connected a Liebig potash bulb containing 10 cc. water and 1 cc. perhydrol free from sulphur. When the loss is comparatively large, two bulbs are needed and the quantity of perhydrol is increased. As a precaution it is well to rinse the combustion tube with water after the experiment. With the conditions recommended, the error from this cause is only 0.6 mg. for 2 g. precipitate, corresponding to 0.03 per cent. of the total sulphur.

5. *The Occlusion of Barium Chloride.*—All freshly precipitated barium sulphate contains some barium chloride. This amounts to only about 0.15 per cent. in precipitates which are slowly formed in sodium sulphate solutions; it introduces no error in the determination, because the chloride is transformed by the occluded sodium sulphate during ignition into barium sulphate and hydrochloric acid, and all but a trace of the chloride is thus eliminated. If the precipitation is rapidly made, the amount of chloride in the precipitate is much greater and several tenths of a per cent. remain in the precipitate after heating to redness. Thus another correction is necessitated.

6. *Effect of the Time of Standing on the Composition of Barium Sulphate Precipitates.*—When precipitates are left to stand in the liquid from which they are thrown down, they slowly change in composition, approaching somewhat nearer to pure barium sulphate. The process is accelerated to some extent by heating, though the addition of a large excess of barium chloride has no effect. In exact determinations of sulphur, therefore the barium sulphate should not be filtered

---

[1] For a full discussion of this subject, see *J. Am. Chem. Soc.*, **32**, 604-6.

at once for in that case the losses from both occlusion and volatilization are higher. 18 hours is a practical time to allow before filtering. The corrections given in this paper imply this condition. The authors have found that the corrections discussed in the preceding paragraphs are quite constant when the prescribed conditions are strictly adhered to. In the analyses which follow, the results have therefore been corrected by the use of constants previously determined under similar conditions.

One analysis each of pyrite and marcasite was made exactly according to the method described above; two others were made by a slightly modified method in which magnesium oxide[1] was used to precipitate the iron. This method has the advantage that the results obtained by it, require only a solubility correction, for magnesium sulphate is carried down by barium sulphate in almost negligible quantity. This error, which lowers the result slightly, is practically compensated by the presence in the precipitate of a little barium chloride (0.10–0.15 per cent.). The volatility loss is a mere trace. The method has the disadvantage that the precipitated iron (or probably the excess of magnesium oxide in it) retains sulphur persistently. Three precipitations were in fact required to recover all the sulphur.

ANALYTICAL DATA I.

Pyrite.—*a.* Sodium carbonate method:

0.5208 g. pyrite gave	2.0184 g. BaSO$_4$.
Corr. for solubility[2] 2.0	
Corr. for occlusion of Na$_2$SO$_4$ ..5.8	
Corr. for volatility..........0.6	
Total corrs.................	0.0084
	2.0268 g. = 53.46% S.

b. Magnesium oxide method:

0.4685 g. pyrite gave ....1.8227 g. BaSO$_4$.	
Corr. for solubility ....0.0036[3]	
	1.8263 g. = 53.53% S.

Marcasite—*a.* Sodium carbonate method:

0.5005 g. marcasite gave ......1.9328 g. BaSO$_4$.	
Corr. as under pyrite (*a*) 0.0084	
	1.9412 g. = 53.28% S.

b. Magnesium oxide method:

0.5026 g. marcasite gave ......1.9476 g. BaSO$_4$.	
Corr. as under pyrite (*b*)......0.0036	
	1.9512 g. = 53.33% S.

A few determinations for the sake of comparison have been made by Fresenius' and by Lunge's method both somewhat modified. The results have also been corrected for the errors already discussed. Even after correction, however, we do not regard the results *on coarse material* as equal in accuracy to those just given.

Corrected Analyses by Fresenius' Method.—It is

[1] The reagent was carefully freed from lime and sulphur.

[2] The correction for solubility is 1 mg. for each of the two solutions. Both were brought to a volume of 350 cc. so that the same correction might be used for both.

[3] The correction obtained experimentally is multiplied by 3 because three precipitations, and therefore three solubility corrections, were necessary.

commonly directed in this method to pulverize the sulphide before fusing with sodium carbonate. But since we have shown that this operation may involve a considerable error, the following analyses were made on the 20-mesh material. Only in details was there any change in the ordinary procedure. For the sake of certainty in correction, we fused with a mixture of 4 pts. sodium carbonate and 1 pt. sodium nitrate (instead of nitre).[1] Six grams of the mixture were used. The fusion was heated in a platinum crucible, first over a burner and finally for a few minutes over the blast; meanwhile, it was protected from the sulphur of the flame by a good-fitting asbestos board. The cooled fusion was extracted with water and the precipitate well washed. The iron was redissolved and reprecipitated as described under the first method. Both filtrates were brought to about 350 cc. and acidified as there described; the remainder of the procedure is also the same in every way. In correcting the weight of the precipitate it must be remembered that the sulphate was precipitated from a solution containing close to 6 g. of sodium chloride, the amount yielded by 6 g. of the above fusion mixture. The presence of this salt makes a considerable difference in the composition of the precipitated barium sulphate and therefore in the corrections to be applied to it. The occluded sodium sulphate amounts on the average to 17.4 mg. (for 2 g. precipitate) and the correction for it (after an allowance of 10 per cent. for incomplete extraction) 12.2 mg.; the average volatility loss is 5.9 mg., while the solubility loss remains unchanged, 2.0 mg. The sum of these corrections is 20.1 mg.[2]

ANALYTICAL DATA II.

a.

0.5031 g. pyrite gave.......1.9346 g. BaSO$_4$.	
Sum of corrs. as above 0.0201	
	1.9547 g. = 53.37% S.

b.

0.4815 g. marcasite gave.......1.8421 g. BaSO$_4$.	
Corrs. as above...............0.0201	
	1.8622 g. = 53.13% S.

c.

0.4758 g. marcasite gave ....1.8194 g. BaSO$_4$.	
Corrs. as above...............0.0201	
	1.8395 g. = 53.11% S.

Corrected Results by Lunge's Method.—The weighed quantity of sulphide crushed to 20-mesh size was allowed to stand over night in the cold with 10 cc. of a mixture of 3 vol. conc. nitric acid and 1 vol. conc. hydrochloric acid. The solution was then evaporated on the steam bath, first without, then several times with hydrochloric acid to remove the nitric acid. The remainder of the analysis was exactly like the method proposed and described above.

[1] The correction constants were determined on precipitates of barium sulphate which were thrown down in solutions containing *only sodium salts.*

[2] The correction constants were determined on precipitates formed in the presence of 5 g. and 10 g. NaCl respectively. The occlusion number is practically identical for both. The volatility losses are 5.2 mg. and 8.8 mg. respectively; by interpolation we obtain 5.9 mg. for 6 g. NaCl.

ANALYTICAL DATA III.

a. 0.5100 g. pyrite gave........ 1.9659 g. BaSO$_4$.
     Corrs. previously given, I..... 0.0084
                             ————

                             1.9743 g. = 53.18% S.
b. 0.5315 g. marcasite gave..... 2.0417 g. BaSO$_4$.
     Corrections as above......... 0.0084
                             ————

                             2.0501 g. = 52.99% S.
c. 0.5127 g. marcasite gave..... 1.9722 g. BaSO$_4$.
     Corrections as above......... 0.0084
                             ————

                             1.9806 g. = 53.07% S.

CORRECTED RESULTS.

	Pyrite.	Marcasite.
Authors' method.......................	53.53	53.33
	53.46	53.28
	———	———
	53.49 Av.	53.30 Av.
Fresenius' method modified...............	53.37	53.13
		53.11
		———
		53.12 Av.
Lunge's method modified	53.18	52.99
		53.07
		———
		53.03 Av.

The concordance in the duplicates given above shows that the determinations were carefully done. We ascribe the lower results by Fresenius'[1] and Lunge's methods to a loss of sulphur during oxidation. In the last determination of the sulphur in marcasite, a little unoxidized sulphur was in fact noticed. The loss probably would not have occurred had the material been finely ground, but if fine grinding is resorted to another error is introduced. The Carius method of oxidation avoids both errors.

Control of Sulphur Determinations.—For the sake of control, 5-g. portions of both pyrite and marcasite were subjected to qualitative analysis. Except for a trace of copper in the marcasite only silica was found: 0.04 per cent. in the pyrite, and 0.20 per cent. in the marcasite. As a final check on the accuracy of the sulphur determination, it seemed desirable to determine also the amount of iron in portions of the same purified pyrite and marcasite.

DETERMINATION OF THE IRON.

1. *Volumetric.*—About 0.25 g. substance was decomposed in the usual way with 10 cc. of a mixture of 3 parts conc. HNO$_3$ to 1 part conc. HCl. The excess of acid was gotten rid of by evaporating with sulphuric acid, first on the water bath and finally over a free flame, until voluminous white fumes appeared. The residue was dissolved and diluted with water to about 200 cc., nearly neutralized with ammonia,[2] reduced with sulphur dioxide,[3] and titrated as usual with permanganate solution, in the presence

of sufficient added sulphuric acid. A weight burette was used throughout. The permanganate solution was standardized by means of sodium oxalate ("nach Sörensen," obtained from Merck), which had been previously heated for an hour at 240°.[1] As a result of several closely agreeing determinations, 1 g. KMnO$_4$ solution = 0.002633 g. Fe. A number of blank experiments were performed, and the amount of permanganate used up in them, varying from 0.05 to 0.07 g., was subtracted from the quantity used in titration. The amounts given below have been corrected in this way.

  (a) 0.2682 g. pyrite required (1) 47.62 g., (2) 47.54 g. permanganate.
  (b) 0.2682 g. pyrite required (1) 47.53 g., (2) 47.63 g. permanganate.

The percentage of iron from these four analyses is therefore: 46.75, 46.67, 46.66 and 46.75; the mean value is 46.72 per cent. Fe, whereas FeS$_2$ requires 46.55 per cent. Fe.

  (a) 0.2576 g. marcasite required 45.62 g. permanganate.
  (b) 0.2719 g. marcasite required (1) 48.01 g., (2) 48.06 g. permanganate.

The percentage of iron from these three analyses is 46.63, 46.49 and 46.54; the mean value is 46.55 per cent. Fe.

2. *Gravimetric.*—The first determinations of the iron were made by the gravimetric method. To our surprise, they were all unaccountably high. As a result of some study it may be said that determinations by this method are invariably too high if certain precautions are not taken, and in view of the importance of the method our experience is here included.

If the precipitation is done in *platinum* by *pure ammonia*, the results leave little to be desired. In the following determinations, the sulphide was dissolved in aqua regia, the excess of acid removed by evaporation, the residue dissolved and filtered into platinum and twice precipitated by pure ammonia. In this precipitation the details given by Lunge were followed, *viz.*, the liquid was heated to a temperature of 40–50°, the ammonia added and the whole then heated to boiling. In the second precipitation macerated filter paper was added to the solution to make the ignited precipitate more porous and to insure the complete reoxidation of any magnetite formed in the burning.[2] The second precipitate was thoroughly washed by the aid of the pump. The ammonia used was purified by distillation, the washed vapors being absorbed by water in a ceresin bottle; 25 cc. of this ammonia gave no weighable residue.

  Pyrite (a) 0.5272 g. gave 0.3504 g. Fe$_2$O$_3$; Fe = 46.46%.
        (b) 0.5344 g. gave 0.3557 g. Fe$_2$O$_3$; Fe = 46.53%.

The mean value, 46.49, agrees very closely with the theoretical number for FeS$_2$, *viz.*, 46.55 per cent. Fe.

---

[1] The possibility that a loss of SO$_3$ may be caused by the contamination of the precipitate by iron should also be considered. In Fresenius' method, a little iron is dissolved when the fused mass is leached by water. This iron would probably be carried down by the barium sulphate as ferric sulphate, which would lose sulphur on ignition. See Jannasch and Richards, *J. pr. Chem.*, **39**, 321; E. A. Schneider, *Z. physik. Chem.*, **10**, 425, 1892.

[2] In presence of much free acid the reduction is incomplete. Private communication from W. F. Hillebrand and R. S. McBride.

[3] In every case complete reduction was assured by testing a drop of the liquid with thiocyanate.

---

[1] This heated salt (as was afterwards observed) reacted very slightly alkaline, due to the formation of a *trace* of sodium carbonate, but cannot account for the fact that the volumetric results are somewhat higher than the final results obtained by precipitation with ammonia. Any other impurity in the oxalate, if neutral to permanganate, would of course make the percentage of iron too high.

[2] W. F. Hillebrand, *Bull. U. S. G. S.* **305**, p. 88.

Marcasite (a)　0.5028 g. gave 0.3344 g. Fe_2O_3; Fe = 46.49%.
　　　　　(b)　0.5209 g. gave 0.3471 g. Fe_2O_3; Fe = 46.57%.

The mean value is 46.53% Fe.

A Common Error in the Gravimetric Determination of Iron.—From several private communications, as well as from our own experience, it appears that the results obtained from gravimetric determinations of iron are generally too high, and by an amount which may well be 2 per cent. of the total iron present. Nevertheless, there appear to be no specific references to this fact in the literature. The first two analyses of pyrite made by us gave identical results, 47.45 per cent. Fe, which are certainly much in excess of the true value. These analyses were performed exactly as described above, except that the iron was precipitated in beakers of Jena glass by means of ammonia, the purity of which had not been recently controlled. This was confirmed by a number of analyses of a solution of ferrous ammonium sulphate, in which the conditions of oxidation and precipitation were varied; the results, however, varied only from 0.004590 to 0.004623 g. Fe per g. solution, as compared with 0.004524 obtained volumetrically.

It was now found by evaporation in platinum that the ammonia left a residue; this ammonia had been redistilled not long before; nevertheless, from 25 cc. of it (about the amount used in a double precipitation), insoluble residues weighing 3.0–3.2 mg., were obtained. Now, since the usual weight of a precipitate of Fe_2O_3 is from 300–350 mg., it is evident that this source alone may be responsible for an error of as much as 1 per cent. of the total iron. The ammonia was therefore subjected to redistillation and the washed vapors absorbed by water in bottles of (1) ordinary glass, (2) Jena glass, and (3) ceresin (such as are used for hydrofluoric acid).

Direct tests made one month later showed the amount of residue from 25 cc. ammonia from each of these to be respectively: (1) 0.7 mg.,[1] (2) 0.4 mg., (3) 0.0 mg. The ceresin bottle is thus entirely satisfactory;[2] the others have been attacked by the ammonia to a slight extent, but sufficient to produce an error in the determination of iron, which is not negligible.

That impurity in the ammonia is not responsible for the whole error is evident from the following analyses, in which the iron was precipitated twice in Jena glass beakers by means of *pure* ammonia: (a) 0.5048 g. pyrite gave 0.3383 g. ppt., whence Fe = 46.85 per cent. (b) 0.5239 g. marcasite gave 0.3514 g. ppt., whence Fe = 46.89 per cent.

[1] The distillation of this ammonia was conducted with very great care. The much larger amount of impurity given above is not to be referred to any special lack of care during the distillation, and that such an amount is not exceptional is shown by the uniformly high results of a number of analyses in which other samples of ammonia were used. However that may be, the figures represent real amounts, which may be encountered by any one who does not specially control the purity of the ammonia he uses.
[2] Such bottles are used to some extent for this purpose. The magnitude of the errors caused by ammonia which has been kept in glass does not appear to have been generally recognized.

Thus the error is still fully 0.6 per cent. of the total iron. Further, special experiments undertaken with the purpose of tracing down this source of error showed that the use of glass beakers was responsible, and that by discarding glass entirely, and by making the precipitations in platinum vessels, satisfactory results are obtained.

The definitive determinations of iron in pyrite and marcasite were made under these conditions, and as we have seen, correct results were obtained. It is evident that it is necessary to guard against these sources of error whenever ammonia is used as a precipitant; they may exert a specially large influence in the determination of aluminum, on account of its low atomic weight and of the fact that it is frequently determined by difference.

If it is necessary to determine both iron and sulphur in the same sample, the use of sodium carbonate for the precipitation of the iron is advisable on account of larger errors otherwise involved. Experience has shown that it is safer to add the sodium carbonate slowly, and in dilute solution (in order to diminish occlusion), and that it may sometimes be necessary to make more than one subsequent precipitation with ammonia, in order to obtain precipitates free from all foreign material.

COMPLETE ANALYSES OF PYRITE AND MARCASITE.

	Pyrite.	Marcasite.
Fe	46.49[1]	46.53[1]
S	53.49[1]	53.30[1]
SiO_2	0.04	0.20
	100.02	100.03

We have selected the gravimetric results for iron as nearer the truth; if the volumetric numbers are used, the summations become 100.25 for pyrite and 100.05 for marcasite.

Comparison of Authors' Method with that of Hintz and Weber.—We have elsewhere shown that the method of Hintz and Weber, though a great improvement on those which preceded it, depends on a compensation of variable errors. The following figures (their best) give an idea of the accuracy.[2]

Assistant I.	Assistant II.
48.25	48.15
48.62	48.41

The variations in the work of each analyst are: I, 0.37 per cent., and II, 0.26 per cent., of the pyrite, or 0.7 per cent. and 0.5 per cent. of the total sulphur. Our own results show variations of 0.07 per cent. and 0.05 per cent. of the sulphide, =0.13 per cent. and 0.10 per cent. of the total sulphur. These are the results obtained by using Carius' method in the oxidation; the results of the other methods, although they indicate a loss of sulphur, show equal *uniformity* in the *determination of the sulphur present.*

Application of the Method to Other Insoluble Sulphides.

[1] Average of two determinations.
[2] *Z. anal. Chem.*, **45**, 44 (1906).

—Although we have not tried the method proposed in this paper in the analysis of other sulphides, the principles which we have discussed, *viz.*, the error involved in the grinding of sulphides, the method of oxidation and the corrections for barium sulphate precipitates, would appear to be of perfectly general application. In the case of sulphides like those of antimony and bismuth in which not all the sulphur would be in soluble form after oxidation, an excess of sodium carbonate would be required to transform it all into sodium sulphate, and the excess of sodium carbonate, of course, would have to be subsequently changed into sodium chloride, which, as we have seen, increases the errors due to occlusion and volatility. The method, however, is still applicable, though the errors would have to be determined for each special case.

SUMMARY.

It has been shown that when the sulphides of iron are ground for analysis, they suffer partial oxidation to sulphur dioxide and ferrous sulphate. If they are finely pulverized this error is not negligible; it may be reduced to 0.05 per cent. by gentle crushing to 20-mesh size, which is sufficiently fine for the proposed method of analysis. Inhomogeneous material, such as would be met with in commercial work, would have to be pulverized for the purpose of accurate sampling. In that case, the error could be determined by washing a weighed portion of the powder with boiled water in an atmosphere of carbon dioxide, and determining the iron in the washings; the operation is rather exacting on account of the readiness with which the moist sulphide oxidizes.

In the proposed method, the sample is oxidized in sealed tubes, according to Carius; this avoids all possible loss of sulphur. Lunge's and even Fresenius' method gave in our hands lower results, a fact which we attributed to a loss of sulphur during oxidation, occasioned by the use of coarse material, or perhaps, in Fresenius' method, to the presence of iron in the barium sulphate.

The iron is removed by two precipitations with sodium carbonate. The object of this is to avoid ammonium salts, which cause much larger losses of sulphur. In precipitating the barium sulphate several conditions must be carefully followed, *viz.*, the free acid must be reduced to a small measured quantity, and the precipitation must be made at a measured rate. These two conditions are necessary because they determine the composition of the precipitate, which is not pure barium sulphate, while the first determines also the loss by solubility.

In every case, three corrections must be made on the weight of the barium sulphate precipitate: (1) a correction for solubility of the precipitate, which depends on the volume of the solution and the quantity of free acid it contains; (2) a correction for the occlusion of sodium sulphate by the precipitate, which depends on many conditions, but chiefly on the quantity of alkali chloride originally present in the solution; (3) a correction for a certain amount of free sulphuric acid lost on ignition. This is not due to any sort of decomposition of the barium sulphate, but to the presence in the precipitate of "free" sulphuric acid, probably in the form of sodium acid sulphate. The most important conditions affecting this error are the quantity of free acid and of sodium chloride in the solution, and the rate at which the precipitation is made; an increase of either acid or sodium chloride increases the error; a rapid rate of precipitation decreases it, but so far as our experiments have been carried, there is not in this case sufficient uniformity in the results to allow of satisfactory corrections. Constants may be used in making all these corrections if the conditions set down are carefully followed, but otherwise they must be determined by methods given in the body of this paper. These corrections have been fully worked out by studying the precipitation of pure sodium sulphate under various conditions. The analytical data on the sulphides appear the more certain since they have been controlled by complete analyses of material which gave both positive and negative evidence of nearly theoretical purity.

The sum of the errors in this method, apart from that involved in the grinding, should not be over 0.2 per cent. of the total sulphur. The extreme variation in our own analyses was less than 0.15 per cent. and the agreement was equally good when other methods of oxidation were combined with our own scheme of precipitation and correction. Hintz and Weber's method for sulphur in pyrite is the best hitherto described; its essential features are oxidation according to Lunge, and a rapid precipitation of the barium sulphate. Their own best published results, however, vary from 0.5 per cent. to 0.7 per cent. of the total sulphur.

Incidentally, it was learned that the precipitation of iron by ammonia involves much larger errors than have generally been supposed, if, as is customary, the ammonia is kept in glass bottles and the precipitation is made in glass beakers. The same error would affect the precipitation of alumina and other similar oxides.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTION OF WASHINGTON,
WASHINGTON, D. C., March 3, 1910.

EXAMINATION OF CANDELILLA WAX.

By R. F. HARE AND A. P. BJERREGAARD.

Description of the Plant.—The wax here reported upon is found coating the entire surface of a plant that grows wild in the semi-arid regions of northern Mexico and southern Texas. The plant is reported

to be abundant over large areas of this section, where it occurs as bunches of leafless, reedlike stems 2 to 4 feet high and from ¼ to ½ inch in diameter. The common name given to the plant by the Mexicans is candelilla. According to competent botanical authorities it is in all probability *Euphorbia anti-syphilitica*.[1]

Preparation of the Wax.—The stems of this plant received by us from Mexico were tied in bundles, thrown into a vessel of cold water and weighted down to prevent them from floating. The water was then heated to boiling, when the wax melted and rose to the surface. After cooling, the impure cake of wax which floated on the water was removed and dried. In this condition it was of a dark brown color, due

90 per cent. benzene mentioned above was found to be an excellent solvent when hot. The hot solution from all of these solvents gelatinized to a pomade-like mass on cooling. Upon slow evaporation from dilute solution it formed white cauliflower-like masses. An examination under the microscope showed no crystals or polarization effect in either the pomade mass or the solid formed from slow evaporation of the dilute solution. The wax obtained in the manner described above had 0.64 per cent. ash which was practically pure calcium carbonate. Some of the physical and chemical constants of candelilla wax are given in the following table along with those of carnauba wax, beeswax and chinese insect wax as given by Lewkowitsch.

CONSTANTS OF WAXES.

| | Candelilla wax. | | | | |
	Original state.	Rendered ash-free.	Carnauba wax.	Beeswax.	Chinese insect wax.
Specific gravity at $\frac{15°}{15°}$ C.	0.9825	..	0.990–0.999	0.964–0.970	0.926–0.970
Melting point.	67–68° C.	..	85–86° C.	61.5–64.4° C.	80.5–83° C.
Solidifying point.	64.5° C.	..	80–81° C.	60.5–62.8° C.	80.5–81° C.
Acid value in mg. KOH.	12.4	17.4	4–7	16.8–21.2	....
Saponification value in mg. KOH.	64.9	84.1	79–95	90–98	80.5–93
Iodine absorption.	36.8	33.6	13.5	7.9–11	....
Unsaponifiable matter, per cent.	91.17	84.2	55	52–56	....
Ash, per cent.	0.34	00.0	0.43	....	....
Fatty acids, per cent.	6.57	....	....	....	....
Refractive index.	At 71.5° C. 1.4555	....	At 80° C. calc. to 40° C. 1.471	At 62° C. 1.4455	....

to presence of minute fragments of bark and other foreign matter. The wax was purified by dissolving in hot chloroform, filtering hot and removing the chloroform by evaporation over the water bath. It was then further purified by dissolving in a boiling mixture of three parts absolute alcohol and two parts of 90 per cent. benzene. This solution was filtered hot and the solvents again removed by evaporation over the water bath. The product thus obtained was a pale grayish yellow, opaque solid, the opacity being caused by a small amount of water. When the sample was melted and dried, it lost 6.36 per cent., became translucent and assumed a brownish yellow color. The amount of wax obtained in this form amounted to about 2.5 per cent. of the partially dried plants.

Examination of the Wax.—The hardness of this wax on the mineral scale was found to be between 1 and 2. It was harder and more brittle than beeswax, but not so hard and brittle as carnauba wax. It had the odor of beeswax, and this is much more pronounced when the wax was warmed. It was but slightly soluble in cold ether, chloroform, alcohol, turpentine, gasoline, carbon bisulphide and acetone, but readily soluble in all of these when hot. Mixing these solvents was not usually found to improve the solubility when cold, but the mixture of alcohol and

It will be seen from the table that the specific gravity, melting point, solidifying point, acid value, and refractive index of candelilla wax is intermediate between beeswax and carnauba wax. The saponification value is lower than either. The iodine absorption (Hanus method) and per cent. unsaponifiable matter are both much greater than either.

The unsaponifiable matter did not increase in weight on attempted acetylation. It was a dull brittle waxy mass of a dark ochre-yellow color soluble in hot absolute alcohol, chloroform and acetic anhydride. The whole solution solidified on cooling to a white pomade-like mass similar to that of the original wax. The unsaponifiable matter dissolved in hot gasoline, and in a hot mixture of chloroform and acetic anhydride, and in both cases the solution remained clear on cooling. Concentrated sulphuric acid added drop by drop to the latter solution caused a purplish red color with faint yellowish green fluorescence. The color did not change on standing but the fluorescence became olive colored. Dissolved in chloroform, cooled and an equal volume of concentrated sulphuric acid added, a yellow color resulted. After shaking and settling the upper layer was very pale yellow and the sulphuric acid layer dark ochre colored. Dissolved in acetic anhydride and a drop of 60 per cent. sulphuric acid added a pale violet pink color appeared (Liebermann-Storch reaction). It dissolved completely in warm concentrated sulphuric acid with a reddish brown

[1] A description of this plant is found in *De Candolle Prodromus*, **15**, Pt. 2a, 69.

color. On dilution and standing several hours the solution became pale lavender, while a dark olive-green semi-solid floated on top. This sample of unsaponifiable matter began to soften at about $75°$ C., but was not sufficiently liquid to flow at $125°$ C. It contained considerable ash not readily soluble in water, but soluble in dilute acid. The ash was found to contain some lime.

The low saponification value obtained by us was probably not due to insufficient saponification, as the wax was digested for five hours in very strong solution of caustic soda prepared by dissolving sodium in alcohol admixed with an equal volume of purified gasoline.

The wax acids separated from the soaps obtained in the saponification were dark brown, softer than the original wax and free from ash.

The wax was prepared ash-free by dissolving in boiling glacial acetic acid and pouring the hot filtered solution into an equal volume of cold dilute hydrochloric acid. After thoroughly washing the wax obtained in this manner with water, some of its chemical constants were determined and are given in the table with those of the wax as examined in the original state. The cause for the differences there shown is not apparent.

The dried and filtered commercial wax yielded on combustion the following average of two closely agreeing determinations:

Carbon, per cent	80.30
Hydrogen, per cent	12.69

A sample of sugar cane wax analyzed by Dumas[1] was found by him to contain 81 per cent. carbon and 14.16 per cent. hydrogen. He regarded this substance as an alcohol of the formula $C_{24}H_{50}O$.

It will be observed that the candelilla wax is somewhat similar to the cane wax in its ultimate composition. The probabilities are, however, that candelilla wax like carnauba wax is a mixture of an alcohol, an ester, and some free fatty acid. If, however, an alcohol is present it should be possible to acetylate the unsaponifiable matter. We attempted the acetylation by the Benedict-Lewkowitsch method, but obtained negative results.

CONSTANTS OF CHINESE WOOD OIL.

By Adolph Kreikenbaum.

Chinese wood oil is a comparatively new article in general commercial use. It is now very much used in the manufacture of varnishes.

In the following work only the results of the determinations of the constants are given and a discussion of the analytical features added. The literature offers comparatively little definite regarding the constants of the oil and at most a considerable con-

fusion of figures together with a wide range given for the various constants.[1] In some cases individual analyses upon some sample of unknown or doubtful source is submitted and in other cases it is evident that a confusion of products is at fault in that Japanese wood oil and Chinese wood oil have been classed alike,[2] being in the opinion of the writer two separate and distinct products. This opinion is based upon references found in literature[3] and not from original knowledge. The values given by Lewkowitsch in the table of constants for Chinese wood oil are evidently some Chinese wood oil and some Japanese wood oil figures. The values given for the specific gravity of Chinese wood oil by Lewkowitsch himself agree with the results obtained in this work. It seems that a distinction should be observed between the two products, Chinese wood oil and Japanese wood oil by all chemists, because the two oils are evidently separate and distinct substances, and the indiscriminate interchange of the figures of the two oils under one synonym *Tung* oil causes an unnecessary confusion and hardship for the analytical chemist, who may be compelled to make use of published data for reference.

The value of the work embodied in this article and the results obtained and submitted in their entirety are due to the fact, that the determinations of the constants have been made upon exact and carefully taken average samples of large commercial shipments of *Chinese* wood oil. This has been done for two years and the samples examined thus show how uniform a product the Chinese wood oil of commerce is. The investigation also reveals the fact that each constant varies but very slightly with the exception of the free acid value. The complete figures for each sample will tell their own story best.

All of the following specimens of the oil represent an average of regular commercial shipments. Several fluid ounces of the oil were taken from each barrel, emptied into a single container, mixed thoroughly and preserved in a tightly stoppered bottle filled close up to the cork and the bottles preserved in a dark, cool cupboard near the floor. More specific details are given directly under the various specimens. The column marked *Age* in the analysis tables indicates the time elapsed between the receipt of the shipment and the date the particular analysis was made.

Number 1.

Shipment received October, 1907. Represents average of about 100 barrels which bore the same brand. Filled one-gallon can full, tightly stoppered; kept in cool place. October, 1908, transferred some of this

---

[1] Quoted by Browne in *Bull.* **91**, Louisiana Experiment Station.

[1] Toch, *Chemistry and Technology of Mixed Paints,* ed. **1907**, p. 99; *Chem. Engr.*, **9**, 186.

[2] *Analyst*, **23**, 113, 118.

[3] *Ibid.*, **23**, 113, 118; Kametaka, *J. S. C. I.,* **27**, abstract of *J. Coll. Science Imp. Univ. Tokyo*, **1908**, p. 25; Lewkowitsch, *Chem. Tech. and Anal. Oils, Fats and Waxes.*

oil into a 16-oz. bottle and filled nearly to the cork. Determinations made from this bottle sample:

Spec. grav.	0.9416	$\frac{15.5}{15.5}$	Pycnometer.		Age 13 mos.	Remarks.
" "	0.9422	$\frac{15.5}{15.5}$	"		2 yrs.	Poured from bottle without shaking.
Free acid 4.8 mgs. KOH.					13 mos.	
Sapon. No.	192.2 / 191.5 }	191.8			24 "	
Iodine......	172.4 / 170.8 }	171.6	Hübl	15 hrs.	13 "	Hübl solution 6 days old.
"	170.0 / 171.8 }	170.9	"	3 "	13 "	Hübl solution 7 days old.
"	168.9 / 169.2 }	169.0	"	18 "	16 "	
"	165.5 / 164.5 }	165.0	"	3 "	16 "	
"	170.0 / 169.5 }	169.7	"	4 "	17 "	
"	170.1 / 170.2 }	170.1	"	18 "	21 "	
"	212.2 / 209.4 }	210.8	Hanus	30 min.	16 "	
"	209.7 / 206.6 }	208.1	"	30 "	16 "	
"	208.3 / 209.0 }	208.6	"	30 "	12 "	
"	196.0	196.0	"	30 "	12 "	

Number 2.

Received October, 1907. Average of 100 barrels, the lightest colored ones found in a total lot of 600 barrels, coming from different shippers. One-gallon can full retained. Transferred some of the oil to bottle October, 1908, from which determinations were made.

Spec. grav.	0.9427	$\frac{15.5}{15.5}$	Pycnometer.		Age 13 mos.	Remarks.
" "	0.9435	$\frac{15.5}{15.5}$	"		24 "	Poured from bottle without shaking.
" "	0.9432	$\frac{15.5}{15.5}$	"		24 "	Bottle shaken, oil well mixed.
Free acid 2.3 mgs. KOH.					13 "	
Sapon. No.	190.7 / 190.5 }	190.6			24 "	
Iodine.....	173.0 / 172.2 }	172.6	Hübl	15 hrs.	13 "	Hübl solution 6 days old.
"	168.3 / 171.3 }	169.8	"	18 "	16 "	
"	163.3 / 164.6 }	163.9	"	3 "	16 "	
"	169.2 / 169.7 }	169.4	"	4 "	17 "	
"	169.6 / 169.1 }	169.3	"	18 "	21 "	
"	196.6 / 197.8 }	197.2	Hanus	30 min.	12 "	
"	194.3 / 196.1 }	195.2	"	30 "	13 "	
"	199.5 / 204.4 }	201.9	"	30 "	16 "	
"	212.8 / 207.6 }	210.2	"	30 "	16 "	
"	207.8	207.8	"	30 "	24 "	

Number 3.

Received October, 1907. Average of 400 barrels darkest colored oil from a total of 600 barrels. One-gallon can of the oil retained. Transferred to bottle October, 1908.

Spec. grav.	0.9436	$\frac{15.5}{15.5}$	Pycnometer.		Age 24 mos.	Remarks. From 1-gal. can half full, exposed to air 1 year.
Free acid 3.3 mgs. KOH.					13 "	
Sapon. No.	192.0 / 191.6 }	191.8			24	From original 1-gal. can half full.
Iodine.....	168.5 / 169.5 }	169.0	Hübl	18 hrs.	16 "	
"	163.9 / 165.1 }	164.5	"	3 "	16 "	
"	169.5 / 169.0 }	169.2	"	4 "	17 "	
"	172.0 / 171.3 }	171.6	"	20 "	21 "	
"	195.3 / 197.7 }	196.5	Hanus	30 min.	12 "	
"	200.4 / 202.4 }	201.4	"	30 "	16 "	

Number 4.

Received October, 1907. Average of 20 barrels marked with a certain brand. Light color. Sample kept in one-quart can in dark, cool cupboard near floor. Can about half-full. Transferred into bottle October, 1908. Bottle completely filled.

Spec. grav.	0.9454	$\frac{15.5}{15.5}$	Pycnometer.		Age 24 mos.	Remarks. First year in 1-quart can half full; second year 1½ inch air space in bottle.
Free acid 1.7 mgs. KOH.					13 "	
Sapon. No.	190.9 / 190.5 }	190.7			24 "	
Iodine.....	162.8 / 163.1 }	162.9	Hübl	3 hrs.	17 "	
"	166.9 / 166.9 }	166.9	"	4 "	17 "	
"	169.9 / 170.9 }	170.4	"	20 "	21 "	
"	192.7 / 196.1 }	194.4	Hanus	30 min.	13 "	
"	193.2 / 197.8 }	195.5	"	30 "	17 "	

Number 5.

Received September, 1908. Average of 88 barrels. Filled 16-oz. bottle and preserved like the rest in dark, cool cupboard.

Spec. grav.	0.9414	$\frac{15.5}{15.5}$	Pycnometer.		Age 12 mos.
Free acid 4.5 mgs. KOH.					10 days
Sapon. No.	191.2 / 191.4 }	191.3			12 mos.
Iodine.....	165.3 / 168.0 }	166.6	Hübl.	3 hrs.	5 "
"	168.8 / 169.5 }	169.1	"	4 "	5 "
"	173.7 / 172.0 }	172.8	"	20 "	10 "
"	196.1 / 195.9 }	196.0	Hanus	30 min.	1 "
"	197.3	197.3	"	30 "	5 "
"	191.2 / 204.1 }	197.6	"	30 "	5 "

Number 6.

Received October, 1908. Average of 400 barrels. Filled some into bottle at once and preserved as usual.

Spec. grav.	0.9411	$\frac{15.5}{15.5}$ Pycnometer.		Age.	16 days
Free acid 5.3 mgs. KOH.					14 "
Sapon. No.	191.6 / 191.9 } 191.7				12 mos.
Iodine.....	169.3 / 169.6 } 169.4	Hübl.	3 hrs.		4 "
"	171.4 / 171.9 } 171.6	"	4 "		4 "
"	170.1 170.1	"	18 "		9 "
"	192.2 / 192.6 } 192.4	Hanus 30 min.			1 day
"	200.0 200.0	"	10 "		2 "
"	192.6 / 199.9 } 196.2	"	30 "		4 mos.

Number 7.

Received October, 1908. Average of 100 barrels. Light color. Bottle sample preserved at once.

Spec. grav.	0.9406	$\frac{15.5}{15.5}$			Age. 2 days.	Remarks. From bottle.
" "	0.9401				7 days	From ½ gal. can of same lot.
" "	0.9407				12 mos.	From bottle.
Free acid 6.1 mgs. KOH.					2 days	
	6.3 " "				5 "	
Sapon. No.	190.5 / 190.7 } 190.6				12 mos.	
Iodine.....	168.7 / 170.2 } 169.4	Hübl.	3 hrs.		4 mos.	
"	173.4 / 173.3 } 173.3	"	4 "		5 "	
"	170.3 / 170.0 } 170.1	"	18 "		9 "	
"	205.3 / 205.9 } 205.6	Hanus 30 min.			2 days	
"	204.5 / 208.1 } 206.3	"	30 "		2 "	
"	201.3 / 191.0 } 196.1	"	"		4 mos.	
"	188.8 / 189.0 } 188.9	"	30 "		5 "	
"	201.0 / 197.2 } 199.1	"	"			Bromine in excess. Linseed, 187.1.

Number 8.

Received June, 1909. Average of 249 barrels. Oil stood in one-gallon can open to air for two weeks before bottle sample was transferred.

Spec. grav.	0.9413	$\frac{15.5}{15.5}$		Age.	2 mos.
Free acid 7.0 mgs. KOH.					2 "
Sapon. No.	190.0 / 189.7 } 189.8				4 "
Iodine.....	170.7 170.7	Hübl.	20 hrs.		1 "
"	170.4 170.4	"	5 "		3 "

Number 9.

Received June, 1909. Average of 200 barrels. Oil left in open pail nine days before bottle sample was transferred.

Spec. grav.	0.9413	$\frac{15.5}{15.5}$		Age.	3 mos.
Free acid 7.1 mgs. KOH.					3 "
Sapon. No.	190.6 / 190.5 } 190.5				3 "
Iodine.....	171.8 / 171.5 } 171.6	Hubl.	18 hrs.		1 "
"	173.1 173.1	"	5 "		3 "

Number 10.

Received September, 1909. Average of 500 barrels. Filled into bottle at once.

Spec. grav.	0.9412	$\frac{15.5}{15.5}$			Age.	½ mo.
Free acid 2.4 mgs. KOH.						
Sapon. No.	190.8 / 190.4 } 190.6					½ "
Iodine.....	171.6 171.6	Hübl.	7 hrs.		½ "	
"	167.9 167.9	"	3 "		½ "	
"	168.6 168.6	"	4 "		½ "	

The results of this work indicate quite conclusively that the Chinese wood oil of commerce is a very uniform product. The constants vary but little. Summarizing the results there are obtained the following figures for the constants:

Specific gravity $\frac{15.5}{15.5}$ by pycnometer 0.941		
Free acid	1.7–7.1 average 4.4 mgs. KOH	
Sapon. No.	average 190.9	
Iodine No.	Hübl	average 170.4%.

The specific gravity of the fresh oil as received is practically 0.941. The minimum observation was 0.9401. In contact with air the specific gravity of the oil increases. Sample 4, which was in contact with much air for 2 years, gave at the end of that period 0.9454 and is the maximum figure obtained; others increased in a less degree. All determinations were made with the pycnometer. The Westphal balance, which gives accurate results upon such liquids as turpentine, benzine, alcohol etc., gives results 1 to 2 points in the third decimal too low when used for linseed oil or Chinese wood oil.

The free acid varied from a minimum observation of 1.7 to a maximum of 7.1 mgs. KOH, with an average of 4.4 for the ten samples.

The saponification number is 190.9, being the average of ten figures, minimum observation 189.8, maximum 191.8.

The iodine number proved to give interesting results, in the first place by giving such uniform results with the Hübl method and giving figures differing from those usually assigned to the oil in literature, and secondly; because the Hanus method was found inapplicable to Chinese wood oil. As a rule, the working of each iodine solution used, whether Hübl or Hanus, was tried for its action and result upon a sample of acid-free linseed oil kept for that purpose. The usual iodine number obtained for the linseed oil sample was 183–184 and the Chinese wood oil results were between 169–171 for these solutions. When the result on the linseed oil reached 185, the Chinese wood oil (see sample 7) showed 173. The Hübl solutions were from 12 to 48 hours old when used, except in the cases where stated otherwise. It can safely be said that the iodine number by the Hübl method is quite uniform in the neighborhood of 170 and age has had practically no effect on it. A three-hour absorption is insufficient, a four-hour absorption giving in most cases almost complete results, assuming 18 hours as standard. For the 18-hour absorption the minimum was 169.0; maximum 173.1.

The average of all Hübl iodine absorptions between 4 and 20 hours is 170.4. The 3-hour absorptions gave an average of 166.9 on 8 determinations, with a minimum of 162.9 and a maximum of 170.9. The 4-hour absorption shows an average of 169.7 on 8 determinations with a minimum of 168.6 and a maximum of 173.3. Two 5-hour absorptions gave 170.4 and 173.1. One 7-hour absorption gave 171.6. It can be assumed from the results of this work and upon the strength of it recommended that a 6- to 7-hour absorption will in all cases give a complete iodine absorption by the Hübl method. The results show that no further remark is necessary than that the Hanus method is not available for Chinese wood oil, although each Hanus solution gave results with the linseed oil sample, which agreed closely with Hübl determinations upon the same, this being a check test nearly always made to prove that the Hanus solution was not at fault.

It is my sincere hope to see a complete research made upon Chinese wood oil, so that the figures, which I submit here, will be verified and that all might be known, which good investigation will bring out, and that we become more enlightened about this most curious of vegetable oils. Further work in confirmation and extension of these results will be taken up by coöperation with other investigators.

CHEMICAL LABORATORY,
THE GLIDDEN VARNISH CO.,
CLEVELAND, O., February 16, 1910.

GAMBOGE.

By F. O. TAYLOR.

Received March 10, 1910.

Of all the resins more commonly used there is none whose ordinary adulterations are more easy to detect than those of gamboge; nevertheless, we find that not only in the powdered state but also in the form of pipes or lumps it is largely adulterated. The adulteration of powdered resins is to be expected, but when the detection of adulteration is so simple a matter as with gamboge, one would imagine that at least more obscure methods of adulteration would be pursued. Such, however, seems not to be the case. For the purposes of this examination, fifteen samples of gamboge were obtained from a variety of sources, eight of these were powdered and seven were either pipes or broken lumps. The appearance of the powdered samples varied from an orange color to lemon-yellow, while of the seven unpowdered samples, five were of first-class appearance and two were considerably lighter in color than a good quality of gamboge should be, one of these being in form of pipe and marked "Saigon Gamboge." The examination of gamboge for adulterations as published in pharmaceutical literature has been chiefly confined to the examination for starch and almost exclusively to the powdered

form. Eberhardt[1] records his results in the examination of a number of samples of gamboge for starch and states that in several years' experience he had failed to discover a powdered gum that would not show at least a slight test for starch; in none of the samples of pipe gamboge did he discover any traces of starch. However, Daniel Base, in a paper before the Maryland Pharmaceutical Association,[2] states that he found, by means of a microscopical examination, a number of samples of gamboge adulterated in this manner, but attributes some of the adulteration to the use of dextrin instead of starch.

The present examination included the percentage of ash, alcohol-soluble matter, acid value and test for starch, the results of which will be found recorded in the table following:

TABLE I.

Sample Number.	Starch Test.	Per cent. ash.	Per cent. alcohol, soluble.	Acid value.
1	Trace (under 1%).................	1.0	79.05	91.6
2	Marked...........................	6.93	61.3	67.7
3	None.............................	0.65	76.15	80.2
4	Very marked......................	11.00	39.25	56.3
5	Trace (faint)....................	0.69	77.0	85.8
6	Heavy............................	1.91	57.6	67.7
7	Very marked......................	6.76	61.0	73.3
8	Trace (under 1%).................	1.02	60.1	64.9
9	Very marked......................	0.93	52.95	80.5
10	None............................	0.45	84.0	95.8
11	None............................	0.54	77.4	85.8
12	None............................	0.32	82.0	88.6
13	Marked..........................	0.71	60.3	73.3
14	None............................	1.26	74.9	81.6
15	Heavy...........................	0.70	49.95	64.9

Starch Test.—The U. S. P., Eighth Revision, includes no test for the presence of starch in gamboge, differing in this particular from the U. S. P., 1890. This was probably done with the supposition that gamboge in pipes, which is the only variety official, is not adulterated with starch. This is unfortunate, as out of seven samples of this character which were examined, two were markedly contaminated with starch, and in such a manner that it was evidently an intentional adulteration. The test given in the U. S. P., 1890, is sufficiently delicate for all practical purposes and is easily applied. Eberhardt (v. s.), while admitting the delicacy of this test, has proposed another based on the destruction of the starch granule with caustic alkali (which at the same time dissolves the gamboge resin), the precipitation of the resin and neutralization of the liquid with acid, and the testing of the filtrate with iodine. This test has the advantage of giving the blue color of starch iodide instead of the green color which appears when this blue is mingled with the yellow of the gamboge. In every case I have used the former U. S. P. test, which will, without difficulty, detect much less than one per cent. of starch.

Not one of the powdered samples showed but a trace of starch. In number 5 this was faint, in num-

[1] *Amer. Jour. Pharm.*, **1896**, p. 371.
[2] *Ibid.*, **1900**, p. 189.

bers 2 and 8 larger but still under one per cent. while in the others the amount of starch was very marked, some indications of the comparative amounts being given by the method of wording of the table. Microscopical examination revealed rice starch in every case except number 4, which contained cornstarch. In the two unpowdered samples, numbers 13 and 15, the starch had evidently been mixed with the melted resin so that part of it was converted into a soluble form, for upon shaking the powder made from these with water, without heat, the presence of starch was distinctly indicated by iodine. The powder made from the remaining samples of pipe gamboge showed absolutely no trace of starch. The cause of the slight trace of starch in some powdered gamboge, so small that it is evidently not an intentional adulteration, has been considered by Eberhardt, but no definite conclusion was arrived at. I have no additional suggestions to offer regarding this, but the fact remains that practically all samples of powdered gamboge will show at least a trace of starch.

Ash.—The U. S. P. requires gamboge to contain not more than three (3) per cent. of ash, but a first-class sample of gamboge comes well below this and the limit could be lowered. But one of the samples of the pipe or lump gamboge had an ash higher than 0.75 per cent., and this one (number 14) was due to the presence of some traces of fine gravel, evidently there as an accidental contamination. A large amount of the ash in numbers 2 and 7 were due to the presence of a considerable amount of fine sand, and the extraordinary quantity in number 4 was caused by the presence both of sand and a marked quantity of lead chromate, an adulteration unique in my experience, and yet one which might be expected. Both gamboge and lead chromate being used as pigments, it is no more than natural to expect that the gamboge intended for use as a pigment would, if adulterated at all, be sophisticated by the addition of the cheaper pigment of similar color (lead chromate), which is at the same time a make-weight for the lighter gamboge. Every sample of powdered gamboge with an ash above one (1) per cent., contained visible traces of sand under the microscope, but the amount was so small that it could scarcely have been used intentionally. It is possible that the gamboge might have been powdered in a ball-mill with stone balls, which would account for the traces of sand. This is the more reasonable when it is remembered how easily powdered gamboge is electrified, so, for the purpose of powdering it, stone would be preferable to metal.

Alcohol Solubility.—The U. S. P. requires gamboge to contain not more than twenty-five (25) per cent. insoluble in alcohol. This was obtained by treating one (1) gram of powdered resin with one hundred (100) cc. of alcohol, letting stand over night with occasional shaking, filtering through a tared filter,

and weighing the washed and dried residue. Six out of the fifteen samples are above this standard, while a seventh (number 14) is so slightly below that it may properly be counted within the standard. Of these seven, two were powdered samples and the remaining five were the five best appearing unpowdered samples. Below this standard the remaining samples ranged in solubility from 61.3 to 39.25 per cent.

Acid Value.—The U. S. P. makes no requirements for acid value, but various observers have made record of this analytical value of gamboge, and the values assigned range between 70 and 90 for unpowdered samples. Von Schmidt and Erban, A. Kremel, and Beckurts and Brüche[1] record acid values on alcoholic extracts of gamboge, but these are not comparable to the results we give. Dieterich[2] in the examination of seven samples pipe gamboge obtained acid values from 71.45 to 86.46, and for the powdered gamboge about 110, the higher value for the powdered variety being due to the presence of rosin. The acid value was determined by the method suggested by Dieterich, digesting one (1) gram of resin with one hundred (100) cc. of alcohol on a steam-bath for fifteen minutes in a reflux condenser, adding fifty (50) cc. of water and cooling before titration. The titration is carried out with some difficulty because of the orange colored solution and the consequent lack of sharpness in the end-point reading. The following method may also be used, and is, I believe, preferable, for it enables the very rapid determination of both alcohol solubility and acid value at the same time.

Two (2) grams of gamboge are digested under a reflux condenser with exactly 150 cc. of alcohol for not less than fifteen minutes, the solution cooled and seventy-five (75) cc. (representing one (1) gram of resin) filtered off through a dry tared filter. This 75 cc. is used for titration of the acid value, which is made direct on this solution, and the filtration is continued so that the insoluble residue may be finally collected on the filter and weighed. This reduces the time for the determination of alcohol solubility to a few hours at most and in the acid value titration gives results agreeing with those obtained by Dieterich's method. This was proved by comparison of this method with Dieterich's on a number of the above samples; the results as a whole, however, had been originally determined by Dieterich's method, and as such they are recorded. The acid value of the samples whose alcohol solubility was up to standard ranged from 80.2 to 95.8. One other acid value above 80 (number 9) had quite a low alcohol solubility, which, in connection with the fact that a large amount of starch was present, indicated colophony. Other acid values ranged downward from this to 56.3.

[1] "Analysis of Resins," Dieterich, pp. 292 and 293.
[2] *Ibid.*, p. 204.

Comparison of Acid Value and Alcohol Solubility.—The comparison of these data is instructive, and from it we may obtain a better idea of gamboge than from either alone. If we take the seven samples whose ash and alcohol solubility are up to standard, and arrange them in the order of their acid value, we will have a table as below.

Sample No.	Acid value.	Alcohol solubility.
10	95.8	84.0
1	91.6	79.05
12	88.6	82.0
11	85.8	77.4
5	85.8	77.0
14	81.6	74.9
3	80.2	76.15

The alcohol solubility, it will be noted, varies in direct proportion to the acid value with a considerable degree of accuracy, excepting number 1, and this, a powdered sample, appears to contain a small amount of colophony, so that though the alcohol solubility is lower than number 12, yet the acid value is higher. The samples of pipe gamboge, however, will excellently bear out this proportional relationship. If now we arrange the remaining samples in the same manner, we will have a table as shown below, from which we may draw conclusions regarding the samples which are adulterated with colophony.

Sample No.	Acid value.	Alcohol solubility.
9	80.5	52.95
7	73.3	61.0
13	73.3	60.3
2	67.7	61.3
6	67.7	57.6
8	64.9	60.1
15	64.9	49.95
4	56.3	39.25

Sample number 9 being heavily adulterated with starch is also undoubtedly adulterated with colophony. Sample number 2 in all probability contains colophony and with more certainty number 6. Number 8, while possibly containing colophony, is by no means as certain as any of the others. The remaining samples may be considered wholly free from this adulteration.

SUMMARY.

Out of the fifteen samples examined, only six are unquestionable, while a seventh offering some grounds for suspicion is yet so good as to be acceptable for ordinary use. Thus we find six out of eight powdered samples and two out of seven samples of pipe or broken gamboge, so heavily adulterated that there would be no question about their rejection for pharmaceutical use. Starch is found in large quantity in seven instances, and in addition to this, sand is present with evident intention in three instances. Number 8 is very low in alcohol solubility and acid value, though containing but a trace of starch; the ash is low, hence the adulterant must be some non-starchy, organic body, whose identity was not determined. Numbers 2 and 3 are interesting by reason of the fact that number 2, a powdered sample, was supposed to be made by powdering number 3. The difference between the two is obvious. Sample number 4 appeared to be of excellent quality upon superficial examination, but proved to be decidedly worse than any other. Starch had been added to a considerable extent, and then to increase the weight some sand was put in, and to correct the light color produced, a small quantity of lead chromate was added. This adulteration has already been referred to, and I can but add that, while somewhat ingenious, it was so crude that its detection was easy. While the use of starch or sand as an adulterant simply decreases the strength of the gamboge, the presence of lead chromate goes further and adds the poisonous action of the lead salt, so causing the gamboge to become not merely inefficient but dangerous.

The alcohol solubility as required by the U. S. P. is, for a test of this character, unusually good for detecting adulteration, and the standard of the U. S. P. needs no change. The ash requirement might well be lowered so that it should read "not to exceed one per cent." The acid value is not essential to detection of most of the adulterated gamboge, but might be added. Lastly, by all means a starch test should be required, and I would suggest that it be worded so as to exclude any gamboge which shows more than a faint green color upon the addition of iodine to a powdered sample which has been boiled with water and subsequently cooled.

LABORATORIES OF PARKE, DAVIS AND CO.

THE DETERMINATION OF SODIUM CHLORIDE IN MILK.[1]

By PAUL POETSCHKE.

The addition of sodium chloride to milk is sometimes practiced with the object of increasing the density and ash content of watered samples. Having had occasion to examine numerous samples of milk for the presence of added sodium chloride, the author has devised a method which not only shortened the time required for this determination but also gave results which are more accurate than direct incineration in a platinum dish. It is customary to estimate chlorine in milk by incineration in a platinum dish, dissolving the ash in nitric acid, and proceeding with the determination of chlorine by Volhard's method. The fact that a loss of chlorine occurs even when the ignition is carried on at temperatures much below those at which chlorides become volatile is well known. This loss appears to be due to the formation of acid products during the ignition, and the loss of chlorine increases with the proportion of organic matter to chlorine. The addition of sodium carbonate prevents this loss, if the proportion of sodium carbonate is five per cent. of the organic matter present.[2] When a large number

[1] Read before N. Y. Section, February, 1910.
[2] Davis, *J. Soc. Chem. Ind.*, **20**, 98 (1901).

of samples are to be examined, considerable time is required in the ashing, especially if sodium carbonate is added, and it becomes necessary to employ quite a number of platinum dishes. Since the presence of copper and those metals whose salts are colorless (with exception of mercury) do not influence the accuracy of Volhard's method, it appeared possible to secure a proper solution for the determination of chlorine in milk by clarification with copper sulphate and sodium hydroxide. The preliminary results given in Table I and II indicated the possibility of applying this method.

TABLE I.

RESULTS EXPRESSED IN GRAMS OF SODIUM CHLORIDE PER 100 CC.

Sample No.	44.145	44.146	44.147	44.310	44.311
Sodium chloride by direct ashing.............	0.168	0.162	0.162	0.198	0.198
Sodium chloride by ashing with sodium carbonate.............	0.178	0.162	0.175	0.207	0.207
Sodium chloride by author's method........	0.180	0.167	0.183	0.208	0.210

TABLE II.

RESULTS EXPRESSED IN GRAMS OF SODIUM CHLORIDE PER 100 CC.

Sample No.	(1)	(2)	(1) plus 0.1000 gram NaCl per 100 cc.	(1) plus 0.2000 gram NaCl per 100 cc	(2) plus 0.1000 gram NaCl per 100 cc.	(2) plus 0.2000 gram NaCl per 100 cc.	(2) plus 0.3000 gram NaCl per 100 cc.
Sodium chloride by direct ashing	0.197	0.164	.....	.....	.....	.....	.....
Sodium chloride by ashing with sodium carbonate.......	.....	0.171	.....	.....	.....	.....	.....
Sodium chloride by author's method......	0.198	0.176	0.293	0.399	0.286	0.385	0.482
Added sodium chloride found.	.....	.....	0.095	0.201	0.110	0.209	0.306

METHOD OF CARRYING OUT THE DETERMINATION.

Solutions Required.

1. Ammonium thiocyanate. A tenth-normal solution.
2. Copper sulphate. Dissolve 34.639 grams of $CuSO_4.5H_2O$ in water and dilute to 500 cc.
3. Ferric indicator. A cold saturated solution of ferric alum in water, to which enough nitric acid is added to cause disappearance of the brown color. Three cc. of this indicator are used for all titrations.
4. Nitric acid. An approximately 5 N solution free from lower oxides of nitrogen.
5. Silver nitrate. A tenth-normal solution.
6. Sodium hydroxide. A half-normal solution.

DETERMINATION.

Twenty-five cubic centimeters of the carefully mixed sample are measured into a 200 cc. graduated flask, diluted with 125 cc. of water, 10 cc. of copper sulphate and 8.8 cc. of sodium hydroxide added. The mixture is diluted to the mark, mixed by inverting the flask ten to twelve times, at the same time shaking gently. It is then poured on a dry, folded filter 19 cm. in diameter and the filtrate collected in a dry flask. The funnel is kept covered with a clock glass and the neck of the flask in which the filtrate is received is loosely stoppered with a plug of cotton to minimize evaporation. The filtrate should have an acid reaction and contain a slight excess of copper. To 100 cc. of the filtrate 5 cc. of nitric acid and an excess of silver nitrate are added, together with 5 cc. of ether[1] which causes the silver chloride to readily coagulate and settle. The silver chloride is now filtered off and after the addition of ferric indicator to the filtrate, the excess of silver nitrate titrated with ammonium thiocyanate. From the amount of silver nitrate required, the amount of sodium chloride is calculated.

Notes.—In order to secure a clear filtrate after clarification, the sodium hydroxide is added gradually while shaking the flask containing the diluted milk and copper sulphate. After diluting to the mark, the contents of the flask are mixed by inverting the flask and shaking gently, since violent shaking caused the filtrate to come through turbid and the filtration to be slow. The first portion of filtrate is rejected since it is usually turbid, the dry flask being placed under the funnel when the filtrate becomes clear. Usually the filtrate is clear after a few cubic centimeters have run through. On the addition of nitric acid a turbidity usually develops which does not interfere with the determination, and for this reason the filtrate from the silver chloride is sometimes slightly turbid.

If great accuracy is desired, normal-twentieth solutions of silver nitrate and ammonium thiocyanate should be used, and corrections applied for the volume occupied by the precipitated fat and proteids. The correction for volume of precipitate can be obtained by the method of double dilution. For this purpose two dilutions are made, one in the regular way as already given and another in which the volume is completed to 100 cc. The volume of precipitate is twice as great in proportion in the 100 cc. as in the 200 cc. flask. The following example shows the method of calculation.

Per cent. sodium chloride by weight found by diluting to 100 cc. = 0.171.

Per cent. sodium chloride by weight found by diluting to 200 cc. = 0.169.

0.171 — 0.169 = 0.002 (half the error in the higher result).

0.171 — (0.002 × 2) = 0.167 corrected percentage of sodium chloride.

The volume as precipitate is calculated as follows:

0.171 : 0.167 : : 100 : x = 97.66 which is the volume of solution in the 100 cc. flask. Therefor the volume of precipitate is 2.34 cc. The results given in Table III indicate that when the volume is made up to 200 cc., the correction of volume of precipitate is well within the ordinary limits of accuracy, and for this reason the volume of precipitate can be neglected in ordinary work. Tables III and IV show the results obtained with the method.

[1] E. Alefeld. *Z. anal. Chem.*, **48**, 79.

TABLE III.

Number and description.		(1) Sample of commercial milk.	(2) Sample (1) plus 0.1000 grams NaCl per 100 cc.	(3) Sample (1) plus 0.2000 grams NaCl per 100 cc.	(4) Sample (1) plus 0.3000 grams NaCl per 100 cc.
N. Y. Bd. of H. lactometer reading at 60° F.		112	114	116	118
Corresponding specific gravity.		1.0325	1.0331	1.0336	1.0342
Fat by Babcock test.		4.3	4.3	4.3	4.3
Total solids.		13.23	13.36	13.43	13.53
Ash.		0.755	0.848	0.949	1.037
Sodium chloride by direct ashing	Per cent. by weight...	0.163	0.258	0.347	0.442
	Grams per 100 cc.	0.168	0.266	0.359	0.457
Sodium chloride by ashing with sodium carbonate.	Per cent. by weight...	0.169	0.270	0.361	0.453
	Grams per 100 cc.	0.175	0.279	0.373	0.469
Sodium chloride by author's method. To volume of 100 cc.	Per cent. by weight...	0.171	0.272	0.366	A. 0.466, B. 0.464
	Grams per 100 cc.	0.177	0.281	0.378	Average 0.465, A. 0.482, B. 0.480
Sodium chloride by author's method. To volume of 200 cc.	Per cent. by weight...	0.169	0.263	0.363	Average 0.431, 0.458
	Grams per 100 cc.	0.175	A. 0.271, B. 0.273	A. 0.378, B. 0.372	A. 0.475, B. 0.472
			Average 0.272	Average 0.375	Average 0.474.
Added sodium chloride found. Grams per 100 cc.	By direct ashing.	..			
	By ashing with sodium carbonate.	..	0.098	0.191	0.289
	By author's method.	..	0.104	0.198	0.294
	To volume of 200 cc.	..	0.097	0.200	0.299

TABLE IV.

Number.	Lactometer reading[1].	Corresponding specific gravity.	Fat by Babcock test.	Total solids.	Sodium chloride by ashing with sodium carbonate. Per cent. by weight.	Grams per 100 cc.	Sodium chloride by author's method. Per cent. by weight.	Grams per 100 cc.
45768	106	1.0307	3.6	11.83	a.0.204 b.0.201	0.210 a.0.197 0.207 b.0.197	a.0.197 b.0.197	a.0.203 b.0.203
45769	110	1.0319	3.7	12.23	0.166	0.171	0.164	0.169
45770	108	1.0313	3.7	12.09	0.177	0.183	0.180	0.186
45771	111	1.0322	3.9	12.54	0.187	0.193	0.187	0.193
45772	108	1.0313	3.6	11.97	0.221	0.228	0.229	0.236
45773	110	1.0319	4.2	12.83	a.0.185 b.0.185	a.0.191 b.0.191	0.177	0.183
45774	107	1.0310	4.1	12.50	0.177	0.183	0.182	0.188
45775	111	1.0322	3.7	12.30	0.170	0.175	0.168	0.173
45776	110	1.0319	3.3	11.75	a.0.207 b.0.201	a.0.214 b.0.207	0.200	0.206
45777	112	1.0325	3.7	12.37	0.240	0.248	0.241	0.249
45778	108	1.0313	3.2	11.52	0.200	0.206	0.202	0.208
45779	113	1.0328	3.6	12.32	0.185	0.191	0.182	0.188
45780	111	1.0322	3.9	12.54	0.177	0.183	0.182	0.188
45781	109	1.0316	3.7	12.16	0.169	0.174	0.169	0.174
45782	110	1.0319	3.6	12.11	0.185	0.191	0.182	0.188
45783	113	1.0328	3.5	12.20	0.186	0.192	0.182	0.188
45784	114	1.0331	3.3	12.11	0.177	0.183	0.172	0.178
45785	106	1.0307	3.5	11.71	0.159	0.164	0.163	0.168
45786	113	1.0328	4.0	12.80	0.174	0.180	0.168	0.174
45787	111	1.0322	3.3	11.94	0.178	0.184	0.182	0.188

From the results in Table III, it will be seen that the figures by ashing with sodium carbonate and the author's method show reasonably close agreement, but that by direct ashing quite a loss of chlorine occurs. It is interesting to note that the addition of 0.1000 gram of sodium chloride to 100 cc. of milk causes an increase of 2° in the lactometer reading or 0.0006 in the specific gravity. In judging whether a sample of milk contains added sodium chloride, the ratio of total ash to sodium chloride can be depended upon to show such addition. In this connection, the figures given in Table V, taken from Table III, show the effect on this ratio when sodium chloride has been added.

From the composition of milk ash, as given by Richmond,[2] the ratio of ash to sodium chloride is

[1] N. Y. Bd. of H. lact.
[2] "Dairy Chem.," p. 32.

4.33. Blyth[1] gives the ratio 3.74. According to Fleischmann and Schrott[2] the ratio is 4.15. Konig[3] gives the ratio 4.52. Through the courtesy of Dr. Deghuee, of the Lederle laboratories, it is hoped to extend the study of this ratio.

TABLE V.

Number and description.	Ash, per cent.	Sodium chloride, per cent. by weight.	Ratio of ash to sodium chloride.
(1) Sample of commercial milk.	0.755	0.169	4.47
(2) Sample (1) plus 0.1000 gram NaCl per 100 cc....	0.848	0.263	3.23
(3) Sample (1) plus 0.2000 gram NaCl per 100 cc....	0.949	0.363	2.61
(4) Sample (1) plus 0.3000 gram NaCl per 100 cc....	1.037	0.458	2.26

LEDERLE LABORATORIES,
39–41 WEST 38TH ST.,
NEW YORK, N. Y.

PHOSPHORUS IN FLESH.

(SECOND PAPER.)[4]

By P. F. TROWBRIDGE AND LOUISE STANLEY.

Hart and Andrews[5] were among the first to show that the phosphorus in foods was present to a considerable extent in the organic form. They claimed that in precipitating the phosphorus from the water solutions in the usual way with the ordinary acid molybdate, a sufficient quantity of acid was present to cause a splitting of the soluble organic phosphorus and a precipitation of it along with the inorganic forms. They proposed to remedy this defect by precipitating with neutral molybdate in the presence of the smallest necessary amount of nitric acid. In their method, as finally worked out, they used 10 grams of ammonium nitrate and 2 cc. of nitric acid. Under these conditions only a very small amount of the

[1] "Foods," 1903, p. 201.
[2] See Wiley's "Agric. Anal.," Vol. III, p. 467.
[3] Chem. Nahr. u. Genussm., 11, 227.
[4] THIS JOURNAL, 1, 675 (1909).
[5] Am. Chem. J., 30, 470 (1903).

molybdate precipitate of inorganic phosphorus was obtained, and upon this they base their assertion that practically all the water-soluble phosphorus in vegetable feeding-stuffs is in the organic form.

As a test of this method a solution of inorganic phosphorus was made up, equal definite amounts were taken and the above method of precipitation tried in comparison with the usual methods. The results are noted in the table below. It is quite evident that the Hart and Andrews method fails to precipitate all the phosphorus even when it is present in the inorganic form. If this be true with simple water solution of inorganic salt, it is not surprising that under the retarding conditions usually present in the water extracts of flesh one should fail to get a complete precipitation with the neutral molybdate.

PRECIPITATION OF PHOSPHORUS BY NEUTRAL AMMONIUM MOLYBDATE.

Molybdate used.	Ammonium nitrate.	Acid added. HNO₃ (sp. gr. 1.42).	Yield of P as Mg₂P₂O₇, gram.
25 cc. of usual acid............	10 grs.	Acidified.	0.076
25 cc. of neutral..............	10 "	2 cc.	0.0461
25 " "	10 "	3 "	0.0615
25 " "	10 "	4 "	0.0634
25 " "	15 "	2 "	0.0444
25 " "	20 "	2 "	0.0484

Emmett and Grindley[1] studied the method with a view to its application in determining the organic phosphorus in cold water extracts of flesh. The presence of the soluble protein made it impossible to apply the method without first removing the coagulable protein. This they did by evaporating the solutions to a small volume, and filtering out the coagulated proteins. The method of Hart and Andrews gave good results with the filtrate and they found that as high as 20 cc. of nitric acid could be used without perceptibly affecting the results.

The work of Emmett and Grindley seemed to show that nearly all the soluble phosphorus in flesh was present in the inorganic form. During the years 1907 and 1908 at the Missouri Experiment Station we used the above method in determining the inorganic phosphorus in the cold water extracts of flesh and our results confirmed the belief that in flesh the soluble phosphorus was almost entirely present in the inorganic form. To illustrate we show in the table below the results of determinations upon cold water extract of flesh for total and for inorganic phosphorus. These results indicate quite clearly that after the treatment to remove the coagulated protein the phosphorus is present in the inorganic form.

Siegfried and Siegwald[2] separated organic from inorganic phosphorus in meat extract by the precipitation of the inorganic phosphorus with barium chloride in solution alkaline with ammonia. They found that this gave a sharp separation and by determining the phosphorus either in the filtrate or in the

[1] *Jour. Am. Chem. Soc.*, **28**, 25 (1906).
[2] *Zeit. Nahr. u. Genussm.*, **70**, 521.

precipitate could get at either the organic or inorganic phosphorus.

Sample.	Per cent. total phosphorus.	Per cent. inorganic phosphorus.
8270 Lean and fat of beef, composite........	*g* 0.1225	*g* 0.1205
	h Lost	*h* 0.1139
	i 0.1180	*i* 0.1144
Average..................	0.1203	0.1163
8271 Lean beef.....................	*g* 0.1609	*g* 0.1615
	h 0.1620	*h* 0.1629
	i 0.1615	*i* 0.1668
Average..................	0.1615	0.1637
8272 Sample of beef fat..............	*g* 0.0312	*g* 0.0388
	h 0.0351	*h* 0.0462
	i 0.0329	*i* 0.0206
Average..................	0.0330	0.0352

A comparison of these two methods gave such strikingly different results that we were led to investigate more thoroughly.

In the preparation of the cold water extracts of the raw meats or of the cooked meats the following method was followed:

120 grams of finely ground lean meat (180 grams if sample was very fat) were distributed in twenty 150-cc. beakers. Each portion was wetted with two or three cc. of netural recently boiled distilled water and mixed to a paste and then more water added to make a total of 50 cc. The water was allowed to stand on the sample for about half an hour with frequent stirring. It was then transferred to a filter and the solution allowed to drain completely. The residue was returned to the beaker and was thoroughly mixed with 25 cc. of the distilled water and again filtered. This operation was repeated with each of the 20 portions of the sample, until a total of 250 cc. of water had been used. Each residue on the filters was then washed twice with 10 cc. of water. The total filtrate was then measured into a large bottle and with rinsings from the 20 flask made up to exactly 6 liters mixed thoroughly without too much aeration and filtered through dry filters. From the filtrate aliquots for the analyses were taken. For total phosphorus 500-cc. portions were evaporated to small volume in beakers on the steam bath, then with fifteen cubic centimeters of sulphuric acid transferred to nitrogen flasks and digested as for nitrogen, using mercury and potassium sulphate. The contents of the flask were transferred to beakers, and the phosphorus estimated in the usual manner as magnesium pyrophosphate after first precipitation with acid ammonium molybdate and re-solution in ammonia.

Other 500-cc. portions of the filtrate were coagulated by evaporation to a small volume filtered and the coagulum thoroughly washed with hot water. The filtrate and washings were then made alkaline with ammonia and the inorganic phosphorus precipitated by the addition of barium chloride. The organic phosphorus was estimated in an aliquot of the filtrates as described above for total phosphorus.

Still other 500-cc. portions were treated with ammonia and barium chloride (without previous heating) for the precipitation of the inorganic phosphorus and the organic phosphorus determined in an aliquot of the filtrate as described above for total phosphorus.

A sample of raw beef (No. 810292) showed 7.15 per cent. of the total soluble phosphorus to be organic when the solution was first coagulated and 85.52 per cent. of the total soluble phosphorus to be organic when the inorganic phosphorus was, removed by the ammonia and barium chloride without heating.

In another sample of raw beef (No. 810295) only 0.86 per cent. of the soluble phosphorus is organic after coagulating by heat and 86.30 per cent. by removing the inorganic phosphorus with ammonia and barium chloride without heating. A portion of this sample was cooked as a beef loaf which was reground, thoroughly mixed and a water extract prepared as for raw meats. In this case 7.4 per cent. of the soluble phosphorus is organic after coagulating by heat and 17.6 by removal of the inorganic phosphorus with barium chloride and ammonia.

In a third sample of raw beef (811x) 6.3 per cent. of the total soluble phosphorus is organic after coagulating by heat and 57.4 per cent. by use of barium chloride and ammonia without heating. A portion of this sample was also cooked as a beef loaf and a water extract prepared as above. Only a trace of organic phosphorus was found after coagulating and 16.5 per cent. of the total soluble phosphorus was organic after separated by barium chloride and ammonia without heating. The following table summarizes the results given above.

From this it would seem that the long-continued heating has either caused a splitting of the simple organic phosphorus compounds and a precipitation of them in the inorganic forms, or else on the other hand the presence of the protein seems to hold back some of the precipitate of barium phosphate.

COMPARISON OF ORGANIC PHOSPHORUS FROM WATER EXTRACTS OF MEAT BEFORE COAGULATING AND AFTER COAGULATING.

Laboratory No.	Sample.	Total phosphorus in extract. Per cent.	Organic phosphorus without coagulating. Per cent.	Organic phosphorus after coagulating. Per cent.	Organic phosphorus in extract without coagulating. Per cent.[1]	Organic phosphorus after coagulating. Per cent.[1]
810292a	Raw chuck loaf	0.163	0.141	0.017	86.503	10.43
810292b	Raw chuck loaf	0.164	0.138	0.007	84.146	4.27
810295	Shank loaf raw	0.162	0.140	0.001	86.420	0.62
810295	Shank loaf cooked	0.151	0.026	0.011	17.219	7.28
811x	Chuck loaf raw	0.168	0.096	0.011	57.143	6.55
811x	Chuck loaf cooked	0.152	0.025	Trace	16.447	Trace.

In another series of experiments the total phosphorus and organic phosphorus were determined in water extract of samples of raw meat, a portion of the same meat was cooked as beef loaf to a definite temperature and a roast of the same cut was taken from the opposite side of the animal. The total phosphorus was determined in the usual way after Kjeldahl digestion of 500 cc. aliquots of the water extract (representing 10 gr. of original meat sample). For the organic phosphorus 600 cc. (12 grs.) were taken to which 10 cc. of barium chloride, 5 cc. of ammonia, and 45 cc. of distilled water were added. This was shaken well, allowed to stand over night and filtered in the morning. 550 cc. of the filtrate (representing 10 grs. of original material) were used for the organic phosphorus. The samples from the raw meats gave very little precipitate and the filtrates were in every case slightly cloudy. The extract from the cooked samples gave a heavy precipitate and in every case the filtrate was clear. The following table gives a summary of the results obtained, being the average of triplicate determinations:

DISTRIBUTION OF THE PHOSPHORUS IN BEEF FLESH.

Lab. Number.	Animal.	Description of sample.	Temperature of cooked meat.[2]	Total phosphorus in meat. Per cent.	Total phosphorus in water extract soluble. Per cent.	Organic phosphorus in water extract. Per cent.	Inorganic phosphorus in water extract. Per cent.	Soluble phosphorus which is organic. Per cent.	Total phosphorus which is soluble. Per cent.
81224–25	504	Round, raw.		0.160	0.145	0.0758	0.0692	52.28	90.625
81245	504	Round loaf.	60° C.	0.192	0.1401	0.0388	0.1013	27.69	72.969
81249	504	Round inside muscle.	68° C.		0.1237	0.0355	0.0882	28.70	
81226–27	504	Loin raw.		0.126	0.0852	0.0520	0.0332	61.03	67.619
81246	504	Loin loaf.	65° C.	0.200	0.1443	0.0331	0.1112	22.96	72.150
81248	504	Loin roast.	60° C.		0.1221	0.0339	0.0882	27.76	
81228–29	504	Rib raw.		0.131	0.0977	0.0692	0.0285	70.83	74.580
81247	504	Rib loaf.	60° C.	0.182	0.1335	0.0319	0.1016	23.87	73.352
81250	504	Rib 11th and 12th standing.	64° C.		0.1386	0.0343	0.1043	24.75	
9168	592	Composite of carcass.		0.174	0.128	0.0333	0.0947	26.02	73.563
91151	592	Composite as loaf.	60° C.		0.1615	0.0253	0.1362	15.67	
91124	48	Round raw.		0.192	0.1513	0.1247	0.0266	82.42	78.802
91152	48	Round loaf.	61.5 C.		0.1643	0.0509	0.1134	30.98	
91155	48	Round inside muscle.	62° C.		0.1426	0.0326	0.1100	22.86	
91126	48	Loin raw.		0.174	0.1365	0.0990	0.0375	72.53	78.448
91153	48	Loin loaf.	60° C.		0.1557	0.0453	0.1104	29.09	
91156	48	Loin roast.	64° C.		0.1451	0.0385	0.1066	26.53	
91128	48	Rib raw.		0.150	0.1217	0.106	0.1111	87.10	81.133
91154	48	Rib loaf.	60° C.		0.1440	0.0407	0.1033	28.26	
91157	48	Rib 11th and 12th standing.	60° C.		0.1275	0.0306	0.0969	24.00	
92152	Jerry	Rib raw.		0.152	0.118	0.1089	0.0091	91.44	77.632
92166	"	Rib loaf.	60° C.		0.1429	0.0337	0.1092	23.58	
92167	"	Rib loaf.	80° C.		0.1468	0.0306	0.1162	20.86	
92168	"	Rib loaf.	98.5° C.		0.1649	0.0162	0.1487	9.82	

[1] In terms of total soluble phosphorus.

[2] The temperature of the cooked meat is that registered by the center of the meat when removed from the oven.

CONCLUSIONS.

Emmett and Grindley's method does not give high enough results for organic phosphorus in cold water extracts of flesh, as the heat of coagulation has changed nearly all of the organic phosphorus to the inorganic form.

Barium chloride in slightly ammoniacal solution precipitates the inorganic phosphorus from water extracts of flesh and gives a satisfactorily accurate separation of the inorganic from the organic form.

There seems to be a progressive splitting up of the organic phosphorus compounds in beef flesh during the process of cooking so that in well done meats practically all the phosphorus is present in the inorganic form.

A study of the tables shows considerable variation in the relative amounts of soluble and soluble organic phosphorus in different cuts and in different animals. Extremes will be noted in rib of Jerry (a fat show steer) in which 91.44 per cent. of the soluble phosphorus is organic and in composite of 592 (an extremely emaciated steer) where only 26.02 per cent. or the soluble phosphorus is organic. This subject is being investigated further.

COLUMBIA, MO., March 9, 1910.

THE GLYCOGEN CONTENT OF BEEF FLESH.

(SECOND PAPER.)

By P. F. TROWBRIDGE AND C. K. FRANCIS.
Received February 17, 1910.

In continuing this study[1] the following points were especially considered.

(1) The disappearance or diminution of the glycogen in the flesh of a starving animal.

Smith's "Veterinary Physiology"[2] contains the following: "The glycogen which is stored up in the liver for future use may be made to disappear by starving and working the animal." The same author on p. 227 says: "The muscles of well fed animals contain a considerable quantity of glycogen. Ordinarily it may be stated that the muscles hold as much glycogen as the liver."

(2) The rapidity with which the glycogen disappears after death.

Roehmann,[3] experimenting with dogs, shows that the hydrolysis after death takes place, but not so rapidly but that the major portion can be recovered as glycogen in from one-half to two hours after death. Under certain conditions rigor mortis may take place without loss of glycogen.[4]

(3) The glycogen in horse flesh as compared to that in beef.

Without indicating the method of analysis, Lebbin[1] has reported horse flesh to contain on an average 0.7 per cent. of glycogen, while Pflüger[2] using the alkali method has found from 1.5 to 2.2 per cent.

"Even after nine days' starvation the muscles of horses have shown a glycogen content of from 1 to 2.4 per cent."[3]

Among the results published in the previous paper[4] we desire to recall to the reader the glycogen determinations on the lean meat from three animals. The percentages of glycogen in these have been averaged and reduced to a moisture- and fat-free condition. Other particulars are indicated in the table below.

TABLE I.—GLYCOGEN IN LEAN CLOD MUSCLE.

Lab. No.	Glycogen in fresh sample, per cent.	Glycogen in sample calculated to fat and H₂O free, per cent.	Kind of animal.	Condition of animal.	Age.
92103	0.697	3.38	Jersey cow	Lean	6 years.
91103	0.663	2.95	Short-horn steer	Very fat	4½ yrs.
9153	0.416	1.82	Hereford steer	Emaciated (starving)	23 mos.

While the amount of glycogen in the lean flesh of the Jersey cow is more than that found in the fat steer, the fact that the cow was in a thrifty condition should be considered. It may be that age is an important factor, or that the function of the animal in milk production bears some relation to the storage of glycogen. The thin Hereford steer was not starving in the sense that all food was withheld, but for eleven months he was so fed as to make him lose one-half pound each day. His condition was such at the time of slaughtering that he could not walk steadily but could get up of his own accord. Notwithstanding this emaciated condition and the fact that the entire carcass contained no fat which could be separated mechanically, the muscle still showed the presence of glycogen in considerable quantity.

The following table shows the glycogen content of the liver from a fat Jersey cow, about 7 years old and not in milk for 12 months previous to the date of slaughtering. The animal was killed at 10:18 A.M. and the liver received at the laboratory at 11:30 A.M. and the first portion placed in alkali at 12:05 A.M. The elapsed time indicates the interval required to remove the organ, grind, weigh and place the sample in the alkali.

TABLE II.—GLYCOGEN IN LIVER OF COW NO. 43.

Lab. No.	Sample.	Glycogen, per cent.	Elapsed time.
91052 x	Liver	2.91	1 hr. 47 min.
91052 y		3.07	1 hr. 51 min.
91052 z		2.83	1 hr. 57 min.

Table III shows the analysis of the liver from another fat Jersey cow, about 9 years old and not in milk for 12 months previous to the date of slaughtering. The animal was killed at 8:10 A.M. and the liver re-

[1] THIS JOURNAL, **2**, 24, (1910).
[2] "Manual of Veterinary Physiology," F. Smith, 3rd Ed. p. 226.
[3] Roehmann, *Biochemie*, **229**, 1908.
[4] *Ibid.*, p. 236.

[1] *Z. Nahr-Genussm.*, **7**, 747.
[2] *Ibid.*
[3] Smith's "Vet. Physl.," p. 227.
[4] *Loc. cit.*

ceived at the laboratory at 9:45 A.M. and the first portion placed in alkali at 10:14.

TABLE III.—GLYCOGEN IN LIVER OF COW No. 4.

Lab. No.	Sample.	Glycogen, per cent.	Elapsed time.
9102 x	Liver	3.09	2 hrs. 6 min.
9102 y		3.18	2 hrs. 13 min.
9102 z		3.12	2 hrs. 21 min.

The remaining portion of the above sample was placed in cold storage for one week, the temperature remaining about 6.5° C. Triplicate determinations were then made which gave results indicated in Table IV.

TABLE IV.—GLYCOGEN IN LIVER OF COW No. 4 AFTER ONE WEEK.

Lab. No.	Sample.	Glycogen, per cent.	Elapsed time.	Condition of sample.
9102 xx	Liver	2.78	1 week	Fresh
9102 yy		2.66	1 week	Fresh
9102 zz		2.57	1 week	Fresh

The remaining portion of the sample was returned to the cold storage and the same temperature maintained for another week. When removed on the 14th day the sample appeared to be in about the same condition, so it was decided to expose it in a sealed bottle to atmospheric temperature before analyzing. The results of the analysis after that time are shown in Table V.

TABLE V.—GLYCOGEN IN LIVER OF COW No. 4 AFTER 15 DAYS.

Lab. No.	Sample.	Glycogen, per cent.	Elapsed time.	Condition of sample.
9102 xxx	Liver	2.06	15 days	Slightly spoiled.
9102 yyy		2.32		
9102 zzz		2.36		

Portion 9102 xxx was intentionally removed from the bottle without its being mixed with the remainder of the sample, as it showed evidence of decomposition, being covered with mold. The results were somewhat higher than we expected after the sample had been exposed for eighteen hours to the temperature of the air. Upon obtaining the records from the local weather bureau a rather interesting fact became apparent: the average temperature for the eighteen hours was 6.6° C. As we have previously demonstrated that low temperatures check the hydrolysis of glycogen, no great change could be expected in this instance.

Experiments with Horse Flesh.—A horse thin but not in starving condition, about twenty years old, was killed and a portion of lean muscle from low in the neck used for the glycogen determination.

In the tables below the elapsed time indicates the

TABLE VI.—GLYCOGEN IN HORSE FLESH.

Lab. No.	Glycogen, per cent.	Elapsed time.	Temperature.	Condition of sample.
91190 x	0.183	30 min.	20°–25°	Fresh
91190 y	0.122	37 "		
91190 z	0.133	41 "		
91190 xx	0.066	22 hrs.	20°	Fresh
91190 yy	0.077	22 "		
91190 xxx	0.014	3 days	20°	Slightly decomposed.
91190 yyy	0.015	3 "		
91190 zzz	0.010	3 "		

time passed after the death of the horse before the sample was placed in alkali. The temperatures mentioned are those to which the sample was subjected for the period given previous to the analysis.

The above results show that horse flesh is subject to an enzymatic hydrolysis similar to that of beef. At the end of 22 hours the loss of glycogen was equal to 51.4 per cent. and at the end of 3 days to 91.1 per cent.

SUMMARY AND CONCLUSIONS.

1. The glycogen content of beef muscle and beef liver varies from 0.1 to 0.7 and 0.2 to 3.8 per cent. respectively.

2. Starvation or extreme debility does not cause entire removal of glycogen from the muscle or liver.

3. The glycogen of beef liver and muscle slowly decreases, but does not entirely disappear, when kept at a temperature of 6.5° C. for over two weeks. Glycogen may be present even when liver has become unfit for food.

4. Horse flesh is subject to an enzymatic hydrolysis of the glycogen similar to that of beef. The glycogen decreases slowly when the sample is exposed to temperatures of about 20–25°.

5. The glycogen content cannot be said to offer an absolute or even approximate basis for distinguishing beef from horse flesh.

COLUMBIA, MO., Feb., 1910.

ADDRESSES.

VEGETABLE TANNING MATERIALS.[1]

By JOHN H. YOCUM, Ladew and Yocum Tanneries, Newark, N. J.

When in the time that our tanners had the virgin forest to depend upon, hemlock and oak bark were the only vegetable tanning materials in use in this country, and they yet remain the source of greatest supply of tannin.

The yearly cut of hemlock bark is between 800,000 and 900,000 tons, and oak bark from 300,000–400,000 tons. The peel of hemlock has decreased about one-third in the last ten years, while the peel of oak bark has remained nearly stationary.

Because of increased production of leather during this period and because of the decrease in the peel of hemlock bark, it has become necessary to reach other sources of tannin supply.

The first development to meet these conditions was the making of chestnut wood extract, which has now reached a very important stage, from 450,000–500,000 bbls. being produced yearly. In addition chestnut wood is being used at many southern tanneries directly in the leaches. Tanners have found that the liquors obtained by this method are insufficient in strength for their purposes, so some of them have added evaporating plants to their leach houses to concentrate their liquors to a sufficient strength for their use.

A barrel of chestnut extract is practically equal to a ton or cord of either oak or hemlock bark, and while the yield from various extract factories differ, generally a cord of wood (128 cubic feet) yields a barrel of the 25 per cent. tannin chestnut extract.

Quebracho extract is made from quebracho wood, a product

[1] Address before New York Section, American Chemical Society Symposium on Leather.

of the River Platte Valley in South America. This wood contains from 18–24 per cent. tannin.

The solid quebracho extract contains about 65 per cent. tannin and is sold on this basis. The yield of extract is generally one ton of solid extract from about three and one-half tons of the wood. One ton of the solid extract is considered equivalent to nine tons of oak or hemlock bark.

There are now being imported about 60,000 tons of this solid extract or its equivalent in wood; as there are two factories manufacturing liquid quebracho in this country, the equivalency of this quantity of quebracho is 540,000 tons of oak or hemlock bark.

The tariff on this product was formerly ½ cent per pound, but it has been raised to ¾ cent per pound in the new tariff bill.

Mangrove bark and mangrove extract are also imported in quantity. Mangrove bark grows on the low shores of salt waters everywhere in the tropics. Along the Gulf of Mexico, mangrove averages, when properly cured, about 30 per cent. tannin; that from the East coast of Africa about 40 per cent. tannin. East Indian and Borneo, between the two; this product enters free of duty, so that no accurate data is obtainable as to the quantity imported, but this no doubt is more than 20,-000 tons annually, equivalent to more than 60,000 tons of oak or hemlock bark.

In the East Indies are two factories making solid extract from this bark, which comes upon our market as mangrove cutch; the quantity being brought in is not large now on account of the duty of 7/8 cents per pound, which the new tariff has placed on this product. It formerly came in free.

Myrabolans are the fruit of an Indian tree, the harvest ranging from 30,000–45,000 tons per year. The United States is taking from one-third to one-half the production. Myrabolans contain about 30 per cent. tannin. What is now being used in the tanning trade in this country will represent at least 45,000 tons of oak or hemlock bark. It comes in free of duty.

Valonia, the cup of an acorn obtained in Asia Minor and Greece, is being imported in quantity; it contains about 40 per cent. tannin. The harvest is from 50,000–60,000 tons per year. What is being brought into this country is equivalent to about 40,000 tons of bark per year. It comes in free of duty.

Divi-divi, wattle bark, etc., do not come into this country in any quantity.

Palmetto extract and canaigre are not produced in sufficient quantities to be commercially considered. Sumac and gambier are imported in large quantities, but do not go into the same trade that uses our native barks and cannot be compared with them.

From the estimates given of what the various tanning materials in use here are equivalent to in bark, it is seen that in total 2,300,000 tons are represented, about one-third being imported materials. At a fair valuation, these materials cost the tanner about $23,000,000, the importations being about $7,000,000 per year.

From a chemical view-point, tannins are divided into pyrogallol tannins, such as those from chestnut wood, myrabolans and valonia; and catechol tannins, such as from quebracho, hemlock, mangrove and oak bark. But from the tanners' view-point, the color and characteristics of the leather made from these various materials is of more importance.

Arranging these materials as to their color, that is from a light yellow to a dark red, we have sumac, myrabolans, valonia, bleached quebracho, oak bark, natural quebracho, chestnut, West Indian mangrove, hemlock, and East African mangrove.

It is important to a tanner of oak so far as color is concerned, that if he uses chestnut, to also use quebracho, so that a duplication of the oak color be obtained. There are many combinations that can be arranged from these materials to duplicate the oak, hemlock or union colors so long established as standards in the sole leather trade.

The color of the leather produced is not the only characteristic which the tanner has to consider in the use of tanning materials; some wish hard leathers, some soft. It is well established that sumac is not suitable for hard leather; it is used on sheep and other soft leather exclusively. Myrabolans are considered a soft tannage. Valonia and chestnut are considered hard tannages. Oak, hemlock, mangrove and quebracho are used on both hard and soft tannages. There seems good reason to believe that by proper manipulation soft leathers can be obtained from any of these materials.

Palmetto extract which often contains as much as 12 per cent. of ash from salts soluble in the extract, the extract containing about 20 per cent. tannin, invariably makes soft leathers when used alone. Sulphited quebracho extracts which contain a large per cent. of ash also make soft leathers, and it is a well-known fact that hemlock liquors treated with common salt will tan sheep skins as soft as does sumac.

From this it is a fair conclusion that salts in tanning solutions have a tendency to soften the resulting leather.

In tanning pickled sheep skins, that is, skins cured in NaCl and H_2SO_4, unless the tanning solution is salted; that is, treated with NaCl, the skins plump and lose their value, becoming hard and tinny when tanned; that is, NaCl counteracts the action of the H_2SO_4 on skins.

The tanners of the hardest sole leather use H_2SO_4 as a plumping agent, using hemlock, oak, mangrove, valonia, chestnut, myrabolans and quebracho in various mixtures and proportions. It follows that the character of leather as to softness or hardness is more dependent on the relation of plumping acids to soluble non-tannins than it is on the character of the tanning material used.

In using the term soluble non-tannins, I wish to include the effect not only of soluble inorganic salts, but also the similar effect of organic non-tannins natural to the tanning material.

The character of the organic non-tannins vary both as to their ability to furnish plumping acids and non-plumping acids, and likewise as to their depression of plumping acid action on the skin.

It is quite true as a rule that the pyrogallol tannins do not give the hard leathers that the catechol tannins produce, yet this may not of itself be due to the character of the tannin, but may result from the fact that gallic acid and non-plumping acid is usually present in the tanning solutions made from these materials.

The subject is a broad one and needs much investigation, but sumacs and nutgalls of the pyrogallols series show the largest changes into gallic acid and give the softest leather, while valonia of the same series shows small changes into gallic acid and gives a firm leather. On the other hand, chestnut extract contains in its extracted form gallic acid, and not subject to much further changes into this acid, gives a firm leather.

Palmetto is of the catechol series, but gives a soft leather, which as I have noted before may be due to the presence of excessive quantities of inorganic salts, yet all the rest of this series are used for heavy leather tannages.

The nature of the combination of hide with tannin is not fully understood at present, but the tanner has had the experienced knowledge of generations in the use of raw vegetable tanning materials. This knowledge seems to have brought the practical tanner to conclusions, and he has determined in his own mind what raw material he wants to use to produce a certain result.

It lies with the chemist to determine the reactions between the different tannins, non-tannins and their relations to salts and acids before the final decision can be reached as to the

weakness or strength of the rule of thumb methods now followed by the tanner in determining the kind of tanning material to be used by him.

DYEING LEATHER.[1]

By F. E. ATTEAUX, President, F. E. Atteaux and Co., Boston.

The art of dyeing leather was known to the early Egyptians over three thousand years ago. They produced finely colored leather, samples of which have been found and preserved.

The Chinese and various Oriental tribes also understood the art, and produced highly colored and embossed leather, similar to morocco. They were the first to introduce colored leather in Europe.

After a time the races of Europe began to learn the process of manufacture and coloring leather for their own consumption. As time went on the art of dyeing leather increased. Processes were improved and at the present time the methods employed are radically different from those used only a few years ago.

Formerly vegetable coloring matters were in great demand for dyeing leather, but now these products have been replaced one by one with the artificial dyestuffs, and to-day only a few vegetable colors are used, the most important of which are logwood and fustic.

Of the artificial or so-called aniline dyes, those especially adapted for leather dyeing are the acid, basic, direct and alizarine dyestuffs.

These act differently on different tannages.

Chrome Tannage.—The process of dyeing the different kinds of chrome-tanned leather such as calf, sheep, goat and heavy leather, also pig and horse hides are similar and the formula used on one may be applied to all, with good results, the only difference being a slight variation in body or shade due to the nature of the skin and the method of chrome tannage.

Before dyeing, the skins should be thoroughly washed and if necessary cleared with dermiforma or lactic acid; then if desired a bottom of some vegetable coloring or tanning matter may be applied, such as gambier, sumac, quebracho or fustic, but this is not necessary only where basic colors are used, when a tannin mordant or bottom is required.

To obtain best results for sumac or gambier bottom, drum for 20 minutes at 100° F., neutral, with 3–6 per cent. of extract, the amount used depending upon the strength of bottom.

The liquor is then run off and $1/2$–1 per cent. tartar emetic is added, dissolved in a sufficient quantity of water, and drummed 15 minutes longer at normal temperature; rinse well before dyeing.

Fustic is applied in the same manner as the sumac with the exception of the tartar emetic bath which may be omitted.

From 1–3 per cent. of the extract may be used. This makes a good bottom for acid, direct or alizarine dyes, but should not be used for basic dyes, as it has but little affinity for them.

On dyeing heavy chrome leather with fustic this process and the fat-liquoring may be combined by first dissolving the fustic and then adding it to the drum together with the fat-liquor and drumming 20–30 minutes.

Alizarine colors can be dyed directly upon chrome leather either with or without a vegetable bottom. They are dyed with the percentage of color required to obtain shade for 20 minutes at 120° F. in neutral or slightly acid bath. If acid is used the best results are obtained by using 1–2 per cent. acetic acid.

These colors are used mostly on calf and heavy leather.

Alizarine orange R and alizarine yellow G are the most extensively used of these colors. By shading with logwood or alizarine blue a variety of tans and browns can be obtained.

Direct colors dye leather in a neutral or slightly alkaline bath.

They are drummed for 20 minutes at 120–130° F. From 1–3 per cent. of color should be used, the quantity depending upon the shade desired. If necessary $1/4$–$1/2$ per cent. of sal soda may be added to drum and this will insure the leather against acidity.

Wash leather well after dyeing.

By using 4 per cent. soluble oil, or some other light fat-liquor in the dye solution it is possible to fat-liquor and dye in the same bath.

Any of the direct colors can be used and by the combination of colors a great variety of shades can be produced.

Direct blacks are now used extensively in combination with logwood for producing black on calf and cow hides.

Basic colors are dyed similar to the *direct* colors only in a neutral bath at 110° F.; by adding $1/4$ per cent. bichromate of potash to drum after dyeing and running 15 minutes longer it will produce darker shades. These colors are used on all classes of chrome-tanned leather.

Phosphine produces various shades of tan ranging from a light yellow to the brown.

Bismarck- and chocolate-browns, malachite-green, fuchsine, auramine, methyl violet and methylene blue are colors of this class. They are fast to nearly all fat-liquors excepting a strongly alkaline fat-liquor which is liable to strip the color.

Acid colors are dyed by using $1/4$–$1/2$ per cent. sulphuric acid with the dyestuff. This is not necessary with all acid colors, some of which will dye neutral but many of them will not color the leather unless acid is used.

Acetic or formic acid may be used in place of sulphuric.

Leather can be drummed in a weak acid solution and color added in small quantities until the desired shade is obtained.

With these colors it is best to use a neutral or light fat-liquor, or fat-liquor before dyeing. Golden and coffee-browns are combinations of dye belonging to this class.

Colors very fast to light and fat-liquor can be obtained by dyeing the leather with 2 per cent. of dye in a drum for 20 minutes at 120° F. in a neutral bath.

The leather is then washed and run through a cold bath, composed of $2^1/2$ per cent. nitrite of soda and 5 per cent. hydrochloric acid for 15 minutes. It is then washed and put through developing bath of 1 per cent. of phenylamine, diamine, metatoluine diamine or some other developer for 15 minutes. The bath should be kept cold because resulting colors are apt to be dull or rusty if temperature of bath is too high.

The leather is then fat-liquored, dyed and finished.

Primuline, boma black BH and developed brown R can be dyed by the above formula, good bright colors resulting.

Sulphur colors can also be dyed on leather by first dissolving the dyestuff in as little sodium sulphide as possible and adding it to the drum with 5 per cent. salt and drumming for 20 minutes at 110° F.

India Tan.—Before dyeing India goat or sheep skins it is best to clear them with $1/2$–1 per cent. tartar emetic or 1–2 per cent. lactic acid, or if necessary re-tan with sumac and then wash thoroughly.

Basic and acid colors are the only class of dyestuffs used upon India skins with satisfactory results.

Direct and *alizarine* colors will not dye to advantage and it is considered a waste of material and time to use them.

Basic colors dye India-tanned leather very easily as the tannage acts as a mordant, and readily takes up the dye. They produce very bright colors, and are dyed by drumming 120° F. in a neutral bath for 20 minutes. 2 per cent. of the dyestuff produces a full shade.

If an excess of color is used bronzing results, but this may be overcome to a certain extent by using a small percentage of acetic acid with the color.

To dye with acid colors, the skins after being cleared are dyed as follows:

For 1 per cent. color use 0.25 per cent. sulphuric acid, the ratio varying with the amount of color used; they are dyed similar to the basic colors with the exception of the addition of acid; the skins which have been previously treated with sumac and sulphuric acid do not require the addition of acid with the color, as the acid retained in the skins is sufficient to drive on the color.

Acid colors are much faster to light than basic colors and produce bright shades.

Leather red 3B, tartrazine, orange A conc., induline and acid green are all extensively used.

Vegetable Tan.—Acid and basic colors can both be used upon sumac, gambier, quebracho and other tannages of this class. They are dyed in the same manner as India-tanned skins.

The various combination tannages are also colored in a like manner. If a basic dye will not color with good results the leather should be drummed with sumac and afterwards treated with tartar emetic. The color will then go on properly.

Bark-tanned sheep leather, hemlock splits, etc., are dyed very easily with acid colors and sulphuric acid. If basic colors are desired the leather should be treated with sumac before dyeing. For clearing bark-tanned skins $1/2$–1 per cent. borax, and the same quantity of Wyandotte tanners' soda gives good results, but if light shades are desired after clearing the skin with borax or Wyandotte tanners' soda then give them sumac and run for a few minutes in a solution of sulphuric acid of 1 per cent. of the weight of stock. Leather will be much lighter in color.

$1\frac{1}{2}$–2 per cent. tin crystals can be used with sumac to good advantage.

Heavy oak or hemlock sole and belting leather are colored by brushing on solution of dyestuff, made up as follows:

$1/2$–2 oz. of color are dissolved in a gallon of water; acetic acid or methyl alcohol renders the color soluble.

Gum tragacanth and caseine can be used as thickeners. Both acid and basic colors can be used with the gum tragacanth but only acid colors with the caseine, as the alkali used to cut the caseine, will precipitate a basic color. For this reason basic colors cannot be used in any finish or seasoning containing alkali.

Potassium titanium oxalate will produce a yellow shade similar to fustic upon any vegetable-tanned leather; it not only acts as a mordant but gives a good yellow bottom for the color. It does not work on chrome leather unless the leather has been previously treated with vegetable tanning material. It is dyed by drumming $1/2$–2 per cent. of the compound in a neutral bath at 100° F. for 20 minutes; by using from $1/8$–1 per cent. chrome with potassium titanium oxalate various shades of tan and light browns can be obtained depending upon the amount of chrome used.

Basic colors can also be used in combination with potassium titanium oxalate.

Alum leather is dyed both in a drum and by brushing on color.

Methylene blue and roseine produce delicate tints of blue and pink which are used for fancy leathers. All the basic colors give fine tints and acid colors can also be used on this class of leather.

Chrome, alum and vegetable ooze leathers are dyed with some class of colors previously given under the head of tannages to which they belong and are dyed in the same manner.

For a *black* ooze, the leather is first drummed with a yellow shade Bismarck or potassium titanium oxalate. A direct yellow-brown can be used on chrome ooze; then the leather is drummed with 2–4 per cent. logwood crystals for 30 minutes, $1/2$ per cent. alkali being added to force on the color.

A striker of acetate of iron or burnt copperas and copper sulphate is then used. It is next fat-liquored and then dyed with $1/2$–1 per cent. of neutral or leather black; drummed for $1/2$ hour at 120° F. and fat-liquored again and then finished.

The amount of aniline color and logwood crystals used depends largely upon the tannage and shade of black desired.

Nigrosines are generally classed as basic colors, but they belong to a series of colors known as ingrain colors. They are extensively used in seasonings and finishes for blacks. They can be dyed on chrome leather, either in a neutral or acid bath, but do not give good results when dyed on vegetable tannages.

A fine blue-black shade is obtained on the flesh side of the leather by using a little nigrosine in with the logwood when dyeing.

A small percentage of nigrosine brushed on alum ooze leather gives light shades of gray and slate.

NOTES AND CORRESPONDENCE.

A MODIFIED SOXHLET APPARATUS.

In order to use as fully as possible the heat from an electric stove for ether extraction a battery condenser was found convenient as it occupied less space than separate glass condensers.

8 inch
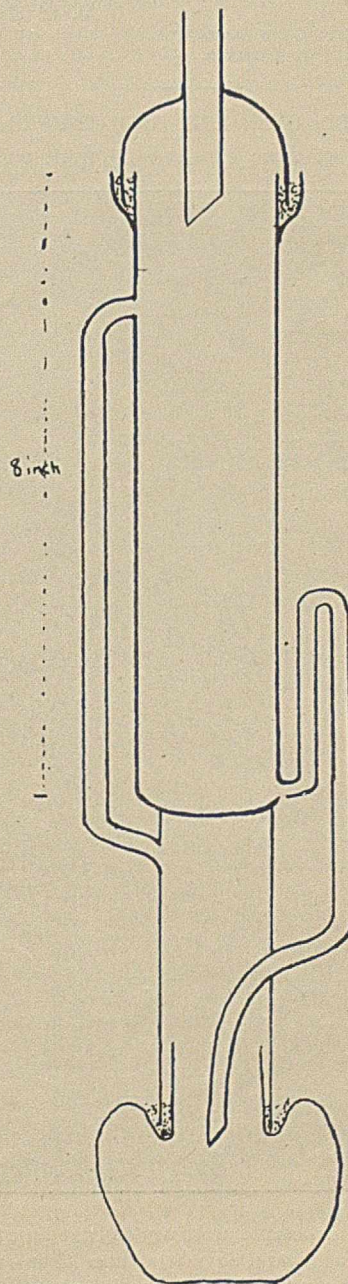
A cheap but efficient condenser was made from a piece of ordinary galvanized iron water pipe into whose ends wooden plugs were inserted through which passed water inlet and outlet tubes and also the block-tin tubes in which the ether was condensed. The water jacket was about 36 inches long. The end plugs were made water-tight by pouring upon their inner surfaces a thick layer of tar. The bottom layer was poured in from the top and the top layer through a hole in the side which was subsequently soldered. The use of such a condenser prevents the employment of ground-joints between condenser and Soxhlet as they are not sufficiently flexible. Knorr's modification was therefore further modified by adding to it a second mercury seal at the upper end. The drawing explains the arrangement. The condenser end was made of glass having the same diameter as the block-tin tubes of the condenser and the junction was effected by first winding on the outside a light cotton soaked in gelatine acetic acid and then covering this while moist with a piece of heavy rubber tube. The rubber tube does not show signs of damage from the ether after several months of use.

V. E. Henderson.

The Pharmaceutical Laboratory.
The University of Toronto.

AN IMPROVED OVEN FOR HIGH TEMPERATURES.

In the course of some experimental work on methods of

In order to obtain a temperature of 250° C. the copper bottom had to be heated to redness. After a week's use this bottom burned through, hence it became necessary to make some changes in the form of oven.

The old copper bottom was cut away, leaving an inch around the edges and the oven then placed on a separate heating base, the construction of which is shown in the accompanying sketch. This base consists of two iron plates the size of the oven, and one one-fourth inch apart, attached at the sides and open at the ends and connected by a number of one-half inch tight-fitting brass tubes. The upper plate is of three-eighths inch cast iron, the lower is of sheet iron and is used to prevent reflection of heat to the bench. The brass tubes allow the circulation of fresh hot air through the oven. The flame of the burners is applied to the bottom of the cast-iron plate through three-inch holes in the lower plate protected from drafts by circular hoods. Parallel grooves are cut in the upper surface of the cast-iron plate, and copper "porcupines" such as are sometimes used in air-cooled gasoline engine cylinders are expanded into them. The copper porcupines increase the radiation of heat and present a large heating surface to the air currents in the oven. The increased efficiency is so great that a temperature of 250° C. can be maintained without heating the base to redness. The oven has been in daily use for several months and shows no ill effects beyond a slight scaling of the porcupines. These can be renewed when necessary at comparatively slight expense. The oven
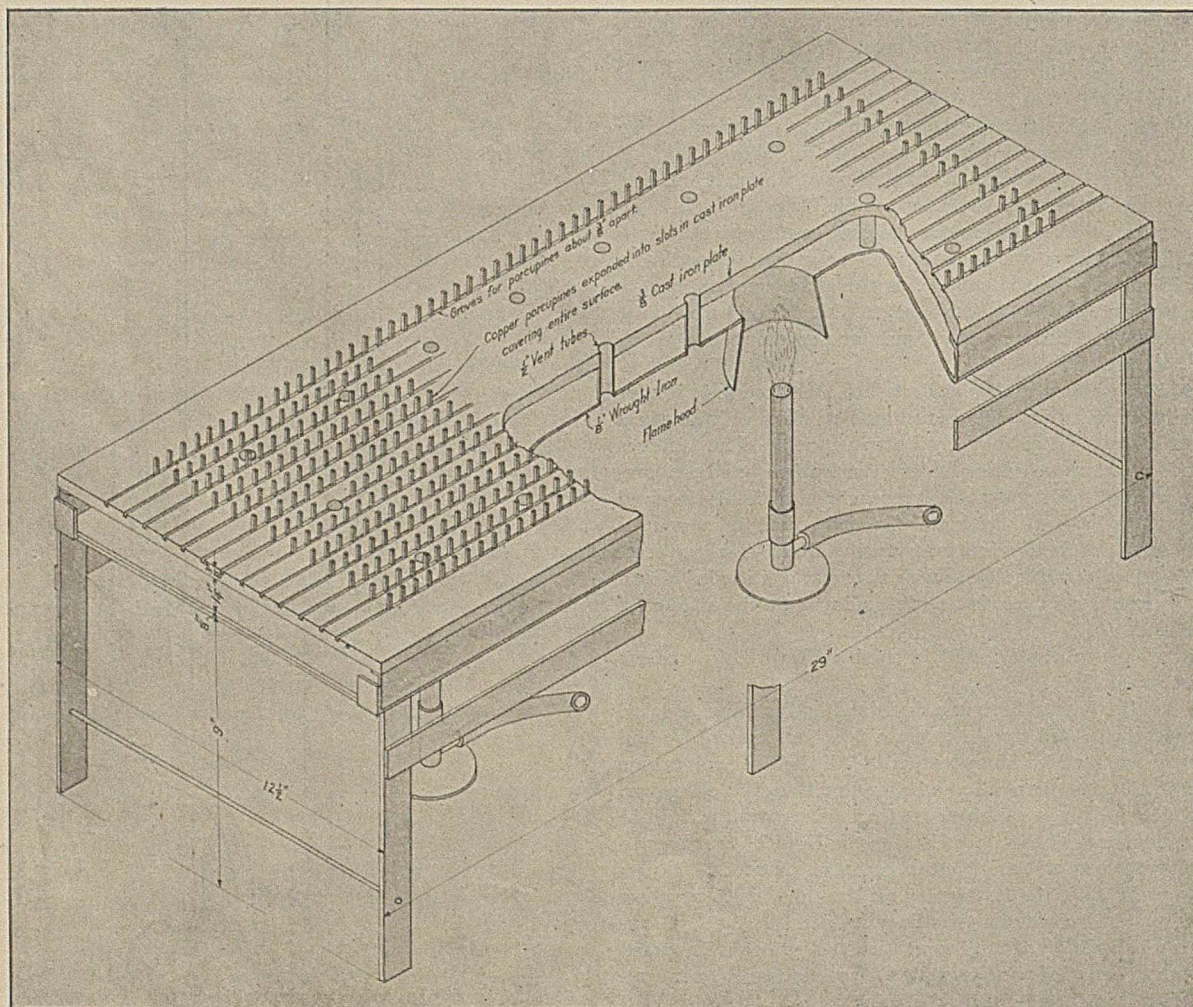
asphalt analysis, it became necessary to have an oven temperature of 250° C. for several days at a time. The oven in use at that time was a new single wall, single bottom, copper oven.

base was made according to our plans by the Hamblet Machine Company, Lawrence, Mass.

H. W. Clark,
George O. Adams.

LENGTH OF A TECHNICAL PAPER.

Editor Journal of Industrial and Engineering Chemistry.

Dear Sir:

In the April issue of THIS JOURNAL, on page 157, is a note by J. W. Turrentine on the "Length of a Technical Paper."

I wish to endorse all that he says therein. There is often too much abbreviation. The technical paper is written for the eyes and use of some one interested practically in the subject, and too much detail can hardly be given. It is too often assumed that well-trained chemists or men of standing are capable of reading between the lines and supplying the details. They may be capable with the hints given of working the process successfully after they have experimented with it and found what was lacking in the article. For instance the methods for crude glycerine analysis might be boiled down to: weigh out 1.5 grams crude glycerine into a 100 cc. flask, precipitate chlorine and act on reducing matters with silver carbonate, subsequently precipitating organic matters with basic acetate of lead. Make up to mark, filter off an aliquot, rejecting the first portions, take 25 cc. in a 250 cc. flask and add about 42.5 cc. of the bichromate solution and 15 cc. of strong sulphuric acid, etc. There are several very essential details left out of the above for a convenient and correct determination of the glycerol, but to the reviewer, who may not be acquainted with or interested in glycerine, the above appears all that is essential for a trained chemist to have. Give us the details in any articles printed in THIS JOURNAL and let the Abstract Journal and Journals on Popular Science or Chemistry handle the articles pruned down to Hints for the Imagination.   Yours truly,

WILSON H. LOW.

New York, March 17, 1910.

Chandler Testimonial. Dear Sir:

After a very long period, almost a lifetime, of the most useful activity as head of the Department of Chemistry and Dean of the School of Mines of Columbia University, Dr. Charles F. Chandler will retire from duties at the end of the coming term, to be appointed Professor Emeritus of Chemistry. We all know the great service rendered by this distinguished man to our science and to the industries of our country, and it is difficult to convey in words the gratitude which so many of us owe to him who has always been ready to give his advice and to lend his assistance in practical ways.

To commemorate this important epoch in the life of our esteemed friend, the following organizations have taken the initiative in planning for a testimonial to be tendered to Dr. Chandler by the chemists of the United States: The Chemists' Club, The Society of Chemical Industry, The American Chemical Society, The American Electro-Chemical Society, The American Institute of Chemical Engineers, The Verein Deutscher Chemiker.

The form of this testimonial has been arranged as follows:

First: *A banquet* at the *Waldorf-Astoria*, on Saturday, April 30th, at 7 P.M. The cost of each dinner ticket will be $5.00, a sum which, while not sufficient to defray the expenses, will we hope insure a large attendance. Ladies will be admitted to the galleries and light refreshment served them at a nominal charge of $1.00 per person.

Second: The *presentation* to our honored guest of a *bronze bust* of himself in heroic size, to be executed by the famous sculptor, Mr. J. Scott Hartley, which bust we expect will finally be presented to the Chandler Museum of Columbia University. A replica of this bust is to be presented to Mrs. Chandler.

Third: The *Creation* of a *Chandler Testimonial Fund* for the purpose of purchasing books for the library of the Chemists' Club.

The *committee solicit your subscription* for the object set forth, and request you to make your contribution a liberal one, so that a large sum may be collected which will be finally used for the development of the *library* of the Chemists' Club, New York, in which, as you know, Dr. Chandler has taken a special interest. This already contains the Perkin Library and is intended to be a reference and circulating library, covering the entire field of theoretical and applied chemistry, which is to be in charge of a salaried librarian, and is to contain duplicate sets, one of which is to be used for circulation among American chemists.

In addition to any personal interest you may take in this testimonial, you are urgently requested to bring the matter of subscribing to this fund, to the notice of any chemical concern with which you are connected, drawing their special attention to the invaluable service which Dr. Chandler has rendered to the industries of this country and to the development of its economic wealth.

Respectfully,

I. F. Stone, Pres. of the Chem. Club,
Ira Remsen, Pres. of the Soc. of Chem. Ind.,
Wilder D. Bancroft, Pres. of the Am. Chem. Soc.,
L. H. Baekeland, Pres. of the Am. Elec.-Chem. Soc.,
Charles F. McKenna, Pres. of the Am. Inst. of Chem. Eng.,
Virgil Coblentz, Chairman of the Verein Deutscher Chemiker.

Committee of Arrangements: *Treasurer*, Morris Loeb, 273 Madison Ave., New York; *Chairman*, I. F. Stone, 100 William St., New York; *Secretary*, Charles F. McKenna, 50 Church St., New York.

BOOK REVIEWS AND NOTICES.

Hygienic Laboratory—Bulletin No. 58. Dec., 1909. Digest of Comments on the Pharmacopoeia of the United States of America and National Formulary. By Murray G. Motter and Martin L. Wilbert.

This volume of 523 pages represents a complete digest of the literature selected from all available sources, relating to the Pharmacopoeia and National Formulary for the year ending 1906, issued under the authority of the Surgeon-General and approved by the Secretary of the Treasury. The recognition of these two standard works through the provision of the Food and Drugs Act, in connection with the U. S. Government becoming signatory with other powers respecting the unification of pharmacopoeial formulae, creates for the U. S. Pharmacopoeia and National Formulary a position of great legal importance. Therefore in the coming decennial revision, it is highly important that the mass of comments and criticisms, more especially those bearing on the relations of these works to the law, are in shape readily available. Also during the interval of 5 years new revisions of several foreign pharmacopoeias have appeared which must receive careful consideration in accordance with the agreement between the United States and the Brussels Pharmacopoeial Conference.

As a work of reference for chemists, physicians and apothecaries, this report is highly recommended since there is scarcely a field in which they are interested not reviewed. In the table of contents appear some of the following headings: Legal Status of Food and Drug Law, Standards, Analytical Data (physical constants, thermometry, polarization, apparatus, color standards), Biologic Products, Vegetable Drugs (valuations, ash determinations, alkaloids, physiologic standardization), Pharmaceutical Preparations, International Standards, Foreign Pharmacopoeias, Rules of Brussels Conference, Comments on Official Standards, etc.

The compilers are to be commended upon the thoroughness and care exercised in this task.   V. Coblentz.

New and Non Official Remedies 1910 Containing Descriptions of the Articles which Have Been Accepted by the Council on Pharmacy and Chemistry of the American Medical Association Prior to Jan. 1st, 1910.

The purposes of this book (256 pp. with index) are explained

in its preface as follows: The Council of Medicine and Pharmacy was established in February, 1905, by the American Medical Association, primarily for the purpose of gathering and disseminating such information as would protect the medical profession in the prescribing of proprietary medicinal articles. In pursuance of this object the Council examines the articles on the market as to their compliance with definite rules which are designed to prevent fraud, undesirable secrecy and the abuses which arise from advertising to the laity. Such articles as appear to conform to the rules are admitted and their essential features are described in this annual publication of the Council. Physicians are to understand that the acceptance of an article does not necessarily mean a recommendation, but that so far as known it complies with the rules of the Council.

Through this means the Amer. Med. Ass'n has endeavored to combat the proprietary medicine evil. The contents embrace practically all of the newer synthetics that have appeared in our market, in addition to organic gland remedials, serums, vaccines and some proprietaries. It is an excellent and authoritative book of reference for the chemist, apothecary and physician since the descriptions, tests of identity and for impurities as well as therapeutics are fully treated.   V. COBLENTZ.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

SEMI-ANNUAL MEETING AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The summer meeting of the American Institute of Chemical Engineers will be held at Niagara Falls, N. Y., June 22–24, 1910.

A prominent feature of the meeting will be visits to the interesting chemical industries in this locality.

An important program of papers is being arranged for by the Committee on Meetings.

COMMITTEE ON RESEARCH PROBLEMS, DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

The Committee on Research Problems of the Division of Industrial Chemists and Chemical Eng'neers realizes that the field open to it is broader than it can possibly cover in its entirety. It feels that it is not within its province to take up specific problems that are of limited interest or that affect merely economic questions of local interest; rather that its work should be on broad lines of questions of general methods of research and of researches that affect the conservation of natural resources by decreasing waste and rendering materials now ignored of use.

We, therefore, ask the members of the American Chemical Society for suggestions of lines on which it is practicable for us to work and that will enable us to be of the greatest assistance. The following seemed to the committee promising ones on which to start, but if we are to succeed in them we must have the coöperation and assistance of the members.

We wish the members to send us statements of the general problems that they are investigating, in order that we may bring in direct communication those who are working on similar lines. We also wish to be in a position to put those who desire advice as to general methods and appliances in direct communication with those who can and will give such information. There are many members of the Society who are so located that they have not access to libraries when they are called upon to make investigations in lines new to them. It will be of great assistance to such men if they can learn who have worked on similar lines and are willing to give them advice and tell them where to look up the particular points they wish to know about. The committee particularly desires to be informed

which members are willing to assist others in this way and on what particular lines.

In a great many cases men have made occasional observations, tests and analyses, which by themselves are only of temporary interest, but if the results obtained by all who have worked on any of these lines were collected and compared, the results would often be of permanent value. As an instance, the collection of routine coal analyses, from which a map was prepared showing the geographical distribution of sulphur and ash in the Welsh coal fields. This map proved to be of great value to the consumers. A similar collection of analyses of our coals, especially if it included the determinations of the fusibility of the ash, would be very useful. The analyses published by the coal companies, and even the Geological Surveys, are often unsatisfactory, as they are usually either those of picked samples or of very large averages that do not correctly represent what the consumer is likely to receive.

In the aggregate the amount of work done by students for their theses is immense, but it is scattered and individual results are often small. The committee believes that if the colleges would coöperate and agree on a list of subjects each year and the results of all the theses on any subject compared, much valuable information would be obtained. In many cases the work done in one year would suggest modifications and extensions of the problems to be taken up the next year. In many cases it is not practicable to publish a thesis, and in many cases they are not of sufficient value to warrant it. Most of them, however, contain some points that are new or interesting, and if a number of those on one subject could be combined they would be well worth publishing, and the men would have the credit for the good work they have done.

If those in charge of such work will let us know whether they consider such coöperation feasible, and if so, how best to bring it about, we, as a committee, will do all in our power to assist them.

(Signed):   GEORGE C. STONE,
            W. R. WHITNEY,
            G. W. THOMPSON.

REPORT ON THE MEETING OF THE SUB-COMMITTEE ON GLYCERINE ANALYSIS AT BOSTON, DECEMBER 29 and 30, 1909.

Organization.—Mr. R. E. Devine resigned from the committee a year ago. His resignation, however, has not to date been accepted and inasmuch as Mr. Devine has again taken up glycerine work and has expressed a wish to resume his work in the committee it was thought that he should still be considered a member.

Dr. Hillebrand was informed of the invitations extended to Dr. A. M. Comey and Mr. S. E. Emery and stated that these gentlemen would be officially notified of their appointment. Mr. B. T. B. Hyde requested that Mr. Loveland take his place.

The committee as at present constituted therefore consists of:

A. C. LANGMUIR, *Chairman*,
ROBERT E. DEVINE,
J. W. LOVELAND,
W. H. LOW,
A. M. COMEY,
S. E. EMERY.

SAMPLING AND ANALYSIS.

Meetings were held at the Hotel Lenox on the afternoons of December 29 and 30, 1909. There were present Messrs. Hyde, Loveland, Low, Comey, Emery and Langmuir.

A general discussion of the methods in use for the valuation of crude glycerine and the results handed in on the analysis of the samples sent out by the chairman, took place. All of those present had had practical experience with both the acetin and

bichromate methods. Some of the members used the acetin method almost exclusively in their work; the others made use of the bichromate process mainly, testing occasional samples by the acetin method. The committee was in substantial agreement as to the details of the acetin process. It had been the experience of those members of the committee who had persevered with the acetin method, that good duplicates were obtainable which agreed with the bichromate on good crudes and distilled glycerines and disagreed on bad crudes. Results obtained independently by members of the committee in the analysis of the pure sample A show that both methods have a tendency toward low results, but that these results are practically identical in the case of pure glycerine. In view of this and the fact disclosed by replies received to the committee's circular letter that a majority of glycerine chemists use the bichromate method and are strongly in favor of it, the committee felt that both methods should be investigated, with the object of recommending the details of each method necessary to achieve the best results and to indicate which process should be employed with impure crudes.

A test which would measure the impurities present and indicate the cases where the bichromate would be unreliable is very necessary. The determination of non-volatile organic impurities leads to discordant results unless conditions are under good control and is not adapted to the general laboratory. The determination of alkali combined with fatty acids is readily carried out and possibly is a guide to the amount of organic impurities present. Messrs. Low and Langmuir undertook to investigate the reliability of this test in various crudes.

The chairman stated that there should be little trouble in reaching an agreement as to the details of the acetin method or the methods of testing dynamite glycerine and advised that the brief time at their disposal be devoted to a thorough discussion of the bichromate method in order to reconcile differences and lay out lines of research.

Correspondence received by the chairman revealed a chaotic condition with respect to the bichromate method, each chemist using modifications of his own with widely different methods of purification and oxidation. Considerable work is necessary to decide which of these modifications are erroneous or superfluous and to evolve a method embodying the best features of the methods submitted.

Sampling from Drums.—No attempt should be made to include salt in the sample, which must be free from solid deposits to insure agreement among chemists. Drums should stand bung up, to permit salt to settle. The sample is taken with a glass tube as large as can be closed by the thumb and long enough to reach to the bottom of the drum, as stratification is possible. If salt is felt the tube must not be pushed into the salt. In removing the tube, the glycerine adhering to the outside is stripped by drawing through the fingers. Every drum is sampled. Sample is delivered into a large preserve jar with compression top, which can be warmed and shaken to mix sample.

Any salt left in the drum after dumping is not washed out, but is weighed with the tare and placed at the disposal of the seller.

For *analysis* a large weight should be taken and reduced by aliquoting.

For purification silver sulphate, basic lead acetate, combinations of the latter with silver oxide or carbonate, and copper sulphate are in use.

Mr. Langmuir promised to make a study of the relative effectiveness of silver sulphate and basic lead acetate.

The committee considered evidence to the effect that silver oxide showed a tendency to oxidize glycerine, particularly in alkaline solutions and concluded that silver carbonate or sulphate would be a superior agent for the removal of chlorine.

On account of its superior solubility silver sulphate should be more effective than the carbonate in removing chlorine. Mr. Low will make a comparison of the two reagents in this respect.

The chairman cited experiments showing that the salt left after treatment with lead acetate alone, did not exceed 3 milligrams in the portion taken for oxidation in the Richardson and Jaffe method and that no measurable error was produced in this way. If silver salts are not required in the removal of chlorine there is no object in adding them unless the purification is more complete, or the precipitate more easily filtered.

Mr. Low's experiments with salt led him to a different conclusion. Mr. Low agreed to test the effect of the small amounts of salt which would escape the lead acetate in the bichromate oxidation mixture.

Mr. Low and the chairman were also at variance in regard to the action of the acetic acid in the small amount introduced by the lead acetate, upon the oxidation mixture and it was agreed that each repeat his experiments.

Mr. Emery undertook to make a comparison of copper sulphate and lead acetate in samples to be sent him by Dr. Comey.

Dr. Comey will make a study of the effect of varying basicity of the lead acetate in the purification of glycerine to determine whether glycerine is retained in the precipitate when the acetate is strongly basic.

In regard to the oxidation, the chairman believed that the problem consisted in so adjusting conditions that all of the glycerine and a minimum of the fatty acids present be oxidized. A reaction may be considered analytically complete if the time is equal to twenty times that necessary to carry it half way. As all know, the oxidation of glycerine is so rapid as to be almost violent when concentrated sulphuric acid is added to the glycerine bichromate, and it would appear that the glycerine oxidation is complete in a few minutes unless intermediate products are formed which are but slowly oxidized. This is an important point and the chairman undertook to determine the minimum time necessary to effect the maximum oxidation with C. P. glycerine.

Once established this time should not be exceeded, in order to reduce the error due to oxidation of fatty acids. This reaction, as may be observed by mixing acetic acid with the bichromate mixture, is a slow one, but may occasion considerable error if the time be unduly prolonged. The speed of a reaction is halved by every 10° C. reduction in temperature. The chairman believes that this error should be diminished to a fourth, as may be done by carrying on the oxidation at 80° C., provided the oxidation of glycerine may be completed at this temperature. He agreed to test the effect of the lower fatty acids in this way.

Independent work on the above lines by other members of the committee is advisable.

If carbon monoxide or formaldehyde are formed and escape in the gases, an error is produced which goes to offset that due to fatty acids. Dr. Comey agreed to test the gases evolved for the above impurities.

A difference in results is possible by varying the initial temperature of oxidation. This may be done by adding dilute sulphuric acid instead of concentrated as in Comey's method. Mr. Loveland will experiment on these lines and will also determine whether there is any difference between delivering the glycerine to be oxidized at the bottom of the hot bichromate sulphuric mixture or adding sulphuric acid in the usual way to the bichromate-glycerine mixture.

The committee agreed that bichromate was the best standard. It should be pulverized and dried at 110–120° C.

The most desirable standard is anhydrous glycerine or glycerine of known strength as determined by an accurate specific gravity table. Messrs. Comey, Low, Emery and Langmuir

will attempt this winter to establish the gravity of anhydrous glycerine.

It was decided to meet again in June and it was hoped that the above research work would be far enough along at that time to enable the committee to make final recommendations.

The chairman had prepared three samples for analysis, marked A, B, and C. "A" contained 76.02 per cent. of anhydrous glycerine, 4.00 per cent. sodium chloride, 1.00 per cent. potassium sulphate, 0.50 per cent. sodium carbonate and 18.48 per cent. of water. These amounts were carefully weighed and thoroughly mixed. The glycerine was prepared from a high-grade C. P. product. The water was first expelled by heating *in vacuo* until the glycerine was boiling freely. The first third of the distillate was rejected. The second third only of the glycerine run was taken. The vacuum was about 12 mm. and special precautions were adopted to exclude moisture. The specific gravity of this glycerine at 15.6/15.6 C. was 1.2651, not corrected *to vacuo.* "B" was a light-colored soap lye crude of good quality. "C" was a dark-colored soap lye crude obtained by thoroughly mixing a number of low-grade samples of domestic and foreign crudes.

BICHROMATE METHOD.

Analyst.	Sample A.	Sample B.	Sample C.	
1	75.55	80.18	78.99	Silver carbonate and basic lead
	75.63	....	....	acetate.
2	74.99	80.24	78.77	Silver sulphate and basic lead
	75.11	79.63	78.83	acetate.
	....	79.65	....	
3	74.07	79.23	78.00	Silver sulphate over night.
	74.51	79.19	78.70	
	74.30	79.29	78.40	
	74.16	78.86	78.36	
4	75.35	79.30	77.70[1]	Silver oxide and basic lead
				acetate.
5	75.86	82.37	79.75	Silver sulphate only.
		80.29		
6	75.36	80.61	79.98	Basic lead acetate hot, double
				precipitation.
7	75.42	80.16	78.96	Silver oxide and basic lead
	75.49	80.12	78.88	acetate.
	75.47	80.09	....	
	75.48	80.18	....	
8	76.20	81.09	79.32	Basic lead acetate 5 hours' diges-
	75.97	80.77	79.09	tion.
9	75.50	79.85	79.00	Basic lead acetate and silver
	75.40	80.01	79.00	acetate 20 minutes' digestion.
	75.50	79.68		

ACETIN METHOD.

Analyst.	Sample A.	Sample B.	Sample C.	
6	75.40	80.13	78.79	Special precau-
		79.46		tions taken to avoid carbonic acid.
7	75.60	80.18	78.36	Small amounts
	75.48	80.28	78.15	carbonic acid may be present.
10	74.34	78.96	76.91	
	74.41	78.96	76.72	
9	75.65		78.69	No carbonic acid
	75.69		78.61	present.

Sp. gr. 15/15	1.2475	1.2905	1.2948	Analyst 7
Non-volatile, 160° C.	5.36%	10.16%	12.48%	" 1.
Ash	5.16%	9.25%	9.48%	" 1
Non-volatile organic	0.20%	0.91%	3.00%	
Hyposulphites	None	Trace	0.09%	

The following chemists, all of whom have had wide experience in glycerine analysis, have tested the three samples and sent their reports to the chairman, who takes this opportunity to express his appreciation of the work they have done and the interest they have shown: W. H. Low and E. F. Lyford, of the Cudahy Packing Co.; W. D. Richardson, E. F. Scherubel and R. H. Fash, of Swift & Co., Chicago and Ft. Worth; C. L. V. Zoul, of Procter and Gamble, Cincinnati; J. W. Loveland and

[1] Analyst No. 4 re-analyzed sample C using silver acetate instead of silver oxide and obtained 78.85 per cent.

G. A. Horne, of Babbitt & Co.; A. M. Comey, Fleming and S. E. Emery, of the Du Pont Powder Co.; F. S. White, E. Nordell and Y. H. Kooyumjian, of Marx and Rawolle; R. E. Divine, Detroit; J. F. Hinckley, New York; Stillwell and Gladding, New York, consulting chemists.

The bichromate equivalent of 1 gram of glycerine varies from 7.462 to 7.486 in the reports received. In order to place the figures on the same basis the chairman has recalculated the results to the equivalent 7.456, in accordance with the 1910 atomic weights.

NOTES: (*a*) Analyst 3 was told that his results were low. The tests were run again and the percentages opposite *a* obtained. This chemist frequently allows the glycerine to stand over night in contact with the silver chloride formed by the action of silver sulphate on the salt.

Mr. W. H. Low obtained materially lower results in the analysis of crudes with silver oxide as a purifying agent, when the mixture stood any length of time, the silver chloride being reduced to metallic silver. Cazeneuve[1] prepared glyceric acid by the action of silver chloride on glycerine in alkaline solution. Unless the glycerine is carefully neutralized these conditions will exist when silver sulphate is permitted to act all night. With silver oxide the error should be more serious as caustic soda is formed as a by-product, which, however, would be removed if lead acetate were subsequently added.

(*b*) Analyst 5 was asked to run sample B again with the result opposite *b.*

(*c*) Three chemists working independently.

(*d*) Analyst prefers this test.

(*e*) Sample A contains 0.50 per cent. soda which probably produced polyglycerols in contact with the glycerine at 160° C. Analyst 7 was unable to obtain good results on this sample until the alkalinity was removed.

(*f*) Two chemists working independently.

Results by the acetin method agree well with the exception of 10 and are uniformly low in the case of "A." Sample C is quite impure as only low-grade crudes were used in its preparation. This is confirmed by the high amount of organic impurities found by analyst 1 above, yet the difference between the acetin and bichromate methods is not marked.

ABSTRACT OF REPLIES RECEIVED TO THE CIRCULAR SENT OUT BY THE SUB-COMMITTEE ON GLYCERINE ANALYSIS.[2]

A. C. LANGMUIR, *Chairman.*

E. COOK & Co., London:

The acetine method gives results below the truth. In order to get accurate results the very greatest care and attention are necessary in all the details. We employ it in cases of divergence as a check test on our regular method—the bichromate. We prefer the latter method, which is standard and which can be easily adhered to in all details. Such a method is a necessity in a laboratory handling a large number of samples of varying raw and finished products. Silver oxide appears to give more accurate results. We measure the bichromate solution as near as possible to 60° F., allowing 15 to 20 seconds to drain. We agree that the bichromate is the most reliable basis, but prefer to standardize each time against Mohr's salt which is kept in solution in *full* bottles in a dark room.

Sampling is very important. Drums should be well rolled. If it is possible to feel much salt at the bottom of the drum sampling cannot be satisfactory.

D. & W. GIBBS, London, G. N. Petty, *Chemist:*

Modified Hehner Method. Clarification effected with copper sulphate and caustic potash. Oxidation 2 hours at 180° F. The bichromate is kept in neutral solution for in this condition its strength does not change appreciably. It is standardized

[1] *Compt. rend.,* **122,** 1206.

[2] See THIS JOURNAL, **1,** 268.

against C. P. glycerin whose strength is determined by specific gravity, using Gerlach's table.

The acetine method is less satisfactory with crude glycerines. The salts present require a higher temperature to keep the mass fused and this sometimes causes a loss of vapor from the top of the air condenser. The end point when neutralizing with 2 per cent. caustic soda is often extremely difficult to determine, probably due to the presence of acid salts such as those of aluminum. This may also occur with lime compounds in saponification crudes. Unless troublesome precautions are taken to exclude carbon dioxide, uncertain results may be obtained during the final titration with acid.

Neither method is quite satisfactory from the distiller's point of view as with low-grade crudes much more glycerine is sometimes shown by analysis than can be recovered by distillation.

J. CROSFIELD & SONS, Warrington, England, J. Allan, *Chemist:*

Weigh 1.2 to 1.5 grams crude glycerine into a 100 cc. flask. Fill flask half full of distilled water, add 1 cc. 10 per cent. caustic soda and then 3 or 4 cc. 10 per cent. copper sulphate solution (or sufficient to neutralize the caustic soda). Fill to the mark with cold water, shake and filter. Twenty-five cc. of the filtrate are added to 40 cc. standard Hehner bichromate in a beaker; add while cooling 17 cc. sulphuric acid. Cover and heat for 2 hours at 80° C. When cool, determine the excess of bichromate in the usual way, using a fresh, strong solution of ferricyanide as indicator.

In this modification chlorides are not removed. Under the conditions laid down and with a temperature not exceeding 80° C. there is no loss of chlorine or chromium oxychloride. Furthermore, at this temperature all the glycerine is oxidized and practically none of the lower fatty acids are acted on.

LEVER BROS., LTD., Port Sunlight, England:

We are in complete accord with you as to the inconvenience caused through differences in results obtained by various chemists due in greater part to the want of standard and uniform methods of analysis and manipulation. We shall bring forward at an early meeting of the glycerin association the question of appointing an expert committee representative of buyers and sellers to consider the whole matter and come to an agreement as regards the British trade. When this has been done no doubt the agreement of a universal scheme with American and Continental makers can be arrived at more simply.

J. LEWKOWITSCH, London:

Refers to the 4th edition of his Chemical Technology for his views. Further comment superfluous.

RICHARD WHEEN & SONS, LTD., London:

We should be glad to know of the establishment of a standard method; we also have had experience of different results from the same glycerin which makes it difficult to have confidence in the present variety of methods.

TYSON RICHMOND & JONES, Liverpool:

We use the acetine method.

T. & H. SOWERBY, London, F. E. Fry, *Chemist:*

Modified Hehner with some of Richardson & Jaffe's modifications. We have come to rely on the standard value of pure bichromate. The duration of the heating has been thirty minutes and we prefer a considerable excess of bichromate to be present. A preliminary blank is essential. 7.464 grams bichromate correspond to 1 gram glycerin.

PRICES PATENT CANDLE CO., LTD., Battersea, J. McArthur, *Chemist:*

Take average of the bichromate and acetin methods as the former overestimates and the latter underestimates the amount of real glycerin present. Bichromate, recently fused, is taken as the standard. 7.486 grams equal 1 gram glycerin. The

Mohr salt solution in each time standardized against the bichromate.

The crude glycerin is purified by basic lead acetate only. A weighed portion of the filtrate, about 25 cc., is oxidized with a weighed portion of standard Hehner acid bichromate, using about 50 per cent. excess over the glycerin present and an equal volume concentrated sulphuric acid is added. Heat 2 hours in a water bath, cool, dilute, add a weighed excess of acidified Mohr salt solution and titrate back with dilute bichromate one-tenth the strength of the standard bichromate solution.

The acetin method is carried out as recommended by Lewkowitsch except that 5 grams instead of 3 grams dry sodium acetate are used. We have experienced no serious difficulty in carrying out this method. In the case of candle crude the bichromate and the acetin methods give results agreeing within 0.2 to 0.5 per cent. but with less pure glycerin the difference may be 1 per cent.

With dynamite glycerin we take the specific gravity and obtain the per cent. from Gerlach's table.

The following results were obtained:

Specific gravity at 60° F.	Glycerol by acetin method. Per cent.
1.2625	98.08
1.2640	98.70

PROCTER & GAMBLE, Ivorydale, C. L. Van Zoul, *Chemist:*

We use the bichromate method with some of our own adaptations.

Weigh 5–10 grams glycerine. Dilute to 500 cc. and take 50 cc. into a 250 cc. flask. Just neutralize the alkalinity with 1 : 4 sulphuric acid. Add powdered silver sulphate a little at a time until the precipitate coagulates, add water to the mark, shake, stand over night or filter and draw off 50 cc. into an Erlenmeyer. Add 25 cc. bichromate and 15 cc. conc. sulphuric acid. Heat 2 hours in a steam bath. Titrate with iron ammonium sulphate in the usual way. Run a blank at the same time.

Bichromate solution—74.88 grams with 150 cc. conc. sulphuric acid in 1000 cc. Iron ammonium sulphate made by dissolving two 12-oz. beakers of Baker's salt in 2000 cc. water. Standardize by the blank. Silver sulphate is made from pure silver nitrate by dissolving 200 grams in water and adding 66 cc. conc. sulphuric acid while stirring vigorously. Cool, decant and wash five times with ice water. Place in funnel and wash three times. Exhaust dry, place in large dishes in hot air bath, then powder fine and preserve in dark bottles. It should have no odor of nitric acid.

To determine organic impurities we would advise the determination of total Na_2O in the ash as well as the free Na_2O in the sample.

Na_2O free:

Take 10 grams, dilute with 50 cc. water, add phenolphthalein and an excess normal acid, boil down to half the volume and titrate back with normal caustic factors equals 0.031. This Na_2O includes free and that combined with light volatile acids.

Na_2O total in ash:

Burn 5 grams in a large platinum dish, add a drop of ammonium nitrate solution. A small amount of alcohol added assists the burning off. Weigh the residue for ash. Dissolve in water and titrate with methyl orange for total.

Na_2O:

The difference showing the combined Na_2O to non-volatile acid and a comparison of the three Na_2O percentages gives a fair valuation of the glycerine.

Dynamite Glycerine.—Salt is determined by dilution and titration in the usual way. This is as accurate as is necessary.

Specific Gravity.—We use the pycnometer at 15/15° C. though at times 20/20° C. and apply a correction. We would

advise the adoption of a uniform temperature for a standard at about 20° C.

. Use a pycnometer with a thermometer and do not close until the temperature inside and that in the outside water bath is the same.

Sampling.—When salt is deposited in the drums we leave same in the drums and weigh it in the tare so that the sample which is taken from each drum with a dipper represents the net weight of stock taken out of the drums.

If a too great excess of silver sulphate is added in removing salt, particularly in spent lyes, an insoluble compound of silver and chromic acid separates from the cooled oxidation mixture, causing high results. The silver salt may be filtered out, dissolved in hot, dilute sulphuric acid, and titrated against iron, when the difference will be made up.

PROCTER & GAMBLE, Kansas City, M. Brayton Graff, *Chemist:*
The acetine method does not appeal to me as a practical method for a laboratory where large numbers of determinations are to be run in the shortest possible time. The bichromate method lends itself more easily to a systematic rapid yet accurate working. I find it easier to get concordant results. Duplicates within $1/10$ per cent. are perfectly possible. With regard to incomplete oxidation to carbon dioxide, I should advise the same dilution on all determinations, say 50 cc. solution containing 0.05 to 0.1 gram glycerine with 25 cc. bichromate and 15 cc. conc. sulphuric acid. Digest 2 hours in steam bath.

Lower fatty acids reduce bichromate somewhat but the amount is negligible if one avoids the introduction of acetic acid by the use of silver sulphate instead of lead acetate.

The bichromate is taken as the standard and we measure it out with a pipette at a standard temperature.

A determination of the sodium carbonate in the ash of soap lye crudes is a good indication of the amount of organic impurities.

Burn the crude to a coke, take up with hot water, breaking lumps, filter and take aliquot parts for titration for salt and carbonate of soda which will constitute most of the ash. Burn the filter and coke for insoluble ash.

CUDAHY PACKING CO., W. H. LOW, *Chemist:*
The average results of the bichromate method to be described are very reliable. Our average agrees well with the averages of foreign chemists although there are some serious differences in individual cases. Good checks, however, are no indication that the actual determination of glycerol is correct. Polyglycerols or glycol would produce results far from the truth, as the glycol in particular appears to be on the increase and the bichromate method is almost valueless for such glycerines. We examine most glycerines by both the bichromate and acetin methods, the difference between the results indicating glycol or polyglycerols. We have come to think more highly of the acetin method and believe that its results are nearer to the truth than the bichromate; much nearer if glycol and polyglycerols are present, although of course still high.

My assistant has made eight acetin tests a day with ease.
Sampling.—Errors here cause more differences than any modifications of the bichromate test. With excessive salt we do not attempt to include it in the sample but test a filtered sample for glycerine and estimate the salt. The sample is well stirred with a long iron wire flattened at the end and any deposit is loosened and well mixed.

Fifteen grams are weighed and washed into a 250 cc. flask and diluted to the mark. Twenty-five cc. are then pipetted into a 100 cc. flask. Rinse in freshly precipitated silver carbonate prepared from 0.5 gram silver sulphate in 100 cc. water by adding 3.5 cc. N sodium carbonate, settling and washing once by decantation with 100 cc. water. This amount applies to the average soap lye crude.

Agitate, stand 10 minutes and add 2.5 cc. basic lead acetate

(see Wiley's "Agricultural Analysis," Vol. III). Agitate well, stand 15 minutes, dilute to the mark, adding 0.2 cc. for the volume of the precipitate, filter through a dry filter and take 25 cc. into a 250 cc. volumetric flask. Add $1/2$ cc. conc. sulphuric acid to precipitate lead. The lead sulphate is not removed; about 42.5 cc. bichromate solution are pipetted into a weight burette and after weighing is added to the purified glycerine solution. Approximately 12.5 cc. excess bichromate solution should be present. 15 cc. conc. sulphuric acid is now added with agitation and the flask, loosely covered, is placed for $2-2^{1}/_{2}$ hours in a boiling water bath. Dilute, cool, make up to the mark, shake and settle out lead sulphate if time permits. Fill into a burette and titrate against Mohr's salt solution (20 cc. = 0.01 gram glycerol).

Silver carbonate is safer than silver oxide, particularly with impure crudes. It is very necessary to remove all chlorine. Using 15 cc. sulphuric acid in the oxidation mixture and 2 hours time is very much safer than the quick digestion of Richardson and Jaffe with 25 cc. acid and 20 minutes. In the latter case oxidation is rarely complete as is shown by the fact that gas is still escaping from the solution after 20 minutes and the results obtained average lower. This may be offset by the oxidation of acetic acid. In the former case acetic acid is not oxidized.

Silver oxide on standing with crude glycerine, particularly if impure, gives rise to false results for the silver chloride first precipitated is more or less decomposed, silver being thrown down and chlorine going into solution.

When using silver carbonate the purified filtrate should always show that an excess of lead has been used, otherwise the results will be too high. Strong bichromate solution contains 74.64 grams and 150 cc. conc. sulphuric acid per liter. Ferrous ammonium sulphate 30 grams with 50 cc. sulphuric acid per liter. Compare on every series of tests with dilute bichromate prepared from 12.5 cc. of the above by diluting to 250 cc. We standardize the bichromate against iron wire.

Note by Mr. Low: We are now weighing out the solid bichromate instead of having a standard solution to work with. We get the best C. P. bichromate, pulverize it finely and dry for several days in a large vacuum desiccator under almost perfect vacuum over strong sulphuric acid. As a check we often standardize with our standard iron wire, but there is practically no difference shown and we only do this as a precaution with a new lot of bichromate after preparation.

The Acetin Process:
1.5 grams crude, 3 grams recently fused sodium acetate and 7.5 cc. acetic anhydride are heated in a 60 cc. flask with ground glass joint and return condenser. A gentle boiling by an electric stove is maintained about $1^{1}/_{2}$ hours. Cool somewhat, pour 50 cc. of water free from carbon dioxide into top of condenser. Heat and agitate until solution is complete. Cool now completely and filter rapidly, using 4–6 inches of suction into a 850 cc. Jena glass Erlenmeyer. Wash up to 300–400 cc., add 2 cc. (1 per cent. in 50 per cent. alcohol) phenolphthalein and titrate $2/_{3}$ normal caustic. The end point is a marked change in the color but should not be a full pink. Small drops should be used at the end from a Muter's oil burette. Add 25 cc. 10 per cent. caustic from a burette, cover and digest in the steam bath, $1/_{4}$ to $1/_{2}$ hours. Run a blank on 10 cc., this being about the excess present with the same volume of water. Cool and titrate excess alkali with N sulphuric acid.

Crystallized sodium acetate fuses in its own water, solidifies again and should then be carefully further heated in a platinum dish until completely melted, avoiding overheating. Every precaution must be taken to avoid loss of triacetin by volatilization; no serious delays should occur to allow hydrolysis after dilution and good agitation must be kept up during titration. Water free from carbon dioxide should be used. It is best

obtained by distillation and condensation under 27–28 inches of vacuum.

Standard alkali is made by mixing C. P. caustic with its own weight of water and after standing cold filtered through asbestos. The filtrate is diluted with pure water.

Standard sulphuric acid is made up by Marshall's specific gravity process.[1]

Ash and Non-volatile Organic Matter at 160° C.:

Take $16^2/_3$ cc. of the original solution of the 15 grams crude in 250 cc. (= 1 gram of the crude) in a 45 cc. platinum milk dish and heat gradually in oven until 160° C. Maintain at this temperature as nearly as possible. This is important. The dish should be level. When dry, cool, add a little water to just dissolve the residue dry in steam bath and return to oven where it is maintained until practically constant weight is found.

Obtain the ash by igniting gently until white or gray. The difference gives the non-volatile matter to which too little attention has been paid in this country.

Du Pont de Nemours Powder Co., Eastern Laboratory, A. M. Comey, *Dir.:*

Both the bichromate and acetin methods are used.

Bichromate Method:

A portion of the well mixed sample is transferred to the weighing bottle by a short length of $1/_4$ inch glass tubing filled with glycerin by suction and wiped free from glycerine on the outside while withdrawing 1.5 to 2.0 grams are required. Rinse into a 500 cc. volumetric flask with 40–50 cc. water. Add a slight excess moist silver oxide and then a slight excess basic lead acetate. Shake and dilute to 500 cc. Filter through a dry filter and take 100 cc. of the filtrate in a 500 cc. flask. Add a weighed amount of dry bichromate, which has been gently fused, ground and dried at 110° C., in amount equal to ten times the weight of the glycerine, as this excess is necessary to insure complete oxidation. Add 75 cc. dilute sulphuric acid 1 : 2; acidification directly with strong acid sometimes decomposes a little glycerine.

Heat exactly 2 hours in a steam bath. This is sufficient for refined glycerine, and any further reduction which may occur in some instances must be due to impurities. Cool rapidly, dilute to about 300 cc. and titrate the excess of bichromate by iron ammonium sulphate added in the dry condition from a weighed amount in a weighing bottle. The salt should have been ground through a No. 30 mesh and well mixed. The addition of the salt is continued until the first appearance of the blue color on a spot test with fresh ferricyanide solution 0.01 to 0.03 per cent. strength.

The value of the iron salt is determined in terms of bichromate by titrating 3.5 grams bichromate in 75 cc. dilute sulphuric acid 1 : 2 and dilution to 300 cc. with the iron salt as above, running the test under the same conditions as to volume and depth of green color due to chromium sulphate.

A saturated solution of the tri-basic acetate is used. 5 cc. of this to 1.75 grams of crude glycerine are never exceeded.

The bichromate is taken as the standard. 1.0 gram = 0.13397 gram glycerine.

Acetin Method:

Essentially that outlined by Hehner in 1889. 1.5 grams of the crude are dropped into $3^1/_2$-4 grams dry sodium acetate in a 100 cc. dry Jena flask from a Lunge pipette, the weight being found by the loss in weight of the pipette. 7 or 8 cc. acetic anhydride are now added and the mixture gently boiled with return condenser $1^1/_2$ hours. Cool and add 50 cc. hot water through the condenser tube. Heat carefully with cautious but thorough shaking until solution is effected. This sometimes requires as much as five minutes and is continued until

a slight froth or a few bubbles persist on the surface for two to three seconds. Cool somewhat, add a few cc. more water through the tube, remove the flask and filter into a 750 cc. Erlenmeyer, wash well, cool well, and neutralize carefully the free acid with 2.5 per cent. caustic and phenolphthalein. (Continue as described under Low's method—*Chairman.*) Make a blank run on 25 cc. of the strong caustic. $N/2$ H_2SO_4 is used throughout.

If when fusing the sodium acetate, the salt is in any way charred, the end point is interfered with. It is not as sharp and in addition a solution of the charred salt shows a yellowish color which deepens that due to the impurities of the glycerin.

The heating under the return condenser should be only sufficient to cause a gentle boiling; a higher rate sometimes results in a decided darkening of the mixture.

A blank is always made with each new bottle of acetic anhydride, following exactly the same scheme as is used when making a glycerine determination. With all samples yet met with, a correction must be applied for a small amount of an ester-like substance which is present and is saponified with the acetin by the caustic soda. In some cases the error amounted to 0.7 per cent. glycerine.

The percentage of carbonate contained in the caustic used is not of any great importance provided it is reasonably low and provided none is lost between neutralization and final titration. Absorption of carbon dioxide *after* adding the strong caustic should be avoided. All water added after neutralization of the free acetic acid or to the strong alkali blank should be free of carbon dioxide.

In regard to the danger of hydrolysis after dilution referred to by Hehner, results obtained when neutralization was not effected until thirty-five or forty minutes after solution of the acetin agreed with the bichromate on the same glycerine.

Swift & Co., Chicago, W. D. Richardson, *Chemist:*

My opinion and that of some six or eight chemists who have been in my employ is that the bichromate is the only satisfactory method to use and that the acetin method is thoroughly unsatisfactory and unreliable.

In recent times we have taken the potassium bichromate as a standard although we sometimes standardize against iron wire.

Solutions.—Potassium bichromate 74.86 grams and 150 cc. conc. sulphuric acid per liter. Standardize against iron wire or Mohr's salt. It expands 0.05 per cent. for every 1° C.

Ammonium Ferrous Sulphate.—59.725 grams with 25 cc. conc. sulphuric acid in water and make up to 500 cc. Make it up fresh daily.

Subacetate of Lead.—To 170 grams lead acetate in a weighed 10-inch dish add 800 cc. boiling water. Add 100 grams finely powdered lead oxide and boil $1/_2$ hour, keeping up the volume. Cool and add enough water to make the product weigh 1000 grams. Filter in well-covered funnel and keep well stoppered, 1 cc. = 0.13 gram sodium chloride.

Weigh 5 grams of the glycerine into a 500 cc. flask, dilute slightly and add 10 cc. lead acetate solution. Shake, let stand $1/_2$ hour and make up to 500 cc. Settle or filter through a dry filter and measure 50 cc. into a 300 cc. Erlenmeyer. Add 50 cc of the bichromate solution from a pipette and 25 cc. conc. sulphuric acid and digest the covered flask 5 hours in the steam bath. Run a blank under the same conditions with 50 cc. bichromate solution.

Remove from bath and pour into a 10-inch porcelain dish containing 1000 cc. water and 25 cc. conc. sulphuric acid. Titrate with the Mohr's salt solution until two drops of the oxidation mixture produce a blue color with dilute ferricyanide on a spot plate.

N. K. Fairbank Co., St. Louis, C. B. Cluff, *Chemist:*

In my own work I use the Hehner method, omitting the use

of the weak bichromate which adds nothing to the accuracy of the work.

On C. P. glycerine this method showed 98.10 per cent. as against 98.15 per cent. from the specific gravity and Gerlach's table. I have always standardized my solution against iron wire but I also find that the bichromate itself is an equally good standard. I use a stock solution, taking the temperature at the time of each test applying the proper correction for this factor. Basic lead acetate alone is enough. We use no silver oxide.

I think the important point to work on is the determination of the concentration temperature and time of heating necessary to get accurate results, also whether silver oxide is necessary or advantageous.

A specific gravity table should be adopted as a standard and think Gerlach's would be satisfactory to practically all chemists.

With regard to the acetin method my experience shows that it gives results about ½ to 2 per cent. lower than the Hehner method on soap lye crude, and it is too tedious and inconvenient for ordinary laboratory use. On very low-grade samples this method may give better results but in such cases the end point is so indistinct as to greatly interfere with the accuracy of the work.

I have made some experiments as to the effect of varying concentration during the oxidation, and find that considerably higher results are obtained by concentrating the solution to about 25 cc. before the adding bichromate. There is often a difference of 1 per cent. between the tests made in a volume of 100 cc. and 25 cc. However, I do not consider the higher results thus obtained as more accurate, as it is generally understood that this process as ordinarily carried out gives results higher than the truth in any case.

J. Eavenson & Sons, Camden, N. J., G. D. Hulley, *Chemist:*
1.5 grams crude glycerin are weighed in a small weighing bottle. Wash into a 4 oz. Erlenmeyer flask with 25–30 cc. water, neutralize to litmus with sulphuric acid and add an excess of moist silver oxide. Stand forty to sixty minutes, filter, make up to 200 cc. and take 50 cc. portions in duplicate in No. 2 beakers. Add 50 cc. conc. bichromate solution from a pipette and then 20 cc. conc. sulphuric acid. Heat on a steam plate fifty to sixty minutes and determine the excess bichromate with ferrous sulphate solution standardized by tenth-normal bichromate tested against iron.

Iron 0.11742 = glycerine.

B. T. Babbitt, G. A. Horne, *Chemist:*
Bichromate Method:
Weigh about 0.8 of a gram in small beaker and transfer to ½ liter flask with water. Add 0.3 of a gram of silver sulphate to ppt. chlorides, giving a swirling motion to the flask, in order to effect precipitation of silver chloride without causing any froth on the liquid. Then add 3 or 4 cc. basic lead acetate solution, and fill flask to the mark. Agitate thoroughly. Filter after allowing ppt. to subside, discarding filtrate until it runs through perfectly clear. Accurately measure 50 cc. of filtrate with a standardized pipette into an eight-ounce Erlenmeyer flask; add 25 cc. of concentrated sulphuric acid. Measure from a burette 50 cc. of a standard solution of potassium bichromate, 1 cc. of which equals 0.002 of a gram of glycerine, into the flask containing sample, and heat for one hour in a steam bath. Titrate excess of bichromate with a solution of ammonium ferrous sulphate, approximately equal in strength to the standard potassium bichromate, using a very weak solution of potassium ferricyanide as indicator.

This standard solution of potassium bichromate is readily sensitive to one drop. It is particularly necessary to add the sulphuric acid before the bichromate, as it has been found that a small amount of lead chromate is thrown down when the bichromate is added first.

Acetin Method:
Weigh one gram of crude into a 75–100 cc. narrow-neck flask having a ground joint to connect with reflux condenser. Add 3 grams of anhydrous sodium acetate and 6 cc. acetic anhydride. Connect with condenser and boil 1½ hours. After cooling, pour warm water through condenser, disconnect flask, and pour contents into a 250 cc. flask, filling to the mark. Pour at once through a dry filter, and carefully pipette 50 cc. of filtrate into a 12-oz. flask. Neutralize acetic acid with half-normal caustic soda. Run into the flask 30 cc. of half-normal caustic soda (from a burette), five drops of phenolphthalein solution and boil 20 minutes. Titrate excess of alkali with half-normal hydrochloric acid, calculate glycerine from amount of caustic soda required to saponify the tri-acetin. A blank test should be made on each new bottle of acetic anhydride. It is absolutely essential to have caustic soda solution perfectly free from carbonate. Water used in process should first be boiled.

Notes, by Mr. Horne:
"Having given the acetin method as described by Hehner a thorough trial, and also modification as described above, I am convinced that the latter is much easier to manipulate, and gives a finer end point, particularly in the case of very dark crudes or foots. In working with 0.2 gram sample on the titration instead of 1½ grams, no difficulty whatever is experienced, due to coloring matter, even in very impure crudes.

"The filtering of the diluted acetin is very rapid, and the neutralization of free acetic acid, which only requires from 25–30 cc. of half-normal caustic soda, seems to me a marked improvement over the tedious process of the original method, where frequently 125–150 cc. are required. It would seem to be more scientific as well as convenient to saponify the acetin with the half-normal alkali instead of the strong 10 per cent. solution, and no blank is required regularly, as the half-normal caustic soda does not change.

"Have made some experiments which show that the acetin diluted with cold water practically suffers no change by hydrolysis, even after several hours."

Marx & Rawolle, A. C. Langmuir, *Chemist:*
Our method is that described in *The Journal of the Society of Chemical Industry*, 1898, p. 330, by Richardson and Jaffe, except that a few modifications have been made in the interest of greater accuracy.

Weigh 25 grams of the thoroughly mixed sample and transfer to a 250 cc. flask. Dilute to the mark with distilled water. Mix well and take 25 cc. with a pipette against which the flask has been standardized. Add 1 to 3 cc. of basic lead acetate[1] for a saponification and 7 cc. for a soap lye crude. Filter through a 12.5 cm. paper for a saponification or a 15 cm. for a soap lye, into a 250 cc. flask. Wash with cold water, stirring up the precipitate thoroughly. To the filtrate, about 225 cc., add 5 cc. of sulphuric acid (1 : 3) and 12 cc. of saturated silver acetate solution. The latter serves to remove the small amount of chlorine present as lead chloride. Dilute to 250 cc., mix well and filter through a dry 15 cm. paper. Take 20 cc. of the filtrate for analysis. The pipette should have a narrow orifice and should check against the 250 cc. flask last used.

To avoid the error involved in measuring out 25 cc. of strong bichromate solution, we prefer to weigh the bichromate for each test. It is pulverized and dried at 110° C. and is taken as pure instead of standardizing against iron. Hehner's solution contains 74.86 grams potassium bichromate and 150 cc. of conc. sulphuric acid to the liter. We, therefore, weigh $\frac{1}{40}$ of 74.86 or 1.8715 grams of bichromate and dissolve it in 25 cc.

[1] *Brit. Pharm.*

of dilute, warm sulphuric acid (150 cc. to a liter). It is convenient to have a weight made of exactly 1.8715 grams and weigh the separate charges of bichromate on a tared watch glass, adjusting the weight to within a milligram, which with practice can be very quickly done. In the long run time can be saved by this method as no attention need be paid to temperature or to standardizing the bichromate solution.

After cooling, 20 cc. of the purified glycerine solution as above are run in. The beaker is covered and 25 cc. concentrated sulphuric acid is run in slowly. Complete the reaction by heating for 20 minutes in a boiling water bath. Dilute, cool by placing the beaker in running water and finally dilute to 250 cc. Mix, pour the solution into a burette and titrate against 25 cc. standard Mohr's salt solution, freshly made, using potassium ferricyanide as an indicator. The titration should follow closely after the oxidation, as dust will gradually reduce the bichromate, giving high results. All apparatus must be scrupulously clean and free from grease or dust.

Taking the molecular weight of glycerine at 92.08 and bichromate at 294.5 we have 1 gram of glycerine equals 7.4627 grams bichromate. This quantity of bichromate is equivalent to 59.6611 of Mohr's salt, taking the molecular weight of the latter at 392.4. We have taken the bichromate equivalent at 7.486 in order to agree with Hehner. Mohr's salt is rarely pure, and we therefore standardize it against bichromate as follows:

Dissolve 5.9661 grams of Mohr's salt in 40 cc. of 15 per cent. sulphuric acid. Add 0.7360 gram bichromate dissolved in 20 cc. water. Titrate the mixture with a solution of 100 milligrams bichromate dissolved in 100 cc. water, using ferricyanide as indicator.

To get the end point make two titrations and add to the first at the end 2–3 cc. excess of bichromate solution. Use drop tests obtained from this solution to compare with spot tests obtained in the second titration. Our Mohr's salt required 5.9 cc. Therefore 5.9661 grams called for 0.7360 + 0.0059 or 0.7419 gram bichromate—0.7419 : 0.7486 : : 0.5966 : $x = 0.6020$ gram.

For the regular analysis, therefore, we weigh 6.02 grams Mohr's salt and dissolve it in 250 cc. of water containing a little sulphuric acid. Take 25 cc. portions for the titration.

A blank should be occasionally run on the water and reagents. To 7 cc. of the basic lead acetate add 5 cc. of the dilute sulphuric acid and 12 cc. of the silver acetate solution, dilute to 250 cc. and filter. Run 20 cc. of the filtrate into a solution of 0.6730 gram of bichromate in 21 cc. water and 4 cc. sulphuric acid. Add 25 cc. conc. sulphuric acid and heat 20 minutes in the boiling water bath. Dilute, cool, dilute to 250 cc. and titrate against 25 cc. Mohr's salt solution as above. Not more than the equivalent, 27.8 cc., should be required. Repeated tests have shown that the acetic acid introduced by the 7 cc. of lead acetate causes no measurable reduction of the bichromate.

The basic lead acetate[1] is made as follows: boil a mixture of 142 grams of lead acetate, 99 grams of litharge and 568 cc. water a half-hour and then make up to 591 cc. Filter.

When the above weights and proportions of crude glycerine are taken, the percentage is given by the following formula:

Per cent. glycerine = 125 — 1250/cc.

STILLWELL AND GLADDING:

Weigh out as quickly as possible exactly 5 grams of the substance on a balanced watch glass. Wash it into a 250 cc. flask with warm water, using about 50 cc. Add a half gram of silver acetate which has previously been triturated with a little water in a mortar. Shake frequently during 15 minutes.

[1] *Brit. Pharm.*

Add water until flask contains 200 cc. Then add subacetate of lead in slight excess. Fill up to mark with water, insert glass stopper and mix thoroughly. Filter through a dry filter paper, take 10 cc. (0.20 gram) of the solution and wash it into a beaker holding about 300 cc. and using about 100 cc. water. Add about 15 cc. concentrated sulphuric acid and 20 cc. of potassium bichromate solution. Add water until the beaker contains from 175 to 200 cc. Cover with a watch glass and place in boiling water for two hours, stirring with a glass rod from time to time. Remove from bath and allow to cool. Add about 50 cc. water to replace that which has evaporated. Titrate with ferrous sulphate spotting on porcelain plate with potassium ferricyanide until the blue color just appears.

Potassium Bichromate Solution:

74.5660 grams 100 per cent. potassium bichromate and 150 cc. conc. sulphurous acid are dissolved in water and made up to 1000 cc. 1 cc. of this solution is equivalent to 0.01 gram glycerine.

Ferrous Sulphate Solution:

240 grams of C. P. ferrous sulphate and 50 cc. conc. sulphuric acid are dissolved in water and made up to 1000 cc.

Standardization:

Standardize the ferrous sulphate against the bichromate solution whenever the test is made.

ROBERT E. DIVINE, Detroit:

Weigh 2 to $3\frac{1}{2}$ grams, rinse into a wide-mouthed flask with 100–125 cc. hot water, heat nearly to boiling and add an excess of a 2 per cent. solution of Merck's tri-basic lead acetate, 10 cc. being usually sufficient, heat about ten minutes, filter and wash well with hot water. Wash lead precipitate back into the flask and heat nearly to boiling, add $N/1$ caustic soda, about 1 cc. for each cc. lead acetate used, heat until ppt. is dissolved.

Now add $N/1$ sulphuric acid in amount equivalent to the caustic soda. The reprecipitated lead salts now free from glycerine are filtered and washed with hot water. The filtrates are combined, acidified with dilute sulfuric acid and evaporated until they can be transferred to the proper flask (200 cc. for 2 to $2\frac{1}{2}$ grams crude and 250 cc. for $2\frac{1}{2}$ to $3\frac{1}{2}$ grams), excess of silver sulphate is added and solution mixed, made up to volume, filtered through dry filter and 25 cc. run into a solution of 3.7308 grams bichromate crystals in 50 cc. water, 30 cc. conc. sulphuric acid added and heated 2 hrs. in boiling water bath.

The bichromate is weighed out for each test.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS.

Those desiring information concerning the prices at which rare elements and special compounds can be furnished provided a considerable market is assured, and the extent of the available supply, are requested to indicate their needs to the Chairman of this Committee as soon as possible. All are invited to make suggestions regarding the scope of the work which has been undertaken.

Prompt responses to this request will greatly facilitate the work of the committee and render needless repetition in correspondence unnecessary.

GELLERT ALLEMAN, *Chairman,*
Swarthmore, Penna.

Committee to confer with manufacturers regarding the supply of, and prices for, rare elements and special compounds.

RECENT INVENTIONS.

947,957. **Process of Recovering Fine Gold.** James H. Alling, San Francisco, California. February 1, 1910.

The object of this invention is to provide a process for the recovery of very fine particles of gold, silver, and platinum.

In practicing the process there is employed a sluice box of the kind shown in the accompanying illustration.

This sluice box is sloped at a greater angle than are the sluice boxes used for the recovery of gold in the ordinary processes.
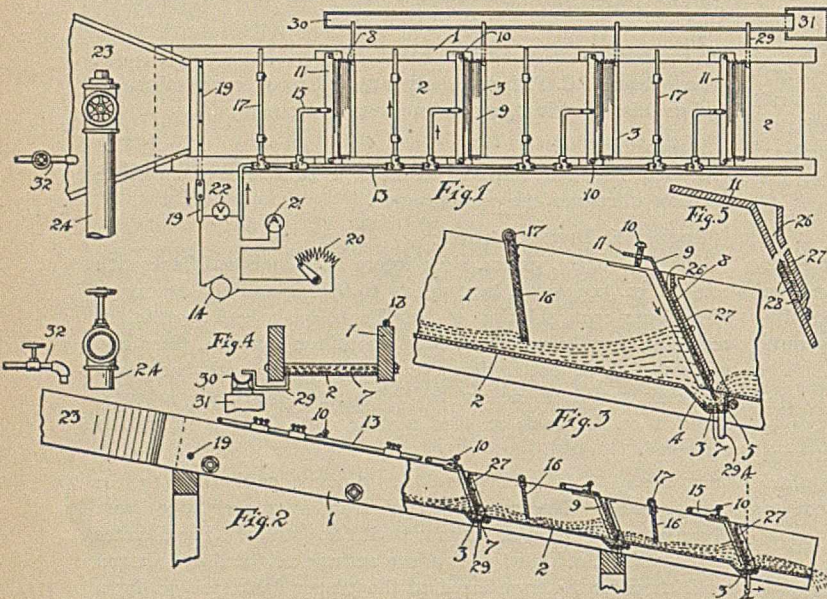
In the bottom of the sluice box is a continuous amalgamating plate formed at suitable intervals into pockets or troughs. Each pocket is formed with a rear wall having a considerable slope, nearly 45 degrees, to the vertical, a front wall sloping slightly backward from the vertical, and a bottom substantially horizontal. In each pocket is placed a sufficient quantity of mercury. The sides of the sluice box are formed with oblique grooves inclined rearwardly upward, and across the sluice box extend anode amalgamating plates with their edges in the grooves. The lower edges of the plates extend to within a short distance, say ⅛ of an inch, from the upper surface of the mercury in the troughs or pockets. The height of each plate can be adjusted by means of adjusting screwed through lips extending from the plates over the sides of the sluice box, the screws resting on the tops of said slides.

Extending along one side of the sluice box is an electric conductor connected to the positive pole of an electric current generator. This conductor is connected by conductors with the several plates, which thus serve as anodes for currents of electricity.

In addition to the anode plates there are provided swinging carbon anodes suspended from bars extending across between the tops of the side of the sluice box, substantially midway between the anode plates.

The cathode plate is connected by a wire to the source of the electric current.

The material, having been first finely pulverized, is fed by a chute into the top of the sluice box. At the same time there is fed a sufficient quantity of water, about 4 tons to 1 ton of material, and through a pipe is fed a small proportion, about 1 to 1000, 2000, or more parts, of a mixture consisting of aqueous solutions of potassic cyanid and mercuri chlorid.

The patentee claims that by his process he has been able to save over 95 per centum of the values of material containing finely divided gold, which cannot be saved by ordinary processes.

948,372. **Process for Producing Oxids of Nitrogen from the Air.** Francis I. Du Pont, Wilmington, Delaware. February 8, 1910

This process consists in subjecting air contiguous to a cooling medium to the action of a moving arc whereby the high temperature of the air produced by the arc is immediately and rapidly reduced, thus producing, the patentee states, the best possible
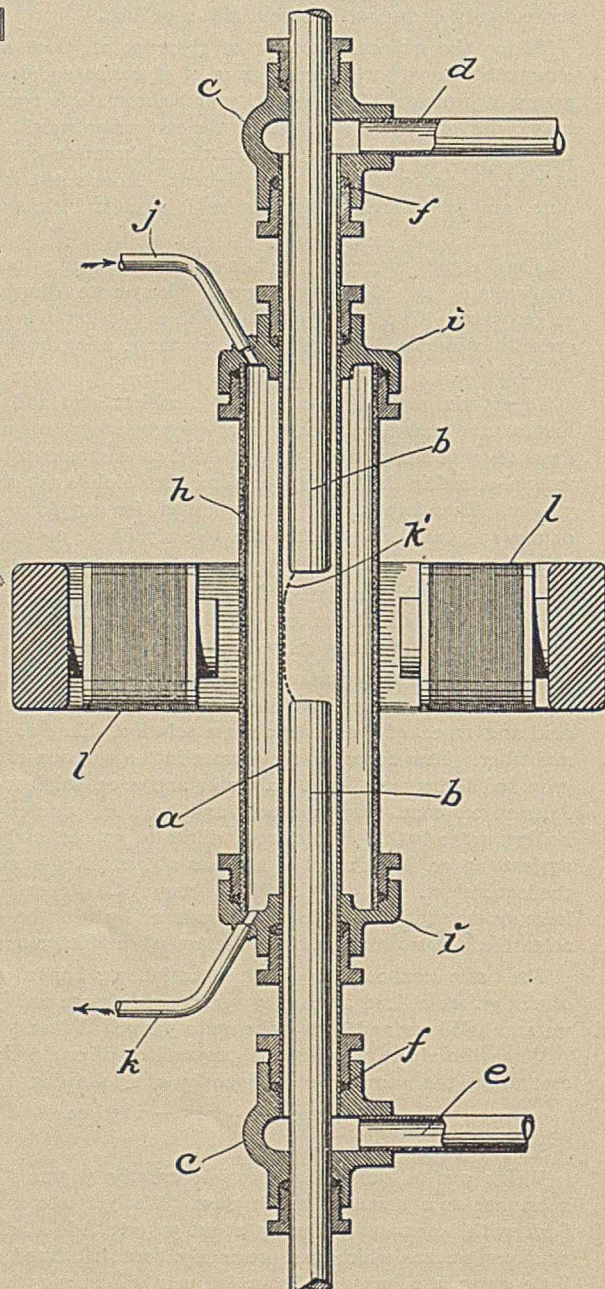
conditions for the production of oxids of nitrogen from the air.

In order to produce a continuous and not disconnected arc, the air container is of silica or other highly refractory material which is not a conductor of electricity. The air is passed through a tube formed of silica in which are electrodes between which an arc is formed. Surrounding this silica tube is a glass tube through which a cooling medium, such, for instance, as a cooling liquid, is passed, thus forming a water jacket, as it were, for the silica tube. Surrounding this cooling tube, in proximity to the arc, is a rotary magnetic field, which rotates the arc around the inner surface of the silica tube. The air passing in contact with the inner surface of the silica tube is, by the rotating of the arc, highly heated, and as soon as the arc passes from any portion of the air, such air is immediately subjected to cooling action and its temperature rapidly reduced.

The accompanying illustration shows the apparatus in which the process is carried out.

In operation air is forced in through the passage into the zone between electrodes. When the arc is produced and the rotary magnetic field is in action, the arc is caused to rotate around the inner periphery of tube *a* coming in contact and acting upon successive portions of the air in contact with said tube. The arc at once highly heats such air. As soon as the arc passes from any portion of the air, such air being in contact with the wall of tube *a*, which is subjected at all times to the action of the cooling medium in tube *h*, has the high temperature produced by the arc immediately and rapidly reduced. By this operation the action of highly heating and cooling any given portion of the air is practically simultaneous, thus more perfectly and with greater certainty forming the oxids of nitrogen from the air. The air is forced in at a pressure from atmospheric to one hundred pounds. The oxids of nitrogen thus produced are the lower oxids and with the air unacted on pass along the tube in the space between the electrode and the wall of the tube escaping by the passage *d* from which they may be led into water where they are converted into nitric acid, in the ordinary manner.

949,474. Process of Refining Iron. Frederick W. Hawkins and George F. Key, Detroit, Michigan. February 15, 1910.

It is the object of this invention to provide a process which is suitable for the refining of iron which, in its crude state, has a high percentage of impurities requiring for their elimination different treatment. For example, iron which contains both silicon and phosphorus, or silicon, sulphur and phosphorus cannot be directly treated in an open-hearth basic-lined furnace, for the reason that the linings would be destroyed by the reactions of the silicon. On the other hand, such metal cannot be refined by the Bessemer process, as this does not extract the phosphorus, and sulphur.

With this process the iron is first treated in a receptacle or furnace to eliminate the impurities which will yield to oxidation and subsequently, but in direct continuation of this first treatment, the metal is subjected to a second treatment, with a basic material, in another furnace or chamber, which removes the phosphorus and sulphur. In the latter step and preferably in both steps of the process all portions of the metal are subjected to uniform treatment by atomizing or breaking up the molten mass into minute particles, this being preferably accomplished by a blast of dry steam, or of dry steam and air, the latter being preferably pre-heated.

With the apparatus shown the refining process is carried out as follows: A suitable quantity of the crude molten metal is first poured into the well *G* while the furnace *A* is arranged in its horizontal position. At the same time air and steam, either in conjunction or separately, as conditions may require, are forced through the tuyeres *E* and *F* so that metal dropping from the well may be blown into fine particles and scattered throughout the length of the furnace *A*. During the passage of the small particles of metal through the atmosphere within the furnace, a large percentage of the silicon, manganese and carbon will be removed by oxidation. The metal will then collect in the bottom of the furnace where it remains until the entire charge has passed therein. The furnace *A* is then revolved on the turntable *C* and tilted upon the trunnions *B* so as to lower its open end over the well *K* on the furnace *H*. This will permit the molten metal within the furnace *A* to be discharged into the well *K* from which it is fed through the restricted passage into the path of the air and steam admitted through the tuyeres *I* and *J*. This will a second time atomize the molten metal with the result that the remainder of the silicon, manganese and carbon will be oxidized.

The bottom of the furnace *H* is covered with a layer of comminuted basic material which is heated to a high temperature by burning gases entering the furnace chamber from end ports *L*. This comminuted basic material forms a filter bed through which the minute particles of molten metal are obliged to percolate and in so doing the metal is brought into intimate contact with the basic material which extracts the phosphorus and sulphur. Thus the metal which finally passes through the filter bed and collects in the bottom of the furnace *H* is purified both from silicon, manganese and carbon, and also from the phosphorus and sulphur.

950,115. Process of Removing Tin from Scrap. Charles J. Reed, Philadelphia, Pennsylvania. February 22, 1910.

This process is intended for the separation of mixed metals, particularly of tin from tinned metals, as for example iron. The process comprises three steps, namely: first, removing the tin in pulverulent or subdivided form from the iron or other coated metal by agitating a charge containing the tinned metal and a subdivided foreign body; second, removing the pulverized tin from the foreign body and from the detinned iron by means of a current of air, steam or gas; third, removing the foreign body from the detinned iron.
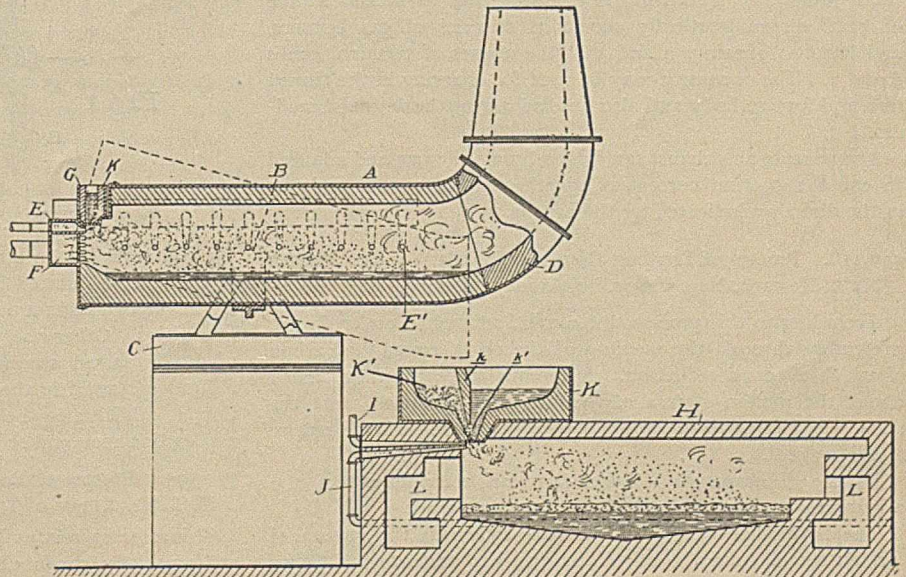
In carrying out the first step in the process advantage is taken of the fact that metallic tin is rendered weak, friable and easily pulverized by heating the charge, preferably to about the melting
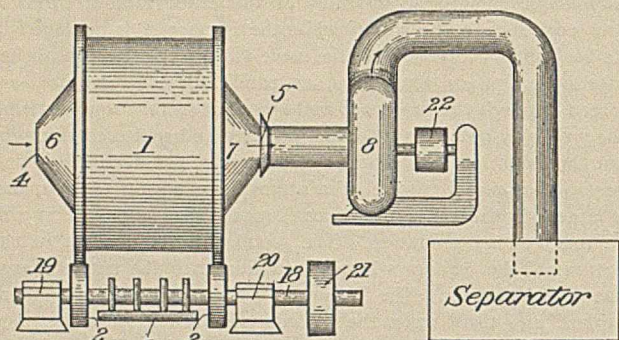
point of tin. The subdivided foreign body used to pulverize or wipe off the fused or softened tin may be any substance which is infusible and non-volatile under the conditions of use.

The amount of the foreign body added to the charge is also variable within wide limits, one to ten and one to one-tenth having been used.

The second step of the process consists in removing the pulverized tin from the foreign body and detinned iron by means of a current of air, steam or gas. This operation may be carried on simultaneously with the pulverizing operation or as a subsequent operation. This is preferably done simultaneously by causing a current of air to pass through the apparatus in which the pulverizing takes place. This current of air is then projected into a separating or settling chamber in which the particles of tin settle by gravity on the floor, or the air is passed through a series of bags or screens of textile or other suitable material in which the tin is collected in the form of a powder of metallic tin or oxid of tin. The air or other gas may be heated to the proper temperature, if desired.

The third step in the process consists in screening the residual mass on a screen capable of allowing the subdivided foreign body to pass through, while rejecting the detinned iron or the principal part of it. The foreign body may then be used over again indefinitely.

A convenient form of apparatus for carrying out the process is shown in the accompanying drawings, in which 1 represents a hollow cylinder of iron or steel mounted to revolve on rollers 2, carried by a shaft 18, supported in bearings 19, 20 and driven by a pulley 21. The drum is mounted over a suitable source of heat, diagrammatically shown as a series of gas burners, and has two openings 4 and 5 at the apexes of terminal cones 6 and 7. The opening 4 may be used for charging in the tinned iron and foreign body and also for discharging the detinned product.

8 represents an exhaust fan driven by a pulley 22 and adapted to cause a suction current of air through the drum and fan in the direction indicated by the arrows.

950,116. Process of Treating Ores and Metals. James Henry Reid, Newark, New Jersey. February 22, 1910.

According to this process, the ore is first melted and reduced, preferably through the medium of the electric arc, the carbon of which effects a reduction. A gaseous reagent is then passed about the molten stream of the resultant metal to treat the same, the character of the treatment depending on the nature of the reagent.

In the accompanying illustration, an embodiment of the apparatus for carrying out the process is shown.

The bottom portion of the furnace in which the stream of molten metal from the arc discharges has preferably a lining d of refractory material, and is provided with a suitable dis-

charge aperture 10. The ore is introduced into the furnace through a hopper, e, at the top thereof, and an exhaust pipe, f, is provided leading from the upper part of the furnace, to suitable exhausting, and if desired, condensing means.

To permit the carrying out of this process, a plurality of apertures 11 are provided in the walls of the furnace below the electrodes, through which the gas may be admitted. The passage of gas through these openings is regulated by an annular plate, 12, having corresponding apertures, 13, which plate is rotatably supported from an annular flange, 14, on the side of the furnace. In order to provide for the admission of different gases to the furnace, an annular conduit is connected to a suitable supply pipe, 16.

In carrying out the process the ore is introduced into the hopper 10 and falls in a continuous stream into the hopper formed by the electric arc and reduced by the carbon of the electrodes, the molten metal and slag dropping through to the bottom of the furnace.

The air or gas to be used in treating the metal is introduced through the apertures 10 and passes around the stream of metal and slag, the movement of the gas being effected by exhausting the upper part of the furnace through the pipe f. This suction, as well as moving the treating gas about the stream of ore, exhausts the upper part of the pool of partly reduced ore on the electrodes. The effect of passing the gas will vary with
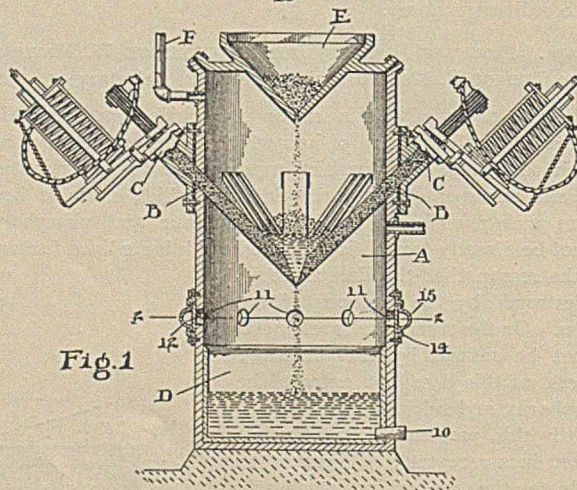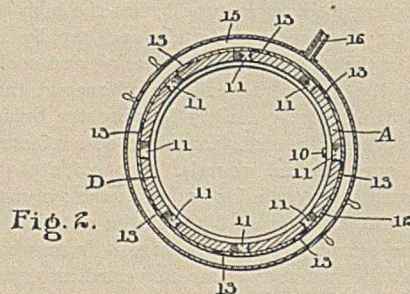
the character of the ore and of the gas. For instance, an ore might first be reduced by the carbon of the electrode and then air might be drawn around the stream of metal to burn out the impurities. Otherwise, a reducing gas, such as carbon monoxid, might be passed around the stream of metal to complete the reduction started in the arc. It will be observed that this suction, in addition to the stream of gas, also will operate to suck any carbon monoxid or dioxid gas in the metal out of the same.

950,595. Process of Reducing Metallic Oxide Ores. Herbert E. T. Haultain, of Toronto, Ontario, Canada, March 1, 1910.

This process relates to the reduction of metallic oxide ores and especially iron ores for the purpose of obtaining steel directly therefrom.

The general purpose of the invention is to provide a process of reducing such ores by which they may be successfully treated in a finely divided condition and which is especially adapted for use with an electric furnace.

In carrying out this process there is utilized an electric furnace having a receptacle of suitable capacity at the bottom to form a bath of molten material.

The ore if not already in the condition of magnetic iron sands is crushed or ground in a finely divided condition. The ore is then treated in a concentrator to separate as far as possible its earthy components. The ore is then so fed into the furnace preferably mixed with a suitable powdered flux as to produce a shower of discrete particles, in which condition the ore is most readily permeable by the reducing agents and is most readily heated. The furnace is so arranged that the ore meets with no

Fig. 2   Fig. 4

obstructions from the time it enters the furnace until it reaches the surface of the bath at the bottom. This bath is suitably heated, preferably by electric energy. Into the shower of finely divided ore, preferably intermediate its point of entry into the furnace and the surface of the bath, there is introduced a shower of carbon, also in a finely divided condition. Carbon monoxide is immediately produced by the combination of the carbon with the oxygen of the ore, which carbon monoxide promptly takes up more oxygen from the ore and becomes carbon dioxide, which in turn takes up carbon and is reduced to carbon monoxide again. This process takes place all through the shower. It has been determined by experimentalists that carbon monoxide alone tends only to partially deoxidize the ore and that the best results are obtained by having solid carbon present with the ore to complete the deoxidation. By this process it will be seen that the carbon being actually present in the shower in a solid condition is ready to hand for combination with the finely divided particles of ore which have been pratically deoxygenized by the reducing atmosphere supplied by the carbon monoxide. There is necessarily a surplus of carbon employed and a consequent surplus of carbon monoxide produced, which must not be allowed to escape and its heating value lost. At the same time air cannot be introduced into the ore shower after its mixture with carbon to effect this combustion as the formation in the ore shower of carbon dioxide instead of monoxide would result. The patentee therefore shapes the lower portion of the furnace so that it extends laterally on each side of the shower and into this portion of the furnace he introduces air which combines with more or less of the surplus carbon monoxide, producing an intense heating effect which is reverberated against the shower and the surface of the bath of molten material by the walls of the chamber which are suitably shaped to produce the reverberating effect. It will be seen that this air does not contact in any manner with the shower of ore

and carbon and it is therefore usefully employed without producing any deleterious effects.

The reactions which take place are stated to be as follows: The shower ore is first calcined and heated as described and after it has passed the calcining portion of the furnace, enters a reducing atmosphere due to the introduction of the shower carbon. By the joint action of the carbon monoxide and the solid carbon the ore is deoxidized and falls into the bath of molten material in the condition of pasty metallic particles mingled with slag. In the bath at, or adjacent to, its surface, the metal is melted and the slag separates collecting on the surface of the bath. This bath has a sufficient capacity to contain a considerable proportion of the daily output of the furnace, and the molten metal is withdrawn from the bath gradually and preferably continuously to a point remote from the place in which the smelting occurs, preferably at the bottom of the bath. This withdrawal is best effected by carrying a suitable conduit from the bottom of the receptacle up to the level of the bath exterior to the furnace. Through this conduit the metal gradually flows off to suitable receptacles. This retaining of the molten metal and its gradual withdrawal equalized any inequalities in the output, which is very important since the proportion of carbon and impurities to the pure metal may be subject to variations, owing to its being continuously produced in small quantities.

The process is carried out in a furnace such as is shown in the accompanying illustration.

951,198. Process of, and Apparatus for, Treating Ores. WALTER G. PERKINS, of Smelter, Nevada, and MARK LAWRENCE REQUA, of San Francisco, California. March 8, 1910.

This invention relates to the treatment of metalliferous ores preparatory to the smelting process, whereby waste of the valuable elements of the ore is reduced to a minimum, and the ore put into suitable condition for smelting in a blast furnace. The best known means of accomplishing this important result,

Fig. 1

is to agglomerate or sinter the ore, which is usually in a finely divided state, by subjecting the same to the action of heat from either solid or gaseous burning products, whereby the metalliferous elements will become agglomerated, or sintered into a solid mass or good-sized pieces or lumps, which are then in condition for further treatment, such as smelting as in a blast furnace, without the risk of waste or loss of the valuable elements of the ore.

In the practice of this process the entire body of the ore is subjected to the action of air or other supporter of combustion, and temporarily to the burning products of the source of heat.

The ore to be treated is placed upon a layer of stones disposed upon a support as shown in the accompanying illustration. And is caused to pass through the ore and during this passage burning gas is passed over the surface of the ore. In this way the ore is agglomerated or sintered. The sintered ore is later separated from the unsintered particles by means of a suitable screen.

951,228. Method of Decomposing Salts. Jasper Whiting, of Boston, Massachusetts. March 8, 1910.

This invention relates to the electrolytic decomposition of salts by methods involving the employment as cathode of a body of liquid metal or alloy. In methods of this character it has been usual heretofore to maintain a substantially continuous circulation of the cathode, but this practice has, it is claimed, proven objectionable by reason of the tendency of the electrolytically separated metal, as sodium, to become oxidized and to re-enter into solution in the decomposing compartment. For example, in the production of caustic soda by electrolysis

of aqueous solutions of sodium chloride in presence of a mercury cathode, the sodium amalgam tends to collect at the surface of the mercury cathode and its removal to the oxidizing compartment is only incompletely effected by the flow of the underlying body of mercury; the sodium of the amalgam is therefore

subject to oxidation by the electrolyte undergoing decomposition, resulting in a reduced efficiency of operation.

According to the present invention the liquid metal is maintained in a state of rest during the charging period or period during which the sodium or other metal is deposited therein, but is at appropriate intervals transferred by gravity to a region of oxidation, the denuded or purified metal being thereafter returned to the decomposing compartment. In the preferred embodiment of the invention the alloy or amalgam from the decomposing compartment is permitted to flow through the oxidizing compartment in contact with carbon surfaces and an oxidizing electrolyte.

The accompanying illustration shows apparatus in which the process may be carried out.

951,272. Obtaining Petroleum Products. Herman Frasch, of New York, N. Y. March 8, 1910.

This is a process of obtaining burning oil (kerosene) from petroleum of the nature of that obtained from the wells near Beaumont, Texas, and from other kinds of petroleum.

On subjecting Beaumont petroleum to fractional distillation (with or without cracking) and subjecting the entire distillate which comes over between the ordinary temperature limits of burning oil (say, from 250–600° F.) to treatment with sulphuric acid of 66° B. (followed by the customary washing with water, and with caustic soda solution, and again with water), the resulting product will be colorless and of a mobility to climb a lampwick; but it will smoke when burned in ordinary petroleum lamps, especially if the flame should be turned low. The raw distillate shows the same smoky flame. The patentee claims to have discovered that such distillate is composed in part only of smoky hydrocarbons and that these and the non-smoking hydrocarbons which accompany them in distillation can be separated from each other by the differentially solvent action of an appropriate menstruum, such as methyl alcohol or ethyl alcohol, not only to a useful extent, but sufficiently to obtain from such smoky distillate a non-smoking burning oil whose hydrocarbons have the same range of boiling points as those of said smoky distillate. The invention consists in the processes of subjecting part at least of either or both of said illuminating oil fractions of Beaumont or other petroleum, as above mentioned, to the action of a menstruum, such as methyl alcohol or ethyl alcohol, which has a different solvent action upon the non-smoking from that which it has upon the smoky hydrocarbons of said burning oil fraction of Beaumont petroleum, and thereby obtaining the results stated. The menstruum may be applied to all or to any desired part of either or both of said illuminating oil fractions before or after the separation of the same from other fractions or parts of the petroleum; but the application would best be made after such separation, the oil treated being in the form of an appropriate distillate. The distillation of the crude oil may, in any case, be performed with or without cracking.

In addition to giving an oil of less ratio of carbon to hydrogen than the oil treated, the separation which is effected by the differentially solvent menstruum also results in an oil of greater ratio of carbon to hydrogen; and this more highly carbonaceous product can be utilized for burning as fuel or for other appropriate purpose.

The solvent action of methyl or ethyl alcohol is greater on the smoky hydrocarbons (or those having a higher ratio of carbon to hydrogen) than on the non-smoking hydrocarbons (or those having a lower ratio); but it is evident that a menstruum having the reverse differential action might serve to separate the two kinds of hydrocarbons; and it is believed that a differential solvent in general has now for the first time been applied as indicated.

Nearly anhydrous methyl alcohol is regarded as the best
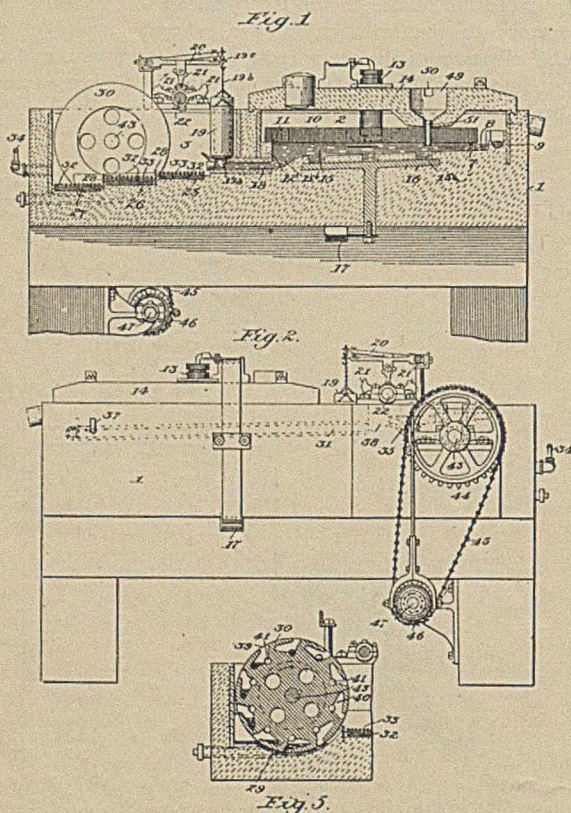
menstruum, but another appropriate menstruum (differential solvent) can be used without exceeding the limits of the invention. As already indicated, ethyl alcohol can be used.

After the desired and feasible separation of the hydrocarbons from each other has been obtained, the menstruum is separated from the hydrocarbons in solution therein in order to obtain purer oil and also to recover the valuable menstruum; and where it and they have sufficiently different boiling points fractional distillation would best be resorted to; but the menstruum separation might be effected in different ways which might vary with the menstruum. Addition of water followed by settling and decantation will separate methyl alcohol or ethyl alcohol from hydrocarbons (of whatever volatility) in solution therein. Methyl alcohol and ethyl alcohol can each of them be separated by distillation from the hydrocarbons which compose the heavier portion of the burning oil fraction of any kind of petroleum. The separated menstruum can be disposed of in any way, but it would best be used over again on a new lot of oil, with or without being subjected to an intermediate treatment.

952,351. Process of Detinning Tin-scrap. WALTER J. PHELPS, of Baltimore, Maryland. March 15, 1910.

It has been demonstrated that tin disintegrates when subjected to extremely low temperatures, as for instance, when brought in contact with liquid air.

Based upon this principle, this process consists in subjecting the tin-coated scraps or tin-bearing material to an extremely low

temperature, while simultaneously agitating the scraps to cause the tin to separate from the steel or other metal coated by the tin.

In practice, the tin-bearing material is supplied to the inner drum of the apparatus shown in the accompanying illustration

through the openings at the top of the inner and outer drums, and after the doors of the openings are closed, the inner drum and agitator are rotated for effectively stirring the tin scraps to bring every portion of the tin-coated surfaces in contact with the liquid air which is supplied by the opening of the valve 22. This liquid air acts on the tin in such a way as to destroy the cohesion between the tin particles and the sheet metal coated thereby, and the particles of tin sift through the perforations of the inner drum and are collected in the space at the bottom of the outer drum. After the agitation has proceeded long enough to remove the tin, the door 7 is first opened to allow the tin to drop out into a suitable receptacle. After this is done, the inner drum is opened when the door thereof is at the bottom, so that the sheet metal from which the tin has been removed can be emptied from the apparatus in preparation for the next charge.

INDUSTRIAL AND TRADE NOTES.

AMERICAN PATENTS IN ENGLAND.

REVOCATION FOR IMPROVEMENTS IN TYPEWRITING MACHINES.

Consul Albert Halstead, of Birmingham, reports as follows concerning the British revocation of letters patent for a typewriting machine manufactured in New York:

A decision of the Comptroller-General of Patents, on December 10, revoked letters patent No. 25382 of 1901 for improvements in typewriting machines, especially referring to an improved key-operating mechanism for the machine manufactured by the Yost Writing Machine Company, of New York. Application was made for the revoking of this patent by Walter Gray Duncan, of Glasgow, on the ground that the article was manufactured mainly or exclusively outside the United Kingdom.

The Yost Writing Machine Company is represented in England by the Yost Typewriter Company (Limited), who are the licensees in England for the sale of the typewriters. The company was represented by counsel. Not only was its patent revoked, but it was ordered by the Comptroller-General to pay the costs of the Glasgow applicant, *viz.*, 30 guineas ($153.29).

This decision is another manifestation of the purpose of British manufacturers to gain every advantage possible under the patents and designs act of 1907, and indicates that many American companies which have developed a large business in the United Kingdom, and which have not undertaken to manufacture in this country the main part of their patented articles sold here, are in grave danger of having their patents revoked and of suffering from the competition of machines made in Great Britain to their designs, machines which, because British-made, in view of the increasing popular prejudice in favor of British-made articles, will become serious competitors.

(An abstract of the decision of the Comptroller-General, transmitted by Consul Halstead, is on file in the Bureau of Manufactures.)

OFFICIAL REGULATIONS AND RULINGS.

NOTICE OF JUDGMENT NO. 216 FOOD AND DRUGS ACT.
Adulteration and Misbranding of Hydrogen Peroxide.

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given that on the 14th day of December, 1909, in the United States Circuit Court for the Eastern District of New York, judgment was rendered in the case of the United States *vs.* Eimer & Amend, a corporation, of New York City, prosecuted for a violation of the aforesaid act upon an information in substance charging
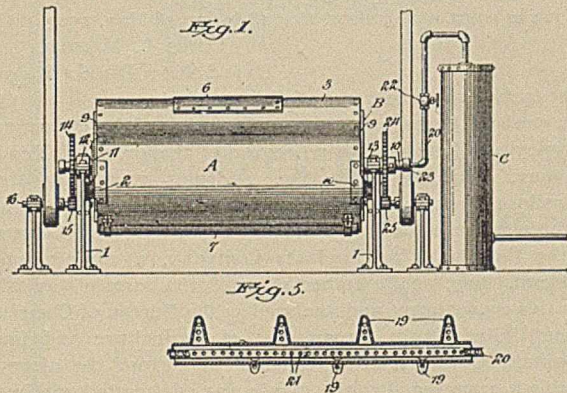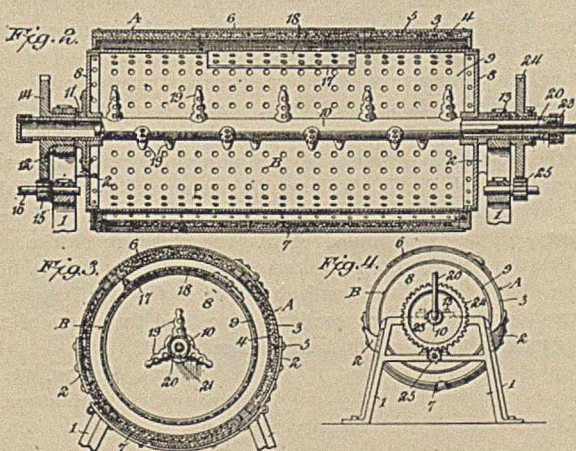
that said defendant filed a guaranty in accordance with the provisions of Section 9 of the said act, which is as follows:

Eimer & Amend,
Manufacturers & Importers of
Chemicals and Chemical Apparatus.

New York, Nov. 14, 1906.

The Secretary of Agriculture,
Washington, D. C.

Dear Sir: We, the undersigned, do hereby guarantee that all the articles of foods or drugs manufactured, packed, distributed or sold by us, including both crude and powdered drugs, alkaloids, chemicals, pharmaceutical preparations, medicinal specialties or proprietary medicines, and any and all articles of foods and drugs as defined by the Food and Drugs Act, June 30, 1906, are not adulterated or misbranded within the meaning of the said act.

Respectfully yours,
Eimer & Amend.
Robert P. Amend,
Treasurer.

Attest
Otto P. Amend [seal],
Secy.

Sworn to before me this 25th day of November, 1906,
[seal]   Jacob B. Toch,
Notary Public No. 39, N. Y. C.,

which said guaranty received a serial number, to wit, 591; and that thereafter the said Eimer & Amend sold and delivered to the Eastern Drug Company, New York City, a certain drug contained in a bottle labeled: "Hydrogen Peroxide 1 pint Eimer and Amend, New York. Guaranteed under Food & Drugs Act, etc., No. 591," which said drug, sold and delivered as aforesaid to the Eastern Drug Company, and afterwards reshipped in its original package by the agent of said company from New York to Boston, Mass., was adulterated in that it was sold under a name recognized in the United States Pharmacopoeia and differed from the standard of quality and purity therein laid down in this, that it contained acetanilid. The information further charged that the said drug was misbranded in that the container thereof, failed to bear a statement of the quantity or proportion of acetanilid contained therein. On December 14, 1909, the defendant pleaded guilty to the information and was fined $5.

The facts on which the prosecution was based, follow:

On June 8, 1908, an inspector of the United States Department of Agriculture purchased a sample of the drug, labeled as heretofore described, from the Eastern Drug Company, at Boston, Mass., which had been sold and delivered by Eimer & Amend to an agent of said drug company, in New York City, who afterwards reshipped the same to his company at Boston, Mass. The sample was analyzed in the Bureau of Chemistry, United States Department of Agriculture, and found to contain acetanilid. The analysis having disclosed that the said drug was adulterated and misbranded the said Eimer & Amend and the said Eastern Drug Company were duly notified thereof, given an opportunity to be heard, and were heard in regard to said adulteration and misbranding. The Eastern Drug Company having established a guaranty from its vendor, and it appearing that there had been a violation of the act, for which Eimer & Amend was responsible, the facts were reported, on April 16, 1909, to the Attorney-General. The case was referred to the United States attorney for the Southern District of New York, who filed the above information, with the result hereinbefore stated.

James Wilson,
Secretary of Agriculture.

Washington, D. C., February 21, 1910.

Notice of Judgment No 220, Food and Drugs Act.
Adulteration and Misbranding of Turpentine.

In accordance with the provisions of Section 4 of the Food and Drugs Act of June 30, 1906, and of regulation 6 of the rules and regulations for the enforcement of the act, notice is given of the judgment of the court in the case of the United States *vs.* 2 Drums Turpentine, a proceeding of libel under Section 10 of the aforesaid act for seizure and condemnation of the said 2 drums of turpentine, lately pending, and finally determined on May 18, 1909, in the District Court of the United States for the District of Vermont by rendition of a decree of condemnation and forfeiture hereinafter fully set out.

The case having come on for final hearing and no one appearing to make any answer to the allegations of the said libel, on May 18, 1909, the court rendered its decree of condemnation and forfeiture in substance and in form as follows:

United States District Court for the District of Vermont.

United States   ⎫
　　vs.　　　　⎬
Two Drums Turpentine. ⎭

This cause came on for hearing on the 18th day of May, 1909, and it appearing that said libel was duly served and returned, and no one appearing to make any answer to the allegations in said libel, and it being made manifest that all and singular the premises aforesaid, are true, and within the jurisdiction of this court, it is thereupon ordered and decreed that the said two drums of turpentine in the information and libel mentioned, be, and the same are condemned as forfeited for the causes in said libel and information set forth.

Done in court at Windsor, this 18th day of May, 1909.

James L. Martin,
United States District Judge.

The facts in the case were as follows:

On or about January 26, 1909, an inspector of the Department of Agriculture found in the possession of the Dr. B. J. Kendall Company, Enosburg Falls, Vt., 2 drums containing about 112 gallons of turpentine, labeled "Spirits Turpentine," which had been manufactured and shipped to said Kendall Company by the Carolina Pine Products Company, a corporation of Cleveland, Ohio, on December 16, 1908. A sample was taken from this consignment and analyzed in the Bureau of Chemistry of the United States Department of Agriculture and found to contain 35 per cent. of mineral oil. From the aforesaid analysis it appeared that the article was adulterated within the meaning of the act in that it was sold under the name of "Spirits Turpentine," which in common parlance means, and is identical with, "oil of turpentine," a name recognized in the United States Pharmacopoeia, while it differed, in fact, from the standard of strength, quality, and purity laid down therein in that a quantity of mineral oil had been substituted in part for the genuine article; and was misbranded within the meaning of Section 8 of the act in that it was labeled "Spirits Turpentine," whereas it was not, in fact, spirits of turpentine, or oil of turpentine, but a mixture of oil of turpentine and mineral oil.

Accordingly, on January 28, 1909, the Secretary of Agriculture notified the United States attorney for the District of Vermont that the aforesaid 2 drums of turpentine were then in the possession of the said Dr. B. J. Kendall Company, Enosburg Falls, Vt., having been shipped as above stated, and that they were adulterated and misbranded within the meaning of the act. On February 1, 1909, the United States attorney filed a libel in the District Court of the United States for the District of Vermont praying seizure, condemnation, and forfeiture of the said goods, with the result hereinbefore stated.

James Wilson,
Secretary of Agriculture.

Washington, D. C., February 23, 1910.

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
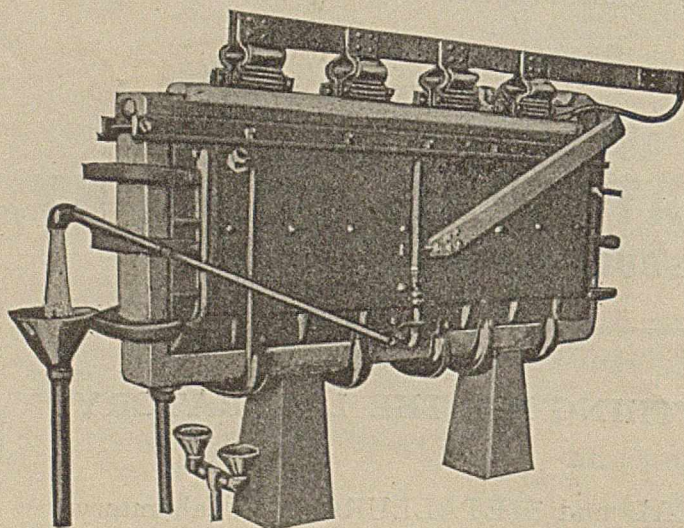
THE TOWNSEND CELL

For the Electrolytic Production of

Alkali and Chlorine

Continuous Operation 3 Years,
1 Month at Niagara Falls, N. Y.

HIGH EFFICIENCY; LOW INITIAL COST;
LOW COST OF MAINTENANCE;
2,500, 4,000, 6,000
AMPERE UNITS.

Chlorination in Metallurgy

LICENSES GRANTED
IN ALL COUNTRIES

Alkali Plants

LICENSES GRANTED IN FOREIGN
COUNTRIES AND TO CONSUMERS
IN UNITED STATES : : : : :

2500-Ampere Cell.

HOOKER ELECTROCHEMICAL CO. FORTY WALL STREET, NEW YORK CITY.

I-11