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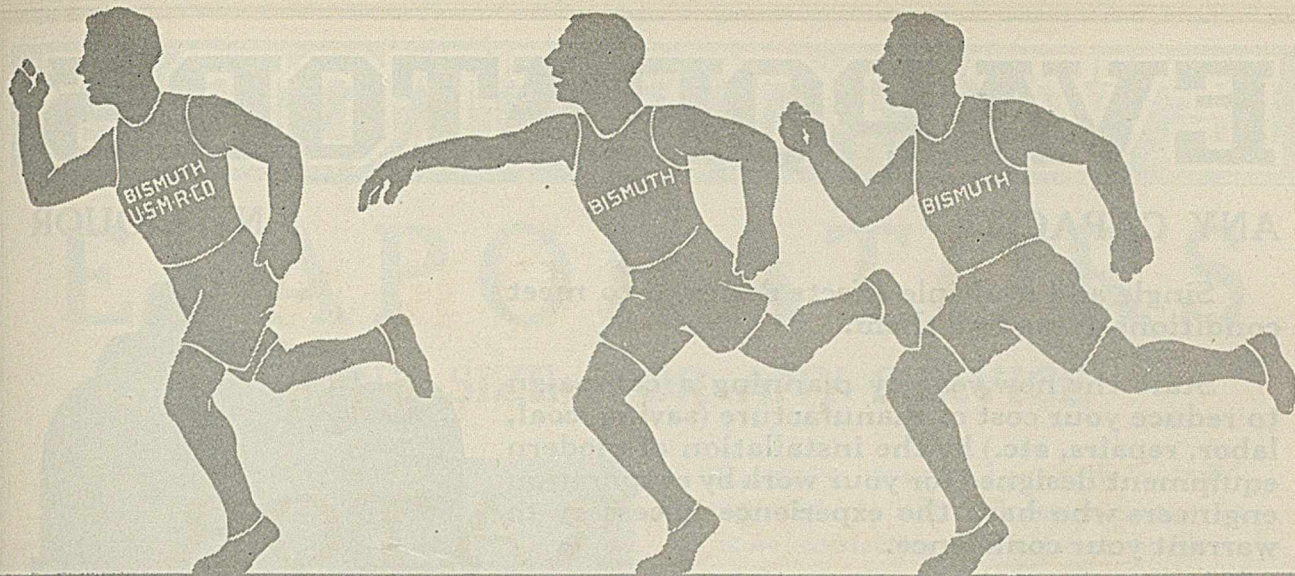
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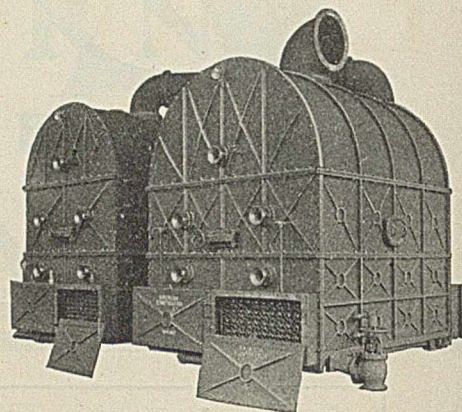
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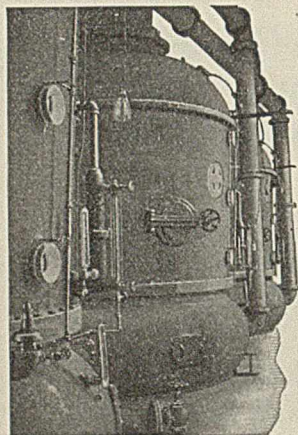
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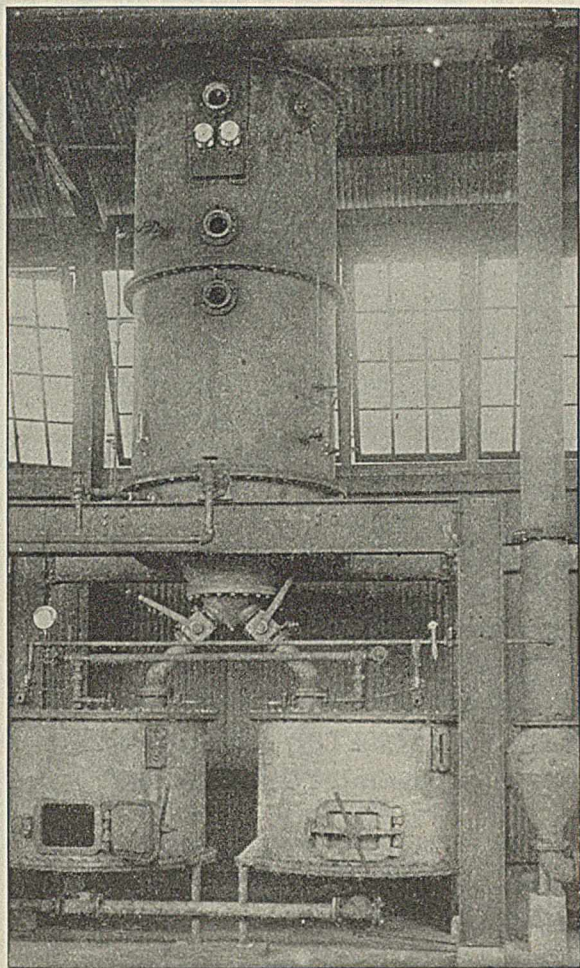
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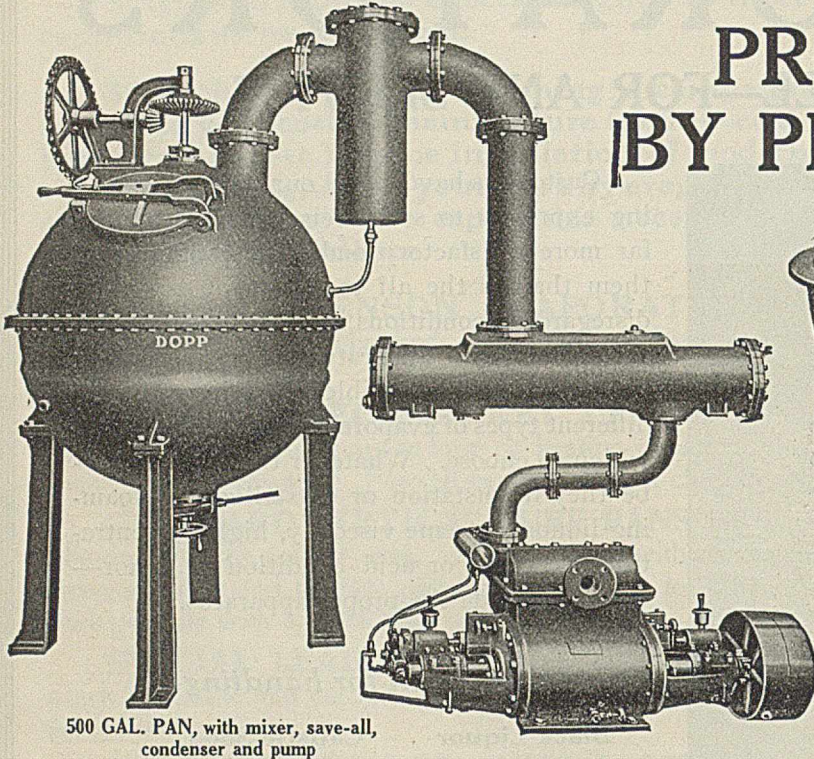
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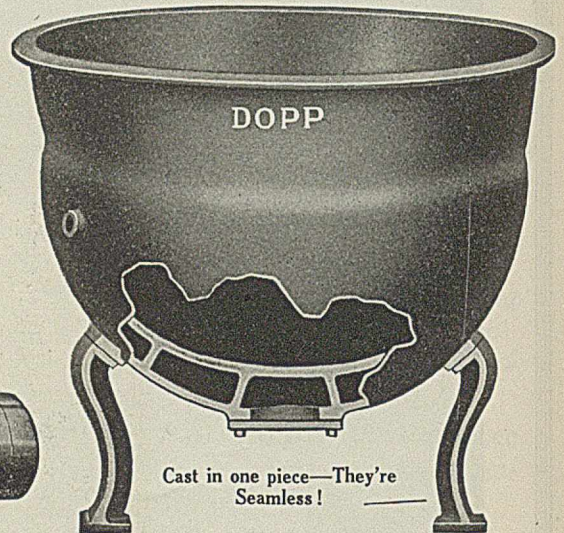


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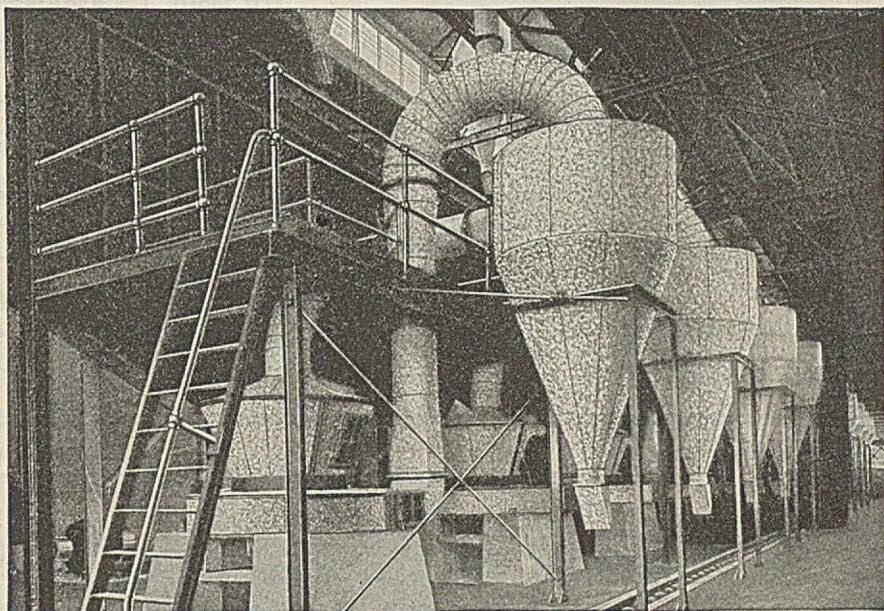
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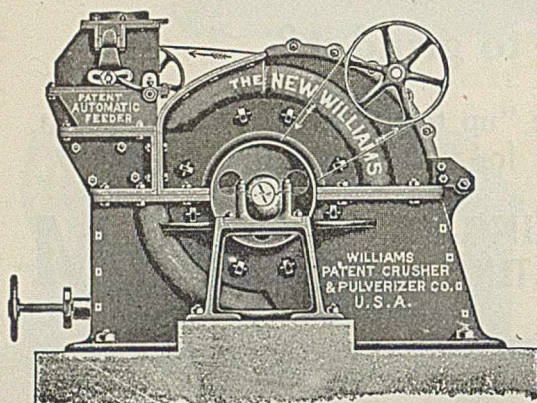
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## EDITORIALS

### THE SEATTLE MEETING

The Fifty-first Meeting of the American Chemical Society, to convene in Seattle on August 31st, with the final social session in San Francisco, offers unusual inducements for a large attendance. The itinerary arranged over the Great Northern Railway, with a special train west of Chicago, was outlined in our last issue. The opportunity to observe such natural scenery, including extensive glaciers, numberless lakes, no end of mountains, and a real live volcano—all "made in America"—is alone ample reason for the trip.

The Exposition in San Francisco, which members can visit at their own convenience after the meeting, has been especially planned to present in detail a broader range of industries than has ever been attempted at any previous exhibit. Scientists and technologists of all classes will find it both instructive and suggestive.

The papers presented at the meeting will of course be interesting and valuable: they always are. Since the majority will eventually appear in the Journals of the Society, however, the main object of their presentation is to bring out discussion. The extent and value of this depends upon the attendance.

The multitude of problems brought forward by the European war has quickened anew the chemical industries of America; these problems must be solved; and they will not be unless the American chemists co-operate. Only by closer intercourse among themselves can they know even their own strength. The informal conferences made possible by the meetings of the Society offer one of the most valuable means of getting into touch with the varied talents of our many Sections.

Hundreds of our members have never attended a general meeting of the Society. And yet no member has ever attended a meeting without being glad of it afterwards, because he realizes that he has been benefited by the invaluable experiences of travel, instruction in his specialty, personal contact with his co-workers and the general broadening of view that is the basis of all progress.

Now that chemists are actually receiving some public recognition, it behooves them to take an added interest in the activities of the Society. In this way they can attain the recognition that is theirs by right, among the professions of the nation.

The Seattle and San Francisco Sections are making preparations for the largest meeting of the Society to date. Are you going to be there?

### THE EXPOSITION OF CHEMICAL INDUSTRIES

No better proof that chemistry and chemists "have arrived" is needed than the fact that a National Exposition of Chemical Industries will be held in New York, September 20th to 25th. The managers report that requests for space are arriving daily and that

the list of exhibitors is already representative of the many great divisions of American industry. The United States Bureau of Foreign and Domestic Commerce is contemplating an elaborate and comprehensive exhibit, which alone will attract thousands of manufacturers anxious to learn the needs of the many markets at present abandoned by the warring nations of Europe.

The time is at hand when the public must be taught that chemists are most often *not* druggists and that there are other chemicals than drugs, dyes and explosives. Furthermore, there are indeed many who still need to be convinced of the truth of President Herty's statement that "Chemistry is no 'black art'."

The all-absorbing nature of the pursuit of chemistry as a profession is responsible for the present conviction of the public that the science is incomprehensible and inaccessible to the lay mind. Until they actually see chemical processes turning out useful and desirable articles and can get some clear idea of the part the chemist plays in this operation, it is useless to expect public support and sympathy for our profession. Those who like the secretive methods of the past are protesting, naturally, against this invasion of their realms, but they will have to submit, for it is now necessary to give the people concrete examples. Since they cannot go into the factories for this information, it must be brought to them. The exposition method is certainly the quickest and most effective manner of accomplishing this result. The value of the chemist is not appreciated because so few people realize that he really works; they think his results are attained by chance or inspiration.

Provision is being made for the illustration of processes by means of working models of machinery, product displays, motion pictures and lantern slides. Rooms have also been provided for meetings of chemical and engineering societies.

Another phase of special importance in this exhibit is that chemical industries are so interlocked that all producers are consumers and *vice versa*. Also, many industries, between whose products there is no relation, make use of similar machinery, so that even the narrowest specialist cannot afford to neglect the study of the methods of other workers.

Concerning the reluctance of many to demonstrate their processes, we venture that no manufacturer will disclose as much as he learns and that many will be surprised to find that some of their most cherished "secrets" are already common property.

In view of the present public interest in things chemical and the inherent value of the exhibits being prepared, we predict that this first National Exposition of Chemical Industries will be successful from every standpoint, and we see no reason why it should not move on to other large cities with profit to its exhibitors and the various communities sufficiently progressive to welcome it.



## ORIGINAL PAPERS

A STUDY OF THE QUALITY OF PLATINUM WARE WITH SPECIAL REFERENCE TO LOSSES ON HEATING<sup>1</sup>

By GEORGE K. BURGESS AND P. D. SALE

There was presented at the 49th Meeting of the American Chemical Society an account<sup>2</sup> of the examination of the purity of a number of platinum crucibles by a thermoelectric method in which the crucible forms one element of a thermocouple. This method has been found useful by ourselves and others for the ready classification of platinum utensils of various kinds and especially for the determination, in the case of purchases of platinum ware, whether or not such articles conform to specifications as to platinum purity. This thermoelectric test, which in no way mars the crucible or other article examined, is now a part of the routine of the Bureau of Standards and many samples of platinum have been so tested the past year; these were secured for the most part through Dr. W. F. Hillebrand, Chairman of the Committee of the American Chemical Society on "Quality of Platinum Utensils."

In Table I is shown the quality of platinum utensils of various sorts expressed in terms of equivalent iridium content as measured thermoelectrically at this Bureau. Of the 164 pieces examined it is seen

TABLE I—CLASSIFICATION OF PLATINUM WARE SUBMITTED TO BUREAU OF STANDARDS FOR THERMOELECTRIC PURITY TEST

CLASS OF WARE } INVESTIGATED	Cru- Crucible			TOTAL No.
	cibles	Dishes	Misc.	
No pieces of each class.....	84	11	22	164
Equivalent Ir-content—per cent	Per cent in each class			
0.0 to 0.5.....	36	9	0	26
0.5 to 1.0.....	17	23	18	20
1.0 to 2.0.....	34	38	9	31
2.0 to 4.0.....	13	13	27	17
4.0 to 25.0.....	0	0	45	6

that nearly 75 per cent have impurities equivalent to over 0.5 per cent of iridium, and of the crucibles, 65 per cent have over 0.5 equivalent iridium content. Dishes and miscellaneous ware, in which stiffness is usually required and which are often not subject to heating and weighing, are heavily charged with impurities, usually iridium, the miscellaneous ware showing, for example, nearly half of the samples with over 4 per cent iridium.

In addition to data on the purity of platinum ware now in use, more exact information was desired by the committee concerning the losses on heating. The experiments here outlined, it is believed, furnish information concerning losses sustained by platinum crucibles of several grades of purity when subjected to continued heating. By suitable acid treatment after heating, it has been possible to give an estimate of the relative amount of iron present, and the crucibles have also been examined microscopically, and through the kindness of Dr. Burrows, magnetically.

As will be shown, a combination of these several methods, or some of them, usually gives sufficient data

<sup>1</sup> Paper read at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915. It will be published in full as a Scientific Paper of the Bureau of Standards.

<sup>2</sup> "A Thermoelectric Method for the Determination of the Purity of Platinum Ware," by George K. Burgess and P. D. Sale, THIS JOURNAL, 6 (1914), 452.

for the ready classification of various grades of platinum ware.

## METHOD OF DETERMINING LOSSES ON HEATING—

For an exact determination of the loss in weight of a crucible on heating, ignition over the blast lamp is not satisfactory. A preliminary series of experiments, using electric resistance furnaces with platinum and other metals as heating coils, carried out by members of the chemical staff of this Bureau, showed that one could not expect to obtain consistently reliable results in a furnace containing metal. A considerable number of measurements of losses on heating at sev-

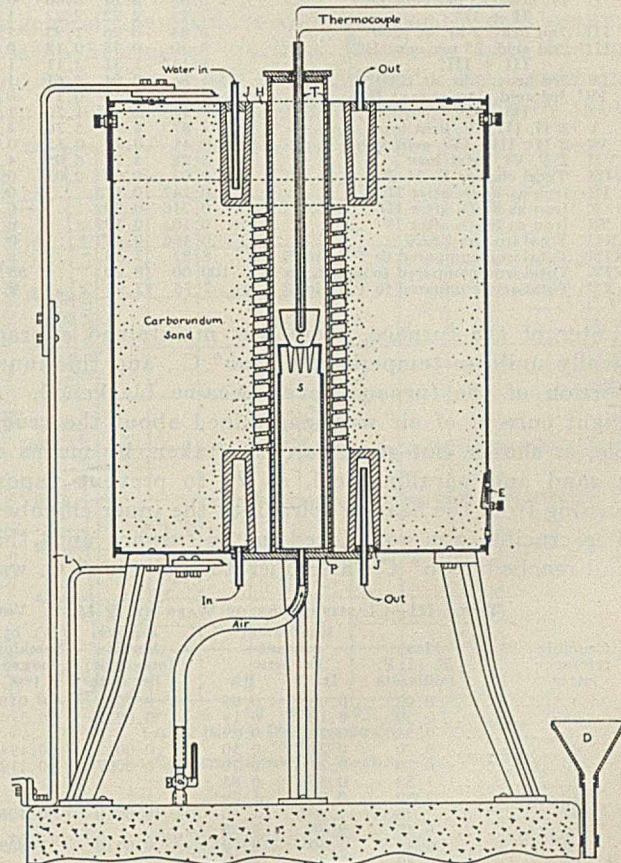


FIG. 1—HEATING FURNACE

C—Platinum Crucible H—Graphite Heater P—Bottom Cover Plate  
D—Water Drain J—Water Jackets S—Crucible Support  
E—Sand Emptying Door L—Current Leads T—Marquardt Protecting Tube

eral temperatures were so taken, but no very definite conclusions can be drawn from these preliminary observations, which were obtained before the thermoelectric method of classification was put into practice.

The method finally adopted for determining heat losses in crucibles is based on the use of a metal-free electrically heated furnace, similar to one which had been in use for other purposes at the Geophysical Laboratory, accompanied by exact weighings of the crucible before and after each heating of 2 hours duration at 1200° C., together with a weighing to determine the iron loss after washing in acid.



The essentials of the furnace are shown in Fig. I. The heating spiral *H* is of graphite set into brass water-cooled terminals. The crucible *C* is supported on a Marquardt porcelain stand, *S*, as shown and enclosed within a tube, *T*, of the same material. Temperatures were measured by a platinum-platinum-rhodium thermocouple enclosed in Marquardt. The furnace takes about 3.5 kw. A. C. at 1200° C.

For a region of about three crucible heights at the

ACID TREATMENT—Iron and other soluble materials were removed, and determined by weighing, after each heating. For several of the crucibles examined, the characteristic reddish coating due to iron oxide appeared after each heating. The acid treatment consisted in boiling the crucible for 5 min. in 25 per cent hydrochloric acid contained in a large covered porcelain crucible. The iron was determined by precipitation with ammonia upon ashless filter paper,

TABLE II—HEATING AND ACID TREATMENT ON PLATINUM CRUCIBLES (MILLIGRAMS PER CM<sup>2</sup>).—(SEE TABLE III FOR KEY TO CRUCIBLES)

Crucible reference letter	E. M. F. measurements: Millivolts at 1100° C., crucible vs. pure Pt (I, I')													
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>
I	0.10	0.50	0.65	0.70	0.70	1.90	2.80	3.00	6.40	6.70	7.00	7.30	9.30	9.70
I'	0.07	0.50	0.62	0.70	0.70	1.85	2.80	2.95	5.95	6.10	6.00	6.50	9.30	9.70
	0.09	0.50	0.64	0.70	0.70	1.88	2.80	2.98	6.18	6.40	6.50	6.90	9.30	9.70
II	2.18	1.98	2.16	1.27	2.46	2.00	1.08	1.38	7.47	1.94	6.24	2.16	1.74	0.61
II'	0.05	0.24	0.06	0.19	0.83	0.16	1.76	3.82	0.81	9.50	1.14	5.33	0.46	0.62
	2.23	2.22	2.22	1.46	3.29	2.16	2.84	5.20	8.28	11.44	7.38	7.49	2.20	0.03
III	0.84	0.96	1.93	1.36	0.26	2.20	2.18	0.43	4.42	4.93	5.45	2.32	1.08	1.44
III'	0.30	0.35	0.18	0.17	0.56	0.09	0.99	1.24	0.16	1.84	0.39	2.47	0.13	0.13
	1.14	1.31	2.11	1.53	0.82	2.29	3.17	1.67	4.58	6.77	5.84	4.79	1.121	1.57
IV	1.85	2.04	1.61	1.65	2.02	2.16	2.36	0.75	4.38	3.23	2.94	5.08	1.00	1.21
IV'	0.06	0.15	0.11	0.09	0.26	0.07	0.40	0.34	0.08	0.66	1.01	2.79	0.10	0.04
	1.91	2.19	1.72	1.74	2.28	2.23	2.76	1.09	4.46	3.89	3.95	7.87	1.10	1.25
V	4.87	4.98	5.70	4.28	4.74	6.36	5.62	2.56	16.17	10.10	14.63	9.56	3.82	3.26
VI	0.41	0.74	0.35	0.45	1.65	0.32	3.15	5.40	1.05	12.00	2.54	10.59	0.69	0.19
VII	5.28	5.72	6.05	4.73	6.39	6.68	8.77	7.96	17.22	22.10	17.17	20.15	4.51	3.45
VIII	0.03	0.00	0.03	0.00	0.00	0.05	0.00	0.05	0.45	0.60	1.00	0.80	0.00	0.00
IX	0.147	0.125	..	0.099	0.544	0.005	1.080	0.794	0.052	2.520	..	..	..	0.090
X	0.216	0.202	..	-0.022	0.357	0.113	0.272	0.714	0.026	0.603	..	..	..	0.168
XI	0.103	0.102	..	0.123	0.628	0.270	0.072	0.454	0.057	0.295	..	..	..	0.004
XII	0.466	0.429	..	0.200	1.529	0.388	1.424	1.962	0.135	3.418	..	..	..	0.262
XIII	8.82	7.50	..	5.16	23.95	5.81	16.25	24.65	0.78	15.46	..	..	..	7.59
XIV	100.00	58.00	..	53.30	92.60	100.00	45.40	36.35	12.87	28.45	..	..	..	100.00
XV	7.76	12.93	..	9.50	25.80	4.78	35.95	67.80	6.10	54.30	..	..	..	5.51

center of the furnace, there was maintained a practically uniform temperature, 1200° C., and this inner portion of the furnace never became blackened. A slight current of air was maintained about the crucible, as shown, but great care was taken, by means of a sand and paraffine seal, at *P*, to prevent vapors passing from the heating spiral into the inner chamber. The crucible was not placed in the furnace until this had reached 1000° C.; a temperature of 1200° C. was

ignited in platinum for 1 min. at about 1200° C., and weighed as ferric oxide.

EXPERIMENTAL RESULTS—Fourteen crucibles were carried through a series of identical operations consisting of a determination of their equivalent iridium or rhodium content by the thermoelectric method<sup>1</sup> (see lines I, I' of Table II); the determination of losses of weight after each of three heatings of two hours each at 1200° C. (see lines II, III, IV, each followed

TABLE III—CLASSIFICATION OF WARE BY E. M. F., VOLATILIZATION, CHEMICAL, MAGNETIC AND PHOTOGRAPHIC DATA

Crucible reference letter	Mean E. M. F. millivolts	Equivalent content Per cent		Equivalent Fe (magnetic) Per cent	Wt. of Fe remaining magnetic test	Maker's chemical statement Per cent	RELATIVE FE BY VI Table II suscep- tibility		CLASSIFICATION with reference to Fig. II Photomicrographs	
		Ir	Rh				Table II	Fig. II	Fig. II	Photomicrographs
<i>a</i>	0.09	0.05	0.05	0.0001	0.018	..	1.0	1.0	Pt	Pt
<i>b</i>	0.50	0.10	0.19	0.0022	0.576	..	1.8	26.0	Rh or Pt	Pt-Rh
<i>c</i>	0.64	0.20	0.29	..	..	..	0.9	..	Pt-Ir	Pt-Ir
<i>d</i>	0.70	0.21	0.30	0.0012	0.194	<0.2 Ir	1.1	14.0	Pt-Ir or Rh	Pt-Ir-Fe
<i>e</i>	0.70	0.21	0.30	0.0007	0.112	..	4.0	8.0	Pt-Ir	Pt-Ir-Fe
<i>f</i>	1.88	0.55	0.85	..	..	0.70 Ir	0.8	..	Pt-Ir	Pt-Ir
<i>g</i>	2.80	0.90	1.29	..	..	..	7.7	..	Pt-Ir-Fe	Pt-Ir-Fe
<i>h</i>	2.98	1.00	1.40	0.0010	0.106	..	8.5	11.0	Pt-Rh	?-Fe
<i>i</i>	6.18	2.30	3.53	..	..	2.37 Ir	2.6	..	Pt-Ir	Pt-Ir
<i>j</i>	6.40	2.40	3.70	0.0110	1.859	0.5 to 1.5 Ir	29.0	125.0	Pt-Ir-Fe	Pt-Ir-Fe
<i>k</i>	6.50	2.42	3.75	..	..	..	6.3	..	Pt-Ir-Fe	Pt-Ir
<i>l</i>	6.90	2.65	4.15	0.0050	0.198	..	26.0	6.0	Pt-Ir-Fe	Pt-Ir-Fe
<i>m</i>	9.30	3.75	7.30	..	..	10.0 Rh	1.7	..	Pt-Rh	Pt-Rh
<i>n</i>	9.70	3.95	7.95	..	..	10.0 Rh	0.5	..	Pt-Rh	Pt-Rh

then attained in about 10 min. and held constant for exactly 2 hrs. and cut off, the crucible being removed 10 min. later or at about 900° C.

Crucible weighings were made on an enclosed precision balance, at first to 0.001 mg. and later to 0.01 mg. as this latter was found sufficient. All weights are reduced to a common basis of loss per 100 cm<sup>2</sup> of total crucible surface.

by determination of loss by acid treatment, lines II', III', IV', and of iron content, lines IX, X, XI). As seen from Table III, these fourteen crucibles range in equivalent iridium content from 0.05 (*a*) to 2.65 (*l*) per cent; crucibles *m* and *n* were supposed to be 90 platinum-10 rhodium; but as measured thermoelectrically, they contain 7.30 and 7.95 per cent

<sup>1</sup> Loc. cit.



rhodium, respectively, the former having been used considerably and the latter an unused crucible; some of the others are of unknown composition and the non-platinum content of each is expressed both in terms of iridium and rhodium (see lines 2 and 3 of Table III). In Table IV the heating and acid losses are given for four crucibles which underwent additional heating.

The microscopic observations were helpful in finally classifying the crucibles in terms of their main impurity—iridium or rhodium (see last line of Table III), as it was found that the crystalline structures

TABLE IV—LOSSES IN WEIGHT DUE TO HEATING AND ACID TREATMENT ON FOUR CRUCIBLES IN MILLIGRAMS, PER 100 CM<sup>2</sup>, AFTER SUCCESSIVE 2-HOUR HEATINGS AT 1200° C

Treatment	CRUCIBLE n			CRUCIBLE l			CRUCIBLE k			CRUCIBLE c		
	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total	Heat	Acid	Total
1st	0.98	0.00	0.98	4.30	0.77	5.07	6.24	1.14	7.38	2.16	0.06	2.22
2nd	2.30	0.18	2.48	2.32	2.47	4.79	5.45	0.39	5.84	1.93	0.18	2.11
3rd	0.61	0.02	0.63	5.08	2.19	7.27	2.94	1.01	3.95	1.61	0.11	1.72
4th	1.44	0.13	1.57	7.40	2.60	10.00	3.78	0.60	4.38	2.34	0.09	2.43
5th	1.21	0.04	1.25	4.04	2.37	6.41	...	...	...	...	...	...
6th	0.81	0.06	0.87	...	...	...	...	...	...	...	...	...
Total	7.35	0.43	7.78	23.14	10.40	33.54	18.41	3.14	21.55	8.04	0.44	8.48
Av.	1.23	0.07	1.30	4.63	2.08	6.71	4.60	0.79	5.39	2.01	0.11	2.12

characteristic of these alloying metals imparted their appearance to the unetched crucible even when present in small percentages. On fresh platinum ware containing considerable rhodium a characteristic bluish color will usually appear after heating to a dull red.

The presence of iron appears to manifest itself in the microphotographs by pitting after heating. The relative amounts of iron in several crucibles were also determined, after the last heating and washing, by measurement of the magnetic susceptibility by a solenoid and balance method in a field of 60 gauss, the crucibles being arranged only approximately in the same order by chemical analysis following heating and by the magnetic measurements (see Table III). It is also of interest to note that iron-free platinum appears to have a susceptibility of zero, and that the susceptibility of "platinum" ranges from 1 to 125. A value of about 20, in the same units, has usually been found for the susceptibility of pure platinum, due undoubtedly to the presence of iron. The total amount of iron in a crucible cannot be determined readily from the magnetic measurements, as is seen by comparison of the magnetic and chemical data of Table III; and the iron, which is supposedly in solution in the platinum, on heating diffuses to the surface as fast as removed by oxidation, thus tending to establish an equilibrium between the iron oxide, oxygen and the iron-platinum solution at the temperature of the experiment. The iron was found non-uniformly distributed in some of the crucibles. The iron washed out in three acid treatments is seen to be greater than the total iron content calculated as iron from the magnetic data, showing that the Fe-Pt alloy containing only a few hundredths per cent iron is paramagnetic and also, from the data, that the susceptibility is not proportional to the iron content.

Considering further the inferences to be drawn from the results recorded in Tables II, III and IV, it is seen that, taking the E. M. F. as a criterion of purity, there is a purification of all crucibles containing over 0.5 per cent iridium after heating. The

platinum-rhodium crucibles (*m* and *n*) do not change composition on heating; that is, the iridium passes out of the crucible and the rhodium does not appreciably.

The losses on heating and after acid treatment are seen to be fairly uniform for each crucible. For some of the less pure crucibles the loss in washing is greater than the heating loss (notably for crucibles *h*, *j*, and *l*). The total heating losses per 100 cm<sup>2</sup>. range from 4.28 to 16.17 mg. for 6 hrs. at 1200°, and the total acid losses (due mainly to iron) from 0.32 to 12.00 mg., for the crucibles containing iridium. For the platinum-rhodium crucibles, *m* and *n*, containing 7 to 8 per cent rhodium, the total losses on heating and washing together are one-fourth less than for the heating loss alone for pure platinum (crucible *a*). In general, there is no relation between the acid loss and loss on heating of crucibles containing both iridium and iron, showing the independence of the determination of loss of soluble and insoluble materials by these

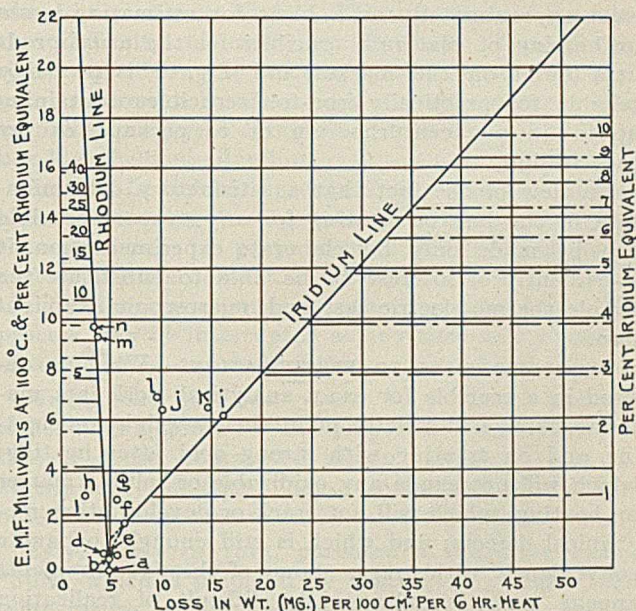


FIG. 2—VOLATILIZATION VS. THERMOELECTRIC FORCE

methods, although relatively large amounts of iron appear to lower somewhat the losses on heating that would otherwise be observed (see crucibles *h*, *j*, *l*). The acid losses are seen to vary from all iron to only 13 per cent iron.

THE PREDICTION OF HEATING LOSSES—The question arises, can the probable loss on heating of a given crucible of unknown composition be predicted from these data? Although a definite answer cannot be given, nevertheless the observations point to a reasonable probability of affirmative reply.

Consider Fig. 2, in which the heating losses are plotted against E. M. F. at 1100° C. against pure platinum for each of the 14 crucibles. The purest crucibles *a*, *b*, *c*, *d* and *e* all lie close together at 5 mg. loss and less than 1 millivolt. The platinum-rhodium crucibles *m* and *n* lie on a line inclined to the left of 5 mg., and which would reach to the heat loss for pure rhodium as a limit. The platinum-



iridium crucibles *f* and *i*, containing negligible iron, lie on a line inclined to the right of 5 mg. The platinum-iridium crucibles containing considerable iron, *h*, *l*, *j* and *k*, lie to the left of the iridium line; *h* may also contain rhodium.

It would follow, therefore, that one would expect a crucible nearly free from iron (which fact is readily tested by heating over the blast lamp) with a measured E. M. F. of say 8 millivolts against pure platinum, to lose 4 mg. per 100 cm<sup>2</sup>. of surface in 6 hours at 1200° C. if made of a rhodium alloy of platinum, and would expect it to lose about 20 mg. if of an iridium alloy. The distinction between these iridium and rhodium alloys may usually be made microscopically, the former having definite smooth crystals with heavy boundaries and the latter a less pronounced and more irregular type of crystals. When iron is present these heat losses will be reduced somewhat and may be halved, since the effective disintegration area is reduced by the layer of iron oxide. Fig. 2 may therefore be used, at least approximately, as a basis for estimating losses on heating of platinum crucibles for the usual products found on the market and Fig. 2 is probably reliable for practically iron-free crucibles containing up to 40 per cent rhodium or to perhaps 10 per cent iridium.

In view of the fact that a satisfactory determination of the loss on heating for any type of crucible can be made only by elaborate experimentation, it is evidently of interest to be able to substitute the simple thermo-electric test and microscopic examination.

**SUGGESTIONS AS TO SPECIFICATIONS**—What is desired in a crucible for exact analytical work is a material which will strictly maintain its weight on heating and on treating with strong acid after heating; which will not exude any oxidizable or soluble matter on heating; which will not crack or develop other mechanical defects; and which is stiff enough to handle conveniently with tongs. Some of these requirements appear to be simultaneously difficult of realization in the present state of our science and of the art of working platinum and its alloys.

Iridium, which adds stiffness to platinum, renders the crucible subject to proportionally greater losses of weight on heating. The presence of iron appears to lower materially the heat losses but is very objectionable on account of the formation of a soluble oxide coating. The purest platinum is usually not stiff enough, although two or three of the apparently purest crucibles here examined were unaccountably stiff, perhaps because of the presence of a small amount of osmium or silica. Rhodium both stiffens the crucible and lowers the heat and acid losses and is much to be preferred to iridium as an alloying element, and crucibles containing small amounts of rhodium, say from 3 to 5 per cent, are to be preferred to crucibles of pure platinum. As the rhodium content is increased the crucible may develop cracks in service.

A requirement which might reasonably be met, at not too great expense for highest grade crucibles, would be: platinum containing 3 to 5 per cent rhodium,

practically free from iron and iridium, and containing no other detectable impurities. For most purposes, these requirements could be checked by assuring one's self that the E. M. F. at 1100° C. against pure platinum was less than 8 and greater than 5 millivolts; that the characteristic crystal structure was that of rhodium and not iridium; and that no iron hydroxide precipitate was obtained after ignition for two hours over strong blast and applying the acid treatment as above described. If pure platinum were preferred, the E. M. F. at 1100° C. should be less than 1 millivolt. If other stiffening ingredients than rhodium be allowed, the 1 millivolt E. M. F. requirement should be maintained.

#### SUMMARY AND CONCLUSIONS

I—There were examined by the thermoelectric method 164 pieces of platinum ware of which 26 per cent contained less than 0.5 per cent iridium and 67 per cent less than 2 per cent of iridium. Of 84 crucibles 36 per cent contained less than 0.5 per cent iridium and 87 per cent less than 2 per cent iridium.

II—A method has been developed for determination of the exact loss on heating of platinum crucibles, by means of a suitable electric furnace containing no heated metal parts.

III—Fourteen crucibles of various makes and grades were examined for loss in weight on heating and after acid treatment following each heating. Their magnetic susceptibilities were also determined. The susceptibility of pure platinum is zero and the range of susceptibility for seven crucibles is 1 to 125.

IV—The heating losses per 100 cm<sup>2</sup>. of practically iron-free crucible surface at 1200° C. ranged from 0.71 mg. to 2.69 mg. per hour, the lesser losses being for crucibles containing rhodium and the greater losses being associated with iridium.

V—Iron appears to lessen somewhat the loss of weight on heating but its presence is objectionable on account of the soluble oxide formed on the crucible surface. The chemical analyses and magnetic measurements place the crucibles in only approximately the same order as to iron content; the magnetic susceptibility is not, however, proportional to the iron content.

VI—It appears to be possible, from a thermoelectric and microscopic examination of a crucible, to predict its probable loss of weight on heating within limits close enough for analytical purposes.

VII—Suggestions are offered concerning the specifications of highest grade platinum crucibles, including the substitution of rhodium to 5 per cent for iridium, and the practical elimination of iron.

VIII—Whether crucibles have been long in use or not, after the first two or three heatings and acid washings, appears to have little or no effect in their behavior as to losses on heating and washing.

We wish to express our obligation to Dr. W. F. Hillebrand who has furnished many valuable suggestions which have aided the progress of this investigation.



## THE PREPARATION, PROPERTIES AND COMPOSITION OF SILUNDUM

By SAMUEL A. TUCKER AND ALEXANDER LOWY

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Silundum is a product of the electric furnace, and was discovered by Bölling,<sup>1</sup> at Frankfort-on-the-Main, Germany. As early as 1900 he began the study of the use of the various silicon carbides as resistors, being led to this work by the fact that these carbides can be subjected to high temperatures without undergoing decomposition. His method was to mix the silicon carbide powder with various binders in order to hold the individual particles together. The mass is a non-conductor at low temperatures, but at about 700–800° C. it becomes conductive, thus being useless at a higher temperature.

By 1904 a process was worked out and patented by which it is possible to convert any piece of carbon, *e. g.*, a crucible, brick, rod, etc., into silicon carbide. By this method resistors without any binding material are obtained, which will stand temperatures as high as 1650–1700° C. Previous to 1904, silicon carbide had been known in two conditions only—amorphous and crystalline—and it was supposed to be formed by the interaction of sublimed carbon and sublimed silicon. Bölling, however, discovered that silicon penetrates carbon when both are in a highly heated condition, but at too low a temperature for the carbon to have any appreciable vapor tension. He claimed that silicon at about 1600° C. exists in the form of vapor. Carbon at this temperature has an extremely small vapor pressure. According to Bölling's definition, silundum is the product that is obtained when carbon is heated in an atmosphere of silicon vapor.

An electric furnace such as is used for the manufacture of carborundum was used for the preparation of silundum. Pieces of carbon pressed to the desired shape were introduced into a mixture of sand and carbon, and this was heated by using as a resistor a granular core of coke. The sand was reduced and the silicon, volatilizing, penetrated the carbon objects and thus "silundumized" them.

Moyat<sup>2</sup> criticized Bölling's work, and claimed that silundum was not a new chemical individual, but merely a new variety of silicon carbide.

Acheson's patent<sup>3</sup> No. 895,531 is interesting, inasmuch as it deals with a similar product. In order to protect crucibles, tuyères, bricks, muffles, and other articles of carbon from destruction at high temperatures in the presence of oxygen, or when exposed to molten metals, Acheson proposes to cover them with a coating of a highly refractory siloxicon, or silicon oxycarbide. This prolongs their life and prevents disintegration. A portion of the carbon on the surface of the article itself is utilized in producing the siloxicon coating. After having been shaped to the form desired, the carbon or graphite article is embedded in a mixture of silica and carbon in the proportion of two parts of sand to five of carbon, and is

exposed to the proper temperature at which silicon, oxygen, and carbon combine to form siloxicon.

The product obtained by this method resembles in appearance the lighter-colored silundum, which is to be discussed later in greater detail.

Tucker and his co-workers<sup>1</sup> in 1909 made an experimental study of the formation of silundum. In their experiments the charge was made up according to the proportion  $\text{SiO}_2 : 2\text{SiC}$ . This charge was heated in a carborundum furnace, the core of which, instead of being of granular carbon, consisted of a number of small carbon plates, pressed together between two horizontal graphite electrodes. Around the core was placed a charge of sand and carborundum, in which were embedded, at varying distances from the core, the carbon articles to be silundumized. These workers also investigated the reactions between sand and carbon. Their experiments showed that silundum can be produced by either of the above reactions, *i. e.*, by the reaction of sand and carbon or of sand and carborundum. They also showed the relative difficulty of oxidizing silundum. Two plates, silundumized on the surface, were heated to a high temperature by means of an electric current. The graphite cores were completely oxidized, leaving only box-like shells of silundum.

Amberg-Bodio<sup>2</sup> also prepared silundum, and states that, "According to the temperature and the time, there is obtained a gray- to metallic-appearing silicon carbide, with a content of silicon greater or less than that which corresponds to the formula  $\text{SiC}$ . The process may be interrupted at any time and a coating of silundum of any desired thickness produced."

Within the past few years, F. J. Tone<sup>3</sup> has obtained four patents for the preparation and manufacture of dense, compacted silicon carbide. From his description, the term "dense compacted silicon carbide" is synonymous with the term "silundum."

Egly,<sup>4</sup> early in 1913, patented a substance called "Silit" which is prepared by heating to a fairly high temperature silicon carbide, silicon, and a binder, until a homogeneous mass results. "Silit" is a good resistor and has many industrial applications.

F. J. Tone<sup>5</sup> describes a silicidized carbon which he calls "Silfrax." In order to show the interior structure of the material, he gives microphotographs of it.

A survey of the literature and a careful preliminary examination of several samples of silundum, indicated to the writers that in all probability the material known as silundum exists in two modifications. The crudeness of the analytical methods used in determining the composition of these refractory materials made it impossible to draw any definite conclusion from the work already published. Moreover, little or no data are available on such important conditions for the preparation of silundum as temperature,

<sup>1</sup> Tucker, Kudlich and Heumann, *Trans. Am. Electrochem. Soc.*, **16**, 207.

<sup>2</sup> Amberg-Bodio, *Z. Elektrochem.*, **15**, 725–727; *Chem. Abs.*, **4**, 149.

<sup>3</sup> Tone, U. S. Patents Nos. 913,324, 992,698, 1,013,700, 1,013,701.

<sup>4</sup> Egly, *Elektrotechn. Zeit.*, **34**, 263–267; *Chem. Abs.*, **6**, 536; **7**, 1142, 2357.

<sup>5</sup> Tone, *Trans. Am. Electrochem. Soc.*, **26**, 181.

<sup>1</sup> F. Bölling, *Chem. Ztg.*, **32**, 1104; *Electrochem. and Met. Ind.*, **7**, 24.

<sup>2</sup> Moyat, *Chem. Ztg.*, **32**, 1166.

<sup>3</sup> Acheson, U. S. Patent No. 895,531; *Electrochem. and Met. Ind.*, **6**, 379.



proportions of reacting materials, and time of heating. It seemed, therefore, that by a careful investigation into the best conditions of temperature for preparing silundum, with an improved method of analysis and a careful examination of properties, considerable light might be thrown upon the question of the composition of silundum. With this purpose in mind the present investigation was undertaken.

Silundum, according to the conditions under which it is formed, exists in two modifications. One of these, a steel-gray variety, is formed at a temperature of about  $1900^{\circ}\text{C}$ . and analyzes very closely to the formula  $\text{SiC}$ ; the other, a slate-green variety formed at about  $1600^{\circ}\text{C}$ ., is an oxycarbide of silicon of the formula  $\text{Si}_4\text{C}_4\text{O}$ . It has been determined that silundum does not decompose below  $2200^{\circ}\text{C}$ . At higher temperatures silicon distills off, leaving a graphite skeleton of the same form as the original silundum, which action would indicate that the graphite does not vaporize at the temperature of decomposition, and would show, further, that silundum is formed by the reaction of silicon vapor and solid carbon, the temperature of formation being lower than the temperature of decomposition.

The action which takes place in the process of silundumization may be summarized as follows: The silicon which is liberated from silica by the reducing action of coke- or sugar-carbon penetrates the solid carbon or graphite objects, and there reacts with the carbon, forming a steel-gray variety of silundum. This takes place above  $1800^{\circ}\text{C}$ . Below this temperature the slate-green variety is formed, most likely by the penetration of the carbon by the silicon vapor and carbon monoxide.

The stumbling block in the analysis of such refractory substances as silundum has been the difficulty of completely decomposing the material and burning all the carbon to carbon dioxide. The silicon may be determined easily by means of the well-known sodium carbonate and potassium nitrate fusion. In order, therefore, to overcome the difficulties hitherto encountered in the carbon determination, various fluxes and oxidizing agents were tried, with the object of replacing the inadequate sodium peroxide and magnesia method<sup>1</sup> previously used. After considerable experimentation litharge was found to be an excellent flux for decomposing the material and partially oxidizing it, complete oxidation being effected by means of a stream of oxygen. Using this method on carborundum crystals, results were obtained that were accurate within 0.3 per cent of theoretical. Considering the nature of the material treated, this was satisfactory. Analyses of silundum samples were made by this new method, and the results checked on duplicates. Therefore, we consider this to be a good method for the accurate determination of carbon in refractory carborundum-like substances.

#### DESCRIPTION OF EXPERIMENTS

**PREPARATION OF SILUNDUM**—In order to obtain sufficient amounts of the substance for the further study of its properties and composition, silundum

was prepared in a coke resistance furnace (Experiments 1 to 7). Since this type of furnace does not lend itself to accurate temperature measurements, the temperatures of formation and decomposition were measured in a separate series of experiments (8 to 13) in the Arsem vacuum electric furnace.<sup>1</sup>

The coke resistance furnace<sup>2</sup> was chosen because with it a range of temperatures up to about  $2600^{\circ}\text{C}$ . can be obtained by varying the amount of electrical energy. The furnace, diagrammatically represented in Fig. 1, consists essentially of a coke resistor enclosed by cemented fire-clay brick walls with magnesia lining. The graphite electrodes extend through the walls into the coke.

The graphite crucible containing the charge and the articles to be silundumized were embedded in the coke core. The energy was supplied by a 50 kw. A. C. generator. The measurements and the

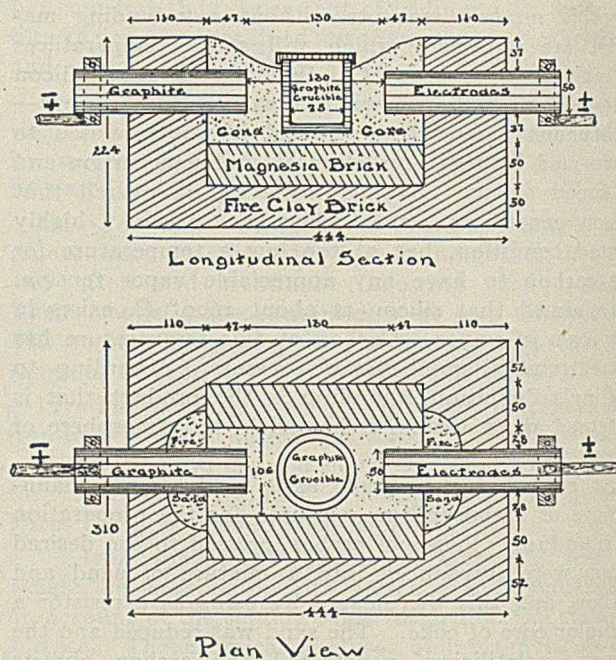


FIG. 1—RESISTANCE FURNACE (DIMENSIONS IN MMS.)

exact details of construction of the furnace are indicated in the diagram.

Carbon and graphite rods varying in diameter from  $1/8$  to  $3/8$  in., and 2 in. in length were used. In a few experiments carbon tubes were used. The charge consisted of clean sand and coke. For the samples that were to be analyzed, special charges, consisting of precipitated silica and sugar-carbon were used, in order to obtain a pure product. The objects to be silundumized in these cases were also made of graphite of the highest purity.

#### EXPERIMENTS IN COKE RESISTANCE FURNACE

Experiments 1 to 7 were conducted in order to find out how the variation of the different factors of time, energy consumption and composition of charge would affect the nature of the product formed.

<sup>1</sup> Arsem, *Trans. Am. Electrochem. Soc.*, 9, 153.

<sup>2</sup> Tucker, *Ibid.*, 11, 307.

<sup>1</sup> Fitzgerald, *Electrochem. Ind.*, 2, 443.



The readings taken during these experiments appear in Table I.

TABLE I—READINGS TAKEN DURING EXPERIMENTS IN COKE RESISTANCE FURNACE

EXPERIMENT No. 1		EXPERIMENT No. 2		EXPERIMENT No. 3		EXPERIMENT NUMBER 5			EXPERIMENT No. 7		
Time	Amperes Volts	Time	Amperes Volts	Time	Amperes Volts	Time	Amperes Volts	Time	Amperes Volts	Time	Amperes Volts
10.00	0 40	1.30	0 35	9.30	0 34	9.55	0 35	10.50	550 28	10.00	0 40
10.10	75 38	1.45	200 30	9.45	200 32	10.05	75 34	10.55	525 28	10.10	100 36
10.20	100 36	1.55	300 30	9.55	310 30	10.10	100 30	11.00	550 28	10.20	200 30
10.30	150 34	2.00	400 30	10.00	405 25	10.15	200 29	11.05	550 28	10.30	500 28
10.40	150 34	2.10	400 26	10.15	400 25	10.20	250 30	11.15	555 28	10.40	500 26
10.50	150 34	2.20	400 26	10.30	410 25	10.25	350 29	11.25	550 28	10.50	550 25
11.00	200 28	2.30	400 26	10.45	410 25	10.30	450 28	11.35	550 28	11.00	650 25
11.10	270 26	2.40	410 26	11.00	400 25	10.35	550 28	11.45	550 28	11.10	650 25
11.20	300 26	2.50	410 26	11.30	400 25	10.40	550 28	11.55	550 28	11.30	650 25
11.30	300 26	3.00	410 26	12.00	400 25	10.45	550 28	12.00	550 28	12.00	650 25
12.00	300 26			12.30	400 25					12.30	650 25
				1.00	400 25						

EXPERIMENT 1—A charge consisting of a mixture of 60 g. coke and 150 g. sand (the theoretical amount to produce silicon) was placed in a graphite crucible. Four carbon rods  $\frac{1}{4}$  in. in diameter and 2 in. long were then embedded in the charge and the crucible tightly covered with a graphite cover. Crucible and contents were placed in the furnace within the coke resistor, and the electric current turned on. After two hours the furnace was allowed to cool, and examination of the contents of the crucible showed that the rods were not silundumized. The sand was fused around the graphite rods. This experiment indicated that a higher temperature was necessary for the accomplishment of the desired reaction.

EXPERIMENT 2 was conducted in order to study the effect of higher temperature on the reaction. The electrical energy consumption was increased, as indicated above, with the object of obtaining this desired higher temperature. The composition of the charge was the same as in Experiment 1. The graphite rods upon fracture were found to be silundumized half way through. The line of demarcation between the silundumized portion and the portion not acted upon was very sharp (see the microphotograph, Fig. 2). The color of this product was slate-green.

EXPERIMENT 3 was intended to produce silundum extending through the entire cross-section of the rods. The charge was made up exactly as in Experiment 1, and the temperature conditions were also duplicated as closely as possible. This experiment, however, was carried on two hours longer than Experiment 2. The rods were completely silundumized, and no graphite core was visible. The color of the rods was slate-green. They were conductors of electricity even at ordinary temperatures.

EXPERIMENT 4 was carried out in order to determine whether there is any difference in the nature of the product obtained when the rods are embedded in the charge and when they are exposed. The charge in this experiment consisted of 120 g. silica and 48 g. coke. The rod was placed in the charge with the upper half extending above the surface of the charge. The other conditions of the experiment were the same as in Experiment 2. The product was of a slate-green color. Fracture showed that the part embedded in the charge was silundumized about half way through, while the part exposed had only a superficial coating of silundum. This experiment shows that more complete silundumization takes place when the rods are embedded in the charge than when they are exposed.

EXPERIMENT 5 was intended to show the effect of

still higher temperatures than were used in the previous experiments. A charge like that in Experiment 1

was used. The rods upon fracture were found to be silundumized about half way through. The color of the product was steel-gray, resembling carborundum. Clearly defined characteristic carborundum crystals were found on the surfaces of the silundumized rods.

EXPERIMENT 6 was similar to Experiment 5 except that the heating was carried on for four hours. Subsequent examination of the rods showed that complete silundumization had taken place. The rods were steel-gray in color, and had small carborundum crys-

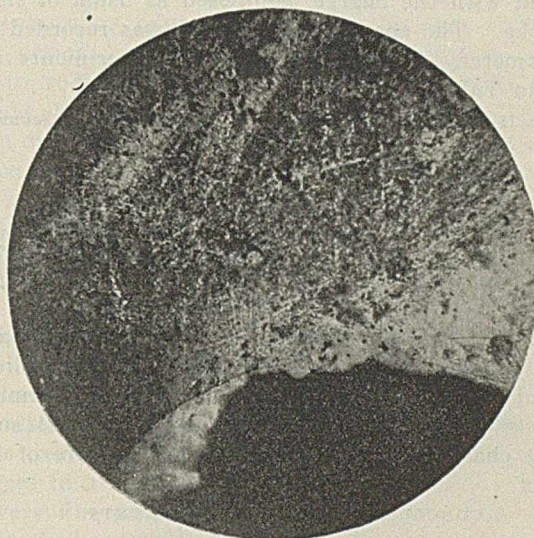


FIG. 2

tals on the surface. They were conductors of electricity even at ordinary temperatures.

EXPERIMENT 7 was designed to study the effect of high temperatures. A rod of silundum of the steel-gray variety was placed in the graphite crucible and heated for two hours under electrical conditions as given in Table I. The silundum rod was found to have lost all its characteristic properties, and on further examination proved to be graphite.

Experiments were also carried out in order to determine what would be the effect of varying the composition of the charge used. It was found, however, that no appreciable difference in the nature of the product resulted from such variation. Some of the sand in the charge sinks to the bottom, and the coke, because of its lower specific gravity, remains at the top. There is never, therefore, any very intimate mixture of the ingredients. It is not surprising, in consequence, that small differences in the ratio of the components of the charge should produce no differences in the results.



## EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

EXPERIMENTS 8 TO 13—As temperature determinations cannot be made with any degree of accuracy in the electric furnace used above, Experiments 8 to 13 were carried out in an Arsem electric vacuum furnace,<sup>1</sup> in order to determine the temperature of formation and decomposition of silundum. Details of the construction of this furnace, which is complex, are out of place in this article, and the reader is referred to the reference below. The temperature was measured with a Wanner optical pyrometer. As pyrometer readings are untrustworthy in the presence of fumes, blank runs were first made without any material in the furnace, noting at the same time the energy consumed and the temperature attained. These temperatures were then taken as the temperatures which would exist in the experiments made under the same conditions of time and energy consumed.

A graphite crucible,  $\frac{3}{4}$  in. diameter and  $2\frac{1}{2}$  in. high, was used. The carbon rod to be silundumized was placed in the center of this crucible and was surrounded with the charge, composed as usual of silica and coke. The energy consumption was recorded by a wattmeter. The results of these experiments are given in Table II.

TABLE II—RESULTS OF EXPERIMENTS IN ARSEM ELECTRIC VACUUM FURNACE

Exp. No.	Temp. ° C.	Ratio of SiO <sub>2</sub> to C in charge	Color of product	Remarks
8.....	1300	30 : 12	.....	No silundum formed
9.....	1606	30 : 12	Slate-green	Surface silundumization
10.....	1712	30 : 12	Slate-green	Surface silundumization
11.....	1845	30 : 12	Steel-gray	Surface silundumization—
12.....	1900	30 : 12	Steel-gray	most of charge volatilized
13.....	Over 2200	30 : 12	.....	Product decomposed

Owing to the fact that a high vacuum was maintained as the temperature rose, some of the silicon distilled from the charge and the depth of silundumization was very small, but the surface layer was sufficiently characteristic to determine the nature of the product.

## CONCLUSIONS FROM EXPERIMENTS

I—The temperature of formation of silundum is above 1300° C. (see Expts. 1 and 8).

II—Up to about 1800° C. the greenish slate-colored variety of silundum is formed (see Expts. 2, 3, 4, 9 and 10).

III—Above 1800° C. the steel-gray colored variety of silundum is formed (see Expts. 5, 6, 11 and 12).

IV—Continued heating above 2200° C. results in decomposition of the silundum with formation of graphite (see Expts. 7 and 13).

V—The extent of penetration of silundumization depends upon the duration of heating (see Expts. 2, 3, 4, 5 and 6).

VI—More complete silundumization takes place when the object is embedded in the charge (see Expt. 4).

## PROPERTIES OF SILUNDUM

According to Bölling,<sup>2</sup> silundum is a form of silicon carbide, and possesses properties similar to those of carborundum. It is capable of being maintained for a long time at temperatures up to 1600° C. without

change, and may be heated for a short time to 1700° C. without deterioration. It is a conductor of electricity, its resistance being about six times that of carbon. At 1000° C. its resistance is one-half to two-thirds of that at room temperature. The electrical resistance is variable, and depends upon the variety and hardness of the carbon used in the preparation, that made from porous carbon having a higher resistance than that made from compact. Silundum cannot be melted; in this respect it resembles carbon. It may be nickel-plated, or covered with a layer of platinum. It is a refractory material, but it is attacked by molten metals at high temperatures. It may be heated to a white heat and plunged into cold water without cracking.

Briefly, the results of the present investigation of the physical and chemical properties of silundum may be summarized as follows:

- 1—Silundum is a good conductor of electricity, with a negative temperature coefficient for its resistance.
- 2—Silundum is a very hard substance—with a hardness on Mohr's scale of about 9.
- 3—The specific gravity of silundum is 2.9 to 3.
- 4—Silundum is not attacked by hydrogen, oxygen, or nitrogen even at 1100° C.
- 5—Silundum is attacked by some fused salts.
- 6—Silundum is not attacked by acids.

ELECTRICAL CONDUCTIVITY—The following is the method for determining the electrical conductivity of silundum: A cylindrical rod of uniform diameter was used. In order to diminish the contact resistance as much as possible the ends were copper-plated, thus: the rods were dipped into paraffine, the ends scraped clean, coated with a very thin layer of graphite, and then copper-plated electrolytically. Copper wires were soldered on, and the rods were cleaned. The resistance was determined at various temperatures with a very accurate Wheatstone bridge.<sup>1</sup>

The rod of the slate-green variety was 1.871 cm. long and 0.635 cm. in diameter. The rod of the steel-gray variety was 2.078 cm. long and 0.348 cm. in diameter. Owing to the fusion of the solder, measurements could not be made above 225° C. The rods were heated in a small Hoskins electric furnace, and

TABLE III—RESISTANCES OF THE TWO VARIETIES OF SILUNDUM  
SLATE-GREEN VARIETY Rod 1.871 Cm. Long and 0.635 Cm. in Diameter  
STEEL-GRAY VARIETY Rod 2.078 Cm. Long and 0.348 Cm. in Diameter

Temp. ° C.	Measured resistance Ohms	Specific resistance Ohms per cc.	Measured resistance Ohms	Specific resistance Ohms per cc.
20	0.91450	0.1546	5.2250	0.2391
25	0.91270	0.1543	5.1886	0.2374
50	0.90000	0.1522	4.9786	0.2278
75	0.89092	0.1506	4.8186	0.2205
100	0.88192	0.1491	4.6291	0.2118
125	0.87212	0.1474	4.4191	0.2022
150	0.86202	0.1457	4.2791	0.1958
175	0.85392	0.1443	4.1541	0.1901
200	0.84522	0.1429	4.0441	0.1850
225	0.83530	0.1412	3.9541	0.1809

the temperature was read by means of an ordinary thermometer with its bulb in the heating chamber. Table III shows the measured resistances and the specific resistances in ohms at the various temperatures. The specific resistances are plotted against the temperatures in Fig. 3.

<sup>1</sup> This was done in the Electrical Testing Laboratory of Columbia University.

<sup>1</sup> Arsem, *Trans. Am. Electrochem. Soc.*, 9, 153.

<sup>2</sup> Bölling, *Loc. cit.*



Attempts were made to spray the ends of the rods according to the Schoop<sup>1</sup> method, but when they were heated, the brass contacts became loosened from the ends of the rods.

It is evident from the above results that the resistance is practically a linear function of the temperature. The temperature coefficient of resistance is negative. The specific resistance is much less than that for carborundum, being, at 25°, 0.1543 ohm per cubic centimeter for the slate-green variety, and 0.2374 ohm per cubic centimeter for the steel-gray variety, while that of carborundum is 50 ohms per cubic centimeter at 25°.<sup>2</sup>

It was attempted to measure the ohmic resistance of the above rods at higher temperatures by clamping them between platinum plates. The resistance varied from 75 ohms to a fraction of an ohm, depending upon the pressure exerted upon the platinum plates, so that measurements of the same order of accuracy as those

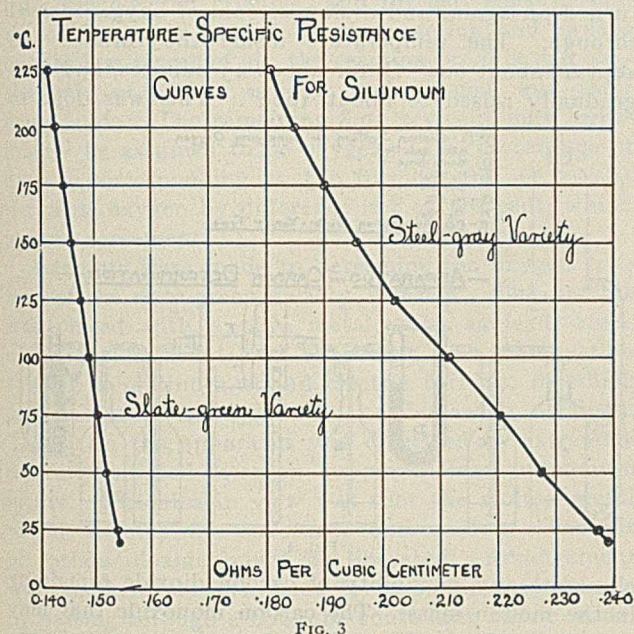


FIG. 3

determined above with plated ends could not be made above 225° C.

HARDNESS and specific gravity measurements are given in Table IV for the two varieties of silundum and for Tone's and Bölling's products.

SPECIFIC GRAVITY was determined by means of a specific gravity bottle, care being taken to expel all air bubbles by careful heating and subsequent cooling.

TABLE IV—HARDNESS AND SPECIFIC GRAVITY OF SILUNDUM

	Specific gravity	Hardness (Mohr's scale)
Tone's "Silifrax".....	2.96	9 plus
Bölling's silundum.....	2.97	9
Greenish variety silundum.....	2.92	8 to 9
Steel-gray variety silundum.....	2.94	9 minus

#### PROPERTIES OF BOTH VARIETIES OF SILUNDUM

**ACTION OF GASES**—Oxygen, nitrogen, and hydrogen have no action on silundum heated to temperatures up to 1100° C. An attempt was made to oxidize silundum in a bomb calorimeter under a pressure of 25

atmospheres of oxygen, in a gelatine capsule containing a mixture of benzoic acid and silundum. The gelatine and the benzoic acid were completely oxidized, but the silundum was unattacked.

**ACTION OF FUSED SALTS, ETC.**—Silundum is not decomposed by the following fused salts: sodium silicate, borax, a mixture of potassium chlorate and potassium nitrate, potassium acid sulfate, cryolite, potassium dichromate.

Silundum is decomposed by fused sodium carbonate, sodium hydroxide, and potassium hydroxide in presence of air, yielding the corresponding silicates and carbon dioxide.

**ACTION OF ACIDS**—Silundum is not acted upon by hydrochloric, nitric, or sulfuric acids, nor by a mixture of hydrochloric and nitric acids, a mixture of chromic and sulfuric acids, nor by fused boric acid. Commercial silundum, however, is slightly attacked by hydrofluoric acid and by a mixture of nitric and hydrofluoric acids, because of the presence of free silicon and silicon dioxide; but pure samples of silundum are not attacked by these acids.

**ACTION OF OTHER SUBSTANCES**—Molten sulfur has no action on silundum. Sodium peroxide oxidizes it to sodium silicate plus sodium carbonate. Lead oxide also oxidizes it, producing metallic lead and carbon dioxide (pp. 566 and 570). Fused sodium in presence of air decomposes silundum, yielding sodium silicate and sodium carbonate. The action in this case is most likely due to the presence of sodium peroxide formed from the sodium.

#### COMPOSITION OF SILUNDUM

In order to obtain silundum as pure as possible for analysis, graphite rods were silundumized according to the previously described methods, in a charge consisting of sugar-carbon and precipitated silica. The resulting silundum was broken up into small pieces in a steel mortar, and subsequently ground to a very fine powder in an agate mortar. The powder was then purified. Depending upon the conditions of preparation, the product obtained was either silicon carbide or silicon oxycarbide, with probable impurities either from the charge or from the reaction, or from the mortar in which the material was ground. The impurities may be silicon, silica, carbon, and iron. Silicon was removed with boiling potassium hydroxide solution, any remaining silica by means of hydrofluoric acid, and the uncombined carbon by long oxidation with a strong blast lamp. Finally, in order to assure complete oxidation the material was boiled with chromic and sulfuric acids, and then with hydrochloric acid in order to remove any particles of iron which may have been abraded from the mortar. The material was then thoroughly washed, and when dried was ready for analysis.

For the silicon determination 0.3 to 0.4 g. of the above purified substance was weighed into a platinum crucible. To this were added 4 g. of chemically pure sodium carbonate and a small crystal of potassium nitrate. The contents were then well mixed and the covered crucible heated, great caution being used to

<sup>1</sup> Met. Ind., 1914, p. 457. THIS JOURNAL, 4, 853; 5, 776; 7, 72.

<sup>2</sup> Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y., 1913



avoid spattering. The heating was continued until a quiet fusion resulted, then strongly increased until all the carbon particles were oxidized, leaving a clear melt. This upon cooling gave a clear, white mass, which was dissolved in hydrochloric acid and evaporated to dryness, dehydrated three times, and the determination of silica made as in rock analysis. The silica was weighed by difference after repeated evaporation with hydrofluoric acid. Duplicate analyses checked within 0.15 per cent. From the amount of silica obtained the percentage of silicon was calculated. The results are given in Table V.

TABLE V—ANALYSES OF SILUNDUM FOR SILICON

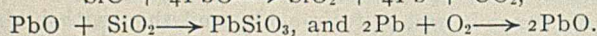
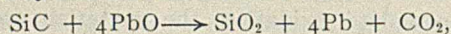
PER CENT SILICON FOUND	THEORETICAL PER CENT SILICON
Steel-gray silundum	in silicon carbide
69.46	70.22
69.59	...
Slate-gray silundum	in Si <sub>2</sub> C <sub>3</sub> O
63.16	63.88
63.28	...

The method<sup>1</sup> formerly employed for the determination of combined carbon in carborundum-like substances was to fuse about 0.3 g. of the substance with 3 g. of calcined magnesium oxide and 6 g. of sodium peroxide in a nickel crucible. A blank test had to be run at each set of experiments to determine the amount of carbon dioxide present in the magnesia and sodium peroxide. Furthermore, it was necessary to heat the crucible with a hydrogen flame until a vigorous reaction occurred, and the crucible while still hot was transferred to a desiccator charged with soda-lime and allowed to cool. The carbon dioxide was then determined by any suitable method.

This scheme is subject to grave error, owing to the appreciable amounts of carbon dioxide present in the magnesia and sodium peroxide. The carbon dioxide content of the sodium peroxide continually increases, and therefore, even with the blank corrections, the results are subject to error. The reaction is generally so violent that spattering is almost unavoidable. Moreover, the process is long, and involves too many operations to yield absolutely quantitative results under the conditions given.

The method worked out in this paper avoids these difficulties.

After preliminary experiments with various oxides, such as pure cupric oxide, ferric oxide, and manganese dioxide, as oxidizing agents, it was found that only molten litharge gave good results on carbon determinations in carborundum-like substances. Molten litharge disintegrates the particles of silundum, and at the same time oxidizes the carbon to carbon dioxide. The reactions may be written as follows:



PROCEDURE—0.20 to 0.25 g. of the sample was weighed out in a watch glass. This was thoroughly mixed with 5 g. of litharge whose carbon dioxide content had been determined in a blank test carried out under the same conditions as the analysis. The mixture of litharge and sample was placed in a C. M. Johnson combustion boat made of vitrified clay, 120 mm. long and 15 mm. wide.<sup>2</sup> Experiments were

also made with combustion boats of porcelain, alundum, nickel, iron, and copper, but all except the vitrified clay were attacked and fused by the molten litharge.

The boat with its charge was placed in the silica tube of an electric combustion furnace, and the air in the furnace displaced by oxygen that had been thoroughly dried in a drying train. The current was turned on and the temperature raised slowly enough to avoid too rapid decomposition, which, if it occurred, would blow the charge out of the combustion boat. A gentle stream of oxygen was passed through the apparatus throughout the determination, and the course of the reaction was followed by observing the rate at which the bubbles of gas passed through the absorption apparatus. As soon as the evolution of carbon dioxide tended to become rapid, the electric current and the flow of oxygen were turned off until the reaction subsided, and no more bubbles of gas passed through the absorption apparatus. Then the current was turned on again, and a slow stream of oxygen passed through. The temperature inside the furnace was kept at about 600° C. for about 45 minutes, and then gradually raised to about 1000°. This was done to

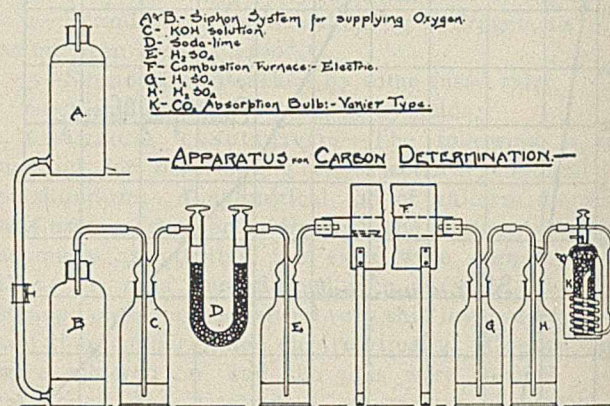


FIG. 4

eliminate any possibility of carbon dioxide remaining in the molten mass. The carbon monoxide that may be given off at this temperature is converted into carbon dioxide by passing over a heated coil of cupric oxide. The carbon dioxide evolved was absorbed in a Vanier KOH absorption apparatus.

The arrangement of the apparatus as set up is indicated in Fig. 4. Analyses made by this method are given in Table VI.

TABLE VI—CARBON IN CARBORUNDUM AND SILUNDUM  
Correction for CO<sub>2</sub> in PbO = 0.0175 Gram

SAMPLE	Weight Sample Grams	Grams CO <sub>2</sub> evolved	Weight CO <sub>2</sub> corrected	Per cent C in sample	Theoretical Per cent Carbon in SiC
Large carborundum crystals..	{ 0.2004	0.2330	0.2155	29.33	in SiC
	{ 0.2142	0.2488	0.2313	29.45	29.78
Steel-gray silundum.....	{ 0.2509	0.2925	0.2750	29.89	in SiC
	{ 0.2214	0.2609	0.2434	29.95	SiC
	{ 0.2187	0.2586	0.2393	29.84	29.78
Slate-green silundum.....	{ 0.2082	0.2308	0.2133	27.94	in SiC
	{ 0.2413	0.2633	0.2458	27.76	Si <sub>2</sub> C <sub>3</sub> O
	{ 0.2265	0.2488	0.2313	27.85	27.09

From the examination of the data in Tables V and VI as summarized in Table VII, it is evident that the percentage of carbon and the percentage of silicon in the steel-gray variety of silundum add up nearly to 100 per cent, indicating that the accepted formula

<sup>1</sup> Fitzgerald, *Loc. cit.*<sup>2</sup> Eimer and Amend, New York



SiC is correct for this modification or variety. On the other hand the silicon and carbon in the slate-green variety of silundum add up to only 91.07 per cent. This variety evidently does not correspond to the formula SiC.

TABLE VII—SUMMARY OF ANALYSES

	Carborundum	Steel-gray silundum	Slate-green silundum
PER CENT FOUND { Si.....	29.39	69.53	63.22
{ C.....		29.89	27.85
TOTAL.....		99.42	91.07
		Silicon carbide	Si <sub>4</sub> C <sub>4</sub> O
PER CENT THEORETICAL { Si.....	29.78	70.22	63.88
{ C.....		29.78	27.09
TOTAL.....		100.00	90.97

It may be assumed from the careful method of preparation, in which only pure silica, sugar-carbon, and graphite were used, that the compound can contain only silicon, carbon, and oxygen. Since a temperature of approximately 1600° C. must be attained for the reaction to begin, practically all the air is expelled from the covered crucible; and further, since carbon monoxide gas is formed by the reaction and sweeps out the last traces of air, the reaction product can consist only of carbon, silicon, and oxygen, and their compounds. The remaining 8.93 per cent may legitimately be assumed to be oxygen. The percentage of oxygen corresponding to the formula Si<sub>4</sub>C<sub>4</sub>O is 9.03 per cent; oxygen by difference is 8.93 per cent, which is good agreement.

Attempts were made to determine the oxygen content of the slate-green variety directly. The sample was placed with a pure metal, such as lead, steel, or copper in a vitrified clay boat in a combustion tube of a platinum-wound electric furnace, in which a temperature of 1300° C. can be easily attained. The air in the apparatus was displaced by extremely carefully purified nitrogen, prepared from ammonium nitrite. The idea in view was that the molten metal would dissolve the substance and carbon monoxide or carbon dioxide might be liberated. Arrangement was made for the monoxide to be oxidized to dioxide by passing through a hot tube containing cupric oxide. Owing to the fact that the sample in each case floated on the surface of the molten metal, no reaction occurred, as evidenced by the fact that the KOH absorption apparatus did not gain in weight.

As regards the relationship of silundum to carborundum, results obtained in this paper indicate that the steel-gray variety is a form of carborundum. The following facts may be mentioned:

- 1—Silundum has the same chemical composition as carborundum.
- 2—Their chemical properties are similar.
- 3—The temperatures of formation and decomposition are practically the same.
- 4—Some of the physical properties measured vary from those given in the literature.<sup>1</sup> This difference most likely is due to the fact that the other workers used different methods for their measurements.

## SUMMARY

- 1—Two distinct varieties of silundum were prepared.

<sup>1</sup> Pamphlet, "Chemical and Physical Properties of Carborundum," published by The Carborundum Co., Niagara Falls, N. Y., 1913.

1—The slate-green variety: formula Si<sub>4</sub>C<sub>4</sub>O.

2—The steel-gray variety: formula SiC.

II—Experiments were made to determine the effect of varying the temperature, duration of heating, and composition of charge.

III—The temperatures of formation and decomposition of the two varieties of silundum were determined.

IV—The physical and chemical properties of both forms of silundum were investigated.

V—Results obtained in this investigation tend to show that the steel-gray variety of silundum is a variety of carborundum.

VI—A quantitative method for carbon determination in carborundum-like substances has been devised.

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## THE CONSTITUTION OF CHINESE WOOD OIL VARNISHES

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The modern varnish operator is well acquainted with the general characteristics of Chinese wood oil, particularly those developed during the heat treatment necessary to the manufacture of high-grade rosin varnishes. He is, however, sometimes puzzled to account for the irregularities exhibited by the different shipments of raw oil, with which he is supplied. There has always been considerable difficulty in determining whether the peculiarities of the particular oil in question are due to unavoidable irregularities of the oil or to an adulteration that has not made itself manifest during the laboratory examination of the shipment.

The past difficulty in the detection of tung oil adulteration is being overcome, due to the development of methods of examination that will detect comparatively small amounts of added material. The 1915 report of Committee D<sub>1</sub>, American Society for Testing Materials, will, no doubt, do much toward standardizing the analytical methods for this oil, and by so doing, will be of considerable assistance to the varnish maker in the regulation of his product.

The most characteristic property exhibited by chinawood oil is its rapid bodying at temperatures considerably below those used for other oils. This increase in viscosity continues to the point of complete solidification, even at a temperature as low as 150° C. The length of time necessary for complete solidification depends upon the temperature and ranges from 30 hours heating at 150°, to 10 minutes at 280°. This solid material, particularly when formed at high temperatures, is a non-tacky, resilient body, practically insoluble in the ordinary solvents. It is saponified only with difficulty, and exhibits other characteristics that denote a complete change in the original glyceride. Although insoluble in most solvents, this material is completely soluble in a number of the organic acids, including rosin.

The presence of air has a decided effect upon the rate of solidification, although, as has been demon-

<sup>1</sup> Holder of Acme White Lead & Color Company Fellowship.



strated at different times,<sup>1</sup> air is not essential to solidification, which takes place perfectly well in a sealed vessel, though a longer time is required for the formation of the completely solid product. The statement of Schapringer that the effect of oxygen is entirely catalytic, and that no oxy-compounds are formed is difficult to verify by experiment. In all cases studied by the authors there have been progressively increasing amounts of oxidized materials formed, whenever wood oil or wood oil mixtures have been heated in the air. Also, if the action of oxygen be entirely catalytic, blowing air through the heated mass would hardly show such a decided effect on the rate of solidification in comparison to the rate during unagitated open air cooking. At 165° C., oil in an open dish will solidify in from 20 to 24 hours, while at the same temperature blown oil will solidify in 4 hours.

Various attempts have been made to prevent or control this solidification at high temperatures, for it is quite generally agreed that chinawood oil should impart the same superior quality to gum varnishes that it has given to rosin-chinawood varnishes as compared to rosin-linseed varnishes. The high cooking temperature of gum varnish has discouraged any extensive use of chinawood oil in this product, as the temperature is beyond the range to which the oil may be heated without solidification, and the fossil gums do not possess the solvent power for the solid material that is shown by rosin.

Several patents have been taken out covering processes to prevent solidification. One, evidently recognizing the very decided accelerating effect of oxy-acids on the time for solidification, recommends the introduction of a strongly reducing metal.<sup>2</sup> Another, possibly in an attempt to make use of the solvent power of free fatty acid, superheats the oil to a temperature of partial decomposition, after which it does not solidify even when heated for a long time.<sup>3</sup>

Investigators are pretty well agreed that the solidification of wood oil comes as a more or less direct result of the polymerization of the glyceride of elaeo-margaric acid, which is the major constituent of the raw oil. This polymerization takes place through a joining at the unsaturated linkings. This, however, is not accompanied by a complete saturation, for a study of the iodine absorption of the raw and heat-treated products shows a difference of only about one-third. The polymerization is not reversed by saponification and subsequent acidification. Inasmuch as the polymerized glyceride is insoluble in the solvents suitable for molecular weight determinations, the best evidence we have that polymerization has really been effected is that the fatty acid from the solidified product has approximately double the molecular weight of the acid from the raw oil.

Morrell<sup>4</sup> has studied the bodying of linseed and poppyseed oils, and has shown that there occurs a

similar heat polymerization with these oils, but that there is no solidification, and that the polymerization is by no means complete.

Various explanations have been offered for the solidification of chinawood oil when subjected to this heat treatment. Some experimenters believe that the solid is a uniform product of a chemical reaction which takes place at a rate dependent upon the temperature of heating and goes to completion under the proper conditions. Others take the stand that the solidification is really the development of a colloidal gel, and is not necessarily a product of complete polymerization.

Wolff<sup>1</sup> claims to be able to extract the unpolym-erized oil from the dry polymerized product, and he shows in his experiments that the extracted material has not increased in molecular weight, and that the polymerized material constitutes only a minor portion of the gel.

Schapringer<sup>2</sup> says that the solid is a final product of a double reaction, and that the polymer is well developed in the primary reaction, but remains soluble until the second reaction starts, when there is a sudden exothermic formation of the gel.

The authors are led to believe from their experiments, that the solidification is due to the formation of a colloidal gel, and although, in the case of heated oils, a direct result of the presence of the polymer, the gel formation does not necessarily accompany the polymerization. The methods for control of solidification are simply means for hindering the gel formation, and exert comparatively little effect upon the polymerization.

A somewhat similar colloidal gel makes its appearance when the oil is treated with a solution of sulfur chloride or iodine. The time for gel formation may be regulated by adjusting the strength of solution used. In the case of the iodine-chinawood gel, the solidification may be entirely prevented by the introduction of a comparatively small amount of alcohol. This does not interfere with the formation of the iodine addition products, but acts to keep the colloid in solution.

The decomposition products formed during superheating of the oil must act similarly toward the oil in preventing solidification during subsequent heating. It is possible, by heating chinawood oil to 350° C. for only a short time, to prevent solidification from heat, even though the oil may be subjected to heating at the ordinary solidification temperatures for long periods. This still liquid product of heat treatment exhibits most of the characteristics of regularly polymerized oil. It contains a large amount of glyceride of high molecular weight, together with some free acid and a considerable quantity of unsaponifiable matter. This unsaponifiable material must exert some influence in preventing the natural solidification of the oil, for it seems hardly possible that the small amount of free acid

<sup>1</sup> Jenkins, *J. Soc. Chem. Ind.*, 16 (1897), 193.

<sup>2</sup> German Patent 219,715, 1910.

<sup>3</sup> German Patent 211,405, 1908.

<sup>4</sup> *J. Soc. Chem. Ind.*, 34 (1915), 105.

<sup>1</sup> *Farben Zeitung*, 18 (1913), 1171.

<sup>2</sup> Dissertation. Translated. Armitage and Stevens, "Chinawood Oil."



present should act in any different manner from the same amount of free acid added to the original oil. It takes considerably more added fatty acid to prevent gel formation than has been shown in any of the superheated products with which the authors have worked.

Undoubtedly the effect of rosin upon heated oil is also one of solution or gel prevention rather than one of suspension of reaction. It should, then, be possible to show the progress of polymerization as influenced by time, temperature, and other conditions, and entirely independent of the rosin present. There might also be other reagents that would exhibit the same ability to control. The development of a nonpolymerizing wood oil will probably be along these lines.

To keep the finished product light in color, and to avoid undue loss from decomposition and volatilization of the gum, it is common practice, in varnish manufacture, to subject the oil to a preliminary heat treatment, to bring it to a body at which the final cook may be comparatively short. In the case of chinawood oil, the polymerization during this preliminary heating must be considerable, and inasmuch as this polymerization reaction is not ordinarily considered to be reversible, the function of rosin in these mixtures must be one of gel prevention.

In the experimental work, of which this paper is a preliminary discussion, the heating was carried out on the mixtures rather than on the individual constituents. The matter of color was of little consequence, and in order to get a more uniform set of results it was thought advisable to permit the rosin to exert its influence during the whole time of heating.

The first problem in the study of the polymerization of chinawood oil in the presence of rosin was the development of a satisfactory method of separation of the various possible constituents of the final mixture.

An attempt was made to use a modification of the Twitchell separation, by forming the ethyl esters of the fatty acids, and their subsequent separation from the rosin and from each other. This method gave a more or less satisfactory separation of the oils from the rosin, but the esters of the polymerized and unpolymerized oils did not show sufficiently pronounced differences upon which to base a method for their separation.

A modification of the method suggested by the authors<sup>1</sup> for the separation of raw chinawood oil from adulterating oils, served the purpose quite well.

The sodium soaps of the fatty acids of both the raw and heat-treated oils are insoluble in absolute alcohol, while sodium resinate is soluble in that menstruum. If proper precautions be taken for the control of temperature and concentration, the soaps of the fatty acids precipitate in a sufficiently granular form to permit of ready filtration and washing.

The subsequently freed fatty acids may be dissolved in warm alcohol of about 80 per cent concentration, from which the comparatively insoluble elaeomargaric acid may be crystallized by cooling.

These characteristic crystals of elaeomargaric acid may be filtered and weighed, or the residue acids may be weighed and the elaeomargaric acid computed by difference. The oxy-acid present may be separated from the residue by precipitation from petroleum ether. In this way it is possible to get an estimation of the total fatty acid, the unpolymerized acid, the oxy-acid, the polymerized acid and the unsaponifiable.

An extensive study of chinawood-rosin heat-treated mixtures, the results of which are now being tabulated, demonstrates quite conclusively that rosin exerts no inhibiting effect upon the polymerization of chinawood oil, either at high or at low temperatures.

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### STUDIES ON THE PRESSURE DISTILLATION OF PETROLEUM HYDROCARBONS

By A. P. BJERREGAARD

Received March 26, 1915

The investigation here reported upon was carried out during the summer of 1914 for the purpose of developing, if possible, a feasible and safe process for the production on a commercial scale of light gravity hydrocarbons, such as gasolines and naphthas, from the heavier and less valuable fractions of petroleum. It has been known for many years that these heavier hydrocarbons, on being subjected to heat and pressure, undergo a decomposition or breaking down into lighter products. This decomposition, whether under pressure or not, has received the name "cracking" in the petroleum industry. It is not the purpose here to go into the history of the process, further than to say that an apparatus somewhat similar to that herein employed was described in U. S. Patents Nos. 342,564 and 342,565, dated May 25, 1886, issued to Geo. L. Benton. In those early days, gasoline was an undesirable by-product, and Benton's process was intended to increase the kerosene fraction. What it actually accomplished is not recorded, so far as I am aware.

#### APPARATUS

The apparatus which was employed (see Fig. 1) consisted of a reaction coil built of one inch double extra strong iron pipe, about 63 ft. long, interior diameter 0.60 in. with walls 0.36 in. thick. This coil was made up of five lengths, each 12 ft. long, with the necessary cross pieces at the ends, each 9 in. long, to make one continuous coil. Extra strong unions were used in each cross piece, and at the ends of each 12 ft. length, so that the whole could readily be opened up for inspection and cleaning. This coil was enclosed in a furnace constructed of fire-brick, asbestos and sheet-iron. It was heated by fourteen large Bunsen burners, each consisting of a horizontally disposed slotted piece of 2 in. pipe, 3 ft. long, fitted at one end with gas and air inlets, and closed at the other end. These burners were arranged under the reaction coil so that the flat sheets of flame issuing from them impinged lengthwise onto the pipes of the reaction coil. Each burner was controlled by a separate gas valve. The fuel was natural gas. Fig. 2 is a general view of part of the furnace, showing some of the gas-controlling

<sup>1</sup> THIS JOURNAL, 6 (1914), 806.



valves. The oil to be subjected to the pressure-cracking process was forced into one end of the coil by means of a hydraulic pump, capable of easily developing a pressure of 4,000 lbs. per sq. in. A pressure gauge reading to 2,000 lbs. was attached to the pipe leading from the pump to the coil. At the other end of the reaction coil was a pressure-release valve controlled by a spring. Various forms of valves were tried. Finally, the one illustrated in Fig.

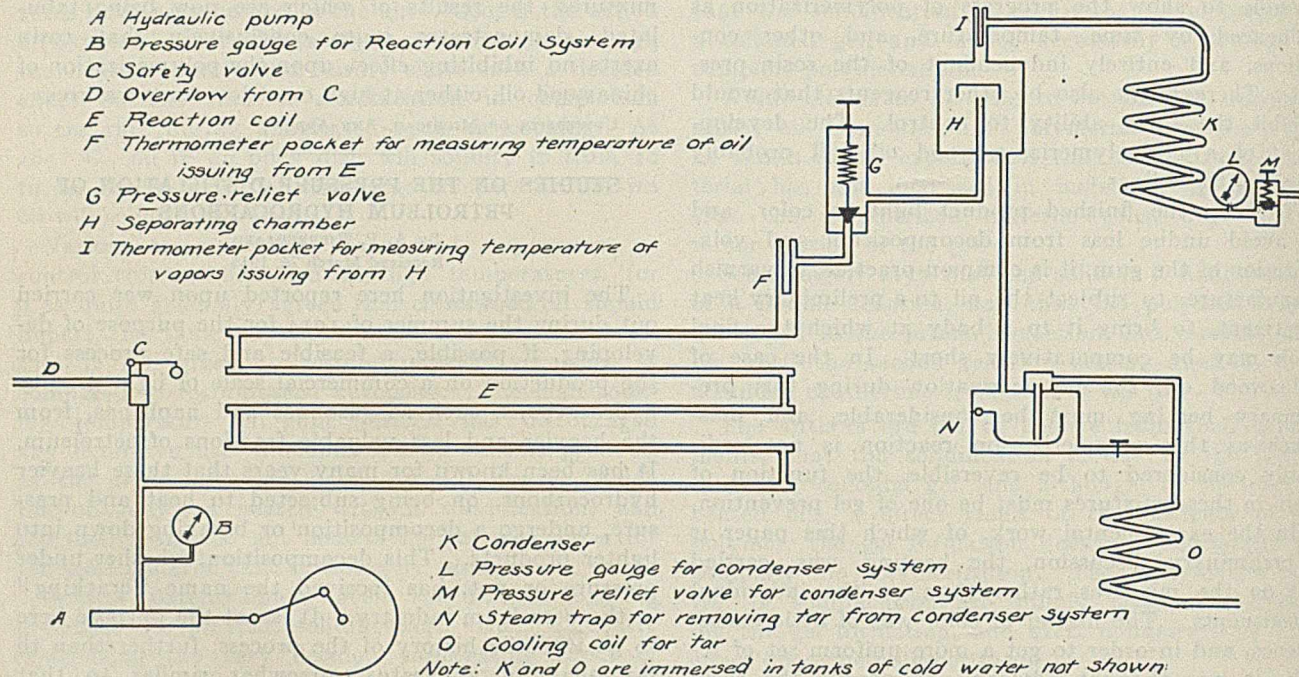


FIG. 1.—DIAGRAM SHOWING ARRANGEMENT OF REACTION COIL AND AUXILIARY APPARATUS

3 was evolved, and this appears to be satisfactory. After leaving the pressure-release valve, the products of reaction passed into a separatory chamber, kept hot enough to allow the lighter vapors, which might be present, to pass out through an opening in the top into a condenser, while the tar, etc., passed out through the bottom. A slight pressure (about 20 to 30 lbs., never more than 40 lbs. per sq. in.) was maintained in the separatory chamber and condenser to facilitate the liquefaction of the most volatile constitu-

it to flow into an appropriate receptacle. The hydraulic pump was the smallest that could be bought, but was much too large for the purpose intended. It was necessary, therefore, to run it extremely slowly. This was accomplished by a system of pulleys and gears. By varying the sizes of the pulleys, different speeds could be given to the pump whereby the oil could be fed to the reaction coil at different rates: an electric motor was the driving force: Fig. 4 shows

TABLE I—DESCRIPTION OF OILS USED IN EXPERIMENTS

Kind of oil	Source of oil	Description of oil	Color of oil	Flash test	Fire test	Begins to boil	Sp. gr.	Viscosity (Saybolt)	Cold test solid at	Amount of distillate
A	Ill. crude	Ordinary 300 oil	Nearly white	110° C.	135° C.	210° C.	0.852	38	-5° C.	
B	Ill. crude	Unpressed acid refined, neutral	Pale yellow	155° C.	175° C.	About 300°	0.873	65	10° C.	Little below 320° C.
C	Ill. crude	Unrefined heavy distillate	Dark brown			About 300°	0.880	Very waxy		Little below 330° C.
D	Pa. crude	Mixture of components from end of kerosene to heaviest distilled over in making cylinder stocks	Light brown			260° C.			Very waxy	10% below 310° C.
E	Ill. crude	Refined kerosene	Water white	70° C.		170° C.	0.820			31% up to 220° C.
F	Pa. crude	Refined kerosene	Water white	65° C.		155° C.	0.788			50% up to 220° C.
Tar	The tar produced in experiments 2708 and 2712 (see Table II)									

uents. A brass pressure-relief valve was attached to the lower end of the condenser to permit the condensed vapors and the permanent gases to escape. The condenser was a coil of 1-in. pipe immersed in a tank of water. The pressure in the cooling system described necessitated the use of a steam trap for the issuing stream of tar; this was of the ordinary floating bucket pattern, and performed its duty excellently. The hot tar was passed through a coil of pipe immersed in a tank of water to cool it before finally allowing

the general arrangement of this part of the apparatus. By means of the separating chamber H (Fig. 1), the crude mixture of reaction products was separated into two parts, and collected separately. The lighter, here called *transformation distillate*, together with whatever permanent gases were produced, flowed from the condenser K (Fig. 1), through the valve M, and the heavier parts, here called *tar*, flowed from the steam trap N, and cooling coil O. The transformation distillates were all yellow in color and when re-

distilled the first fractions were colorless; usually by about 150° C. the fractions began to be slightly yellow and by 200° very distinctly yellow.

The tars were all deep brownish red by transmitted light and they all had a dense green fluorescence, similar to that of Pennsylvania crude oil. No effort was made to ascertain the nature of the substances which imparted these characteristics to the tar.<sup>1</sup> When re-distilled, the distillates from the tar were always yellow.

<sup>1</sup> See Brooks and Bacon, THIS JOURNAL, 6 (1914), 623.



On account of the frequent stoppages by the coke deposits described further on in this report, the 1-in. pipe was removed after most of the experiments herein were performed, and a piece of 2½-in. double extra strong pipe, 12 ft. long, was substituted; its internal diameter was 1.77 in., its walls 0.55 in. thick. Only one trial was made in this, namely, No. 2750.

The various oils used in the experiments are described in Table I. All viscosity tests mentioned were made with the old style Saybolt viscosimeter. All flash and fire tests were made in the open cup.

TABLE II—RESULTS OF EXPERIMENTS

No.	Kind of oil	Rate of feed Gals. per hr.	Average pressure lbs. per sq. in.	Average temperature ° C.	Per cent yield up to 150° C.	Per cent yield up to 220° C.	Total yield to 220° Per cent	Per cent loss
A—HIGH BOILING POINT OILS								
2701	A	3.7	275	350	23.0	17.3	40.3	.....
2717	C	3.7	400	350	24.0	8.6(a)	32.6	.....
2750(b)	D	3.7	450	440	18.5	15.0	33.5	7.8
2699	A	3.7	700	340	21.4	10.4	31.8	.....
2729	D	3.7	900	360	17.7	13.4	31.1	16.8
2702	A	3.7	900	340	23.3	11.2(a)	34.5	15.7
2730	D	3.7	1000	395	27.9	14.4	42.3	15.0
2716	C	11.5	400	433	4.8	1.5(a)	6.3	.....
2715	Tar	11.5	550	430	4.5	1.7(a)	6.2	.....
2725	D	11.5	875	430	3.4	8.6	12.0	.....
2712	B	11.5	1300	430	6.7	3.8(a)	10.5	1.6
2708	A	11.5	1375	430	8.6	5.4(a)	14.0	.....
2711	B	11.5	1400	430	8.2	3.9(a)	12.1	1.9
B—NO YIELD OF LIGHT HYDROCARBONS								
2706A	A	12.25	800	355	0	0	0	.....
2706B	A	12.25	1400	360	0	0	0	.....
C—KEROSENES								
2732	F	3.7	1000	360	24.8	21.5	46.3	29.6
2736	F	3.7	775	365	22.0	33.6	55.6	15.4
2739	F	3.7	775	365	10.0	42.0	52.0	11.4
2728	E	3.7	900	360	15.7	36.1	51.8	10.2
2727	E	11.5	875	435	3.3	31.5	34.8	1.9

(a) Tar not examined for low boiling components.

(b) 2½ in. reaction coil.

Table II gives a summary of the experiments tried, together with a brief statement of the results obtained.

It will be noticed that three rates of feed were employed, and that there is a sharp distinction between the temperatures used with the two speeds of Table IIA. At the faster rate, it was found necessary greatly to increase the temperature in order to develop any "cracking." This is plainly shown by comparing Table IIB with A. Again, for some reason not clear, the larger sized pipe used in No. 2750 required the higher temperature, although the speed was set at the slower rate. It is also noticeable that the yields of low boiling point hydrocarbons and the gas loss was very much greater at the slowest speed. Neither the kind of oil nor the pressure seems to have any pronounced influence on the yield of low boiling hydrocarbons in the trials at the slower rate of feed. But at the higher rate, there seems to be a little better yield at the greater pressures. Even once-run tar when re-run yielded the same results as fresh oil run under the same conditions—compare Nos. 2715 with 2716.

In respect to the apparent large yields from the kerosenes (Table IIC), it is to be noted that the oil used in the first three cases contained before use 50 per cent boiling below 220°, while the other oil contained 31 per cent.

The percentages of yields in all cases (except those where the tar was not examined) is the sum of what was found in both the transformation distillate and the tar. The latter rarely contained anything boiling below 150°.

The figures in Table II show plainly that the time factor is a most important one, and that the yield is at least roughly proportional to the time the oil is subjected to the influence of heat and pressure, since the slower the rate of feed of the raw material, the longer the oil is in the reaction coil.

In two experiments an attempt was made to apply catalyzers, or at least to see if the substances employed would have any effect on the reactions involved. In No. 2736, one pound of highly magnesium calcium hydroxide to 50 gals. oil was used. In No. 2739 zinc oxide was similarly used. Neither increased the yield of gasoline; indeed, both appeared to decrease both that and the gas loss, the zinc oxide more so than the lime. The larger amounts of fraction 150°–220° in these two

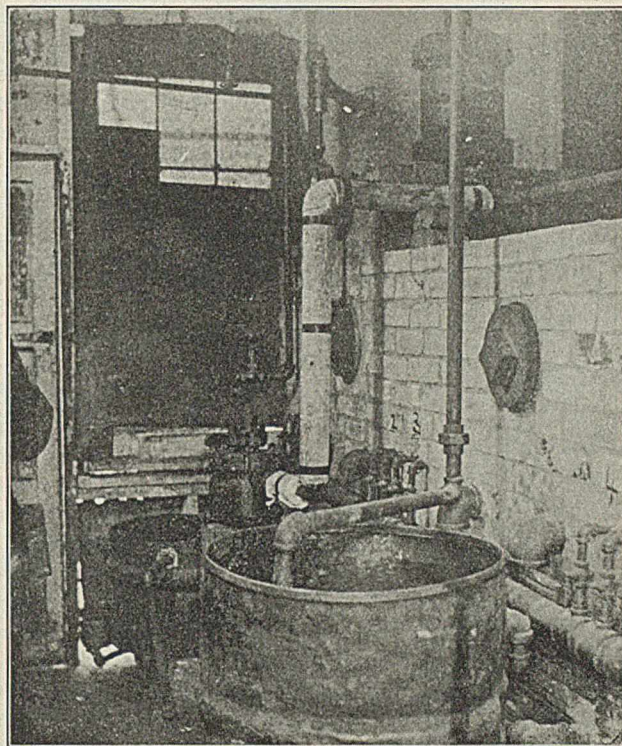


FIG. 2.—CONDENSER IN FOREGROUND, WALL OF FURNACE TO RIGHT WITH GAS SUPPLY COCKS AND LARGE ROUND LIGHTING-UP DOORS. ASBESTOS COVERED PIPE IS FOR LEADING THE HOT TAR FROM THE SEPARATING CHAMBER (NEAR TOP) TO THE STEAM TRAP

trials also indicate less cracking action, since there already was 50 per cent of this fraction present in the raw material.

A dense deposit of so-called coke formed on the inner surfaces of the pipes in the reaction coil. Because of the stoppage caused by this coke plugging up the pipes, prolonged use of the pipes was impossible. This carbon is quite hard, moderately brittle and breaks with a glossy conchoidal fracture like gilsonite or anthracite. Carbon bisulfide extracts only a very small part of it, forming a deep brownish red solution having a deep green fluorescence. That which is insoluble in carbon bisulfide is heavier in gravity than that liquid; it is insoluble in boiling aqua regia and almost incombustible when ignited on platinum foil. The aqua regia extract gives faint



reactions for iron. The carbon adheres with great tenacity to the iron of the pipes.

The carbon set free not only accumulated in the form of coke, but some seemed to be forced into combination with or into solid solution in the iron of the pipes. At any rate, whatever may be the cause of it, the iron became brittle so that when after about 15 runs an attempt was made to unscrew a fitting from one of the pipes, the pipe broke off with a crystalline fracture. But little torsion had been applied before the break took place. Shortly after that, one of the double extra strong 1-in. pipes burst during an experiment, at a time when only 400 lbs. pressure was being applied. There was no evidence that this part of the pipe had been greatly overheated and thus weakened. It did not look burnt, nor was it swelled

as though it had been soft; on the contrary, a scarcely perceptible crack about 1½ in. long opened up. The coil was always tested before each run to 2,000 lbs. pressure, cold. According to U. S. Patents 822,460 and 1,013,191, dated June 5, 1906, and January 2, 1912, respectively, issued to A. W. Machlet, iron articles are case-hardened by subjecting them to the action of light petroleum hydrocarbon vapors under heat and pressure. A similar action must have gone on in these trials, but penetrating into the iron of the pipes to a much greater depth under the influence of a very much longer time of exposure.

In several of these runs, measurements were made of yields during the run for the purpose of finding out whether the rate of production of transformation distillate was uniform throughout the run. It was found that in every case there was a distinct falling off in rate during the time of the run. This is attributed to the partial

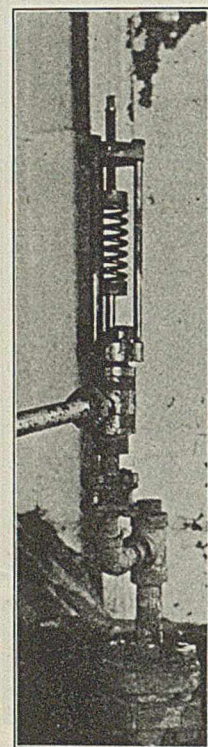


FIG. 3—PRESSURE-RELIEF VALVE

closing up of the pipe by the coke formed, causing a more rapid flow of the oil through the reaction coil and thus diminishing the time during which the oil was acted upon by the heat and pressure.

The yellow color of the transformation distillate is not removed by treatment with concentrated sulfuric acid in the usual petroleum refining process. Considerable heat is generated when these distillates are shaken with the acid. They become very dark, but after removing the acid and washing with water, the yellow color is restored. On now distilling the liquid, it passes over almost white even up to 220°.

Mercurous nitrate solution added to the yellow transformation distillate causes the formation of an abundant bright yellow precipitate; indeed with sufficient mercurous solution the whole mass becomes a yellow paste; large proportions of olefines must,

therefore, be present. Ammoniacal silver nitrate was not reduced and gave no precipitate; acetylenes are, therefore, absent. Iodine and bromine are freely absorbed from their aqueous solutions by transformation distillates; this greatly modifies their odor, but not their color.

In order to find out just how transformation distillate would act under the usual refinery process for producing ordinary gasoline, 24½ gals. were distilled with live open steam from a laboratory still of about 50 gals. total capacity, no other heat being applied. The first 39 per cent that came over was colorless and had sp. gr. 0.721 (64.6° Bé.); it left a residue of 5.2 per cent at 150° C; it was, therefore, a good gasoline. The next 12.3 per cent that came over was faint yellow: it had sp. gr. 0.761 (54.5° Bé.) and distilled between 90° and 200° C., and, except for the color, was a good naphtha. The next 17.4 per cent that came over was distinctly yellow, had sp. gr. 0.784, and distilled between 130° and 220° C.; its flash point was 36° C. The residue left in the still, amounting to 41.5 per cent (by difference) of the charge, was dark yellow, sp. gr. 0.835, and distilled between 180° and 320° C.

In another trial 17 gals. were similarly distilled.



FIG. 4—GENERAL VIEW OF HYDRAULIC PUMP (TO LEFT), ELECTRIC MOTOR (TO RIGHT) AND PULLEY, SPROCKET AND GEAR ARRANGEMENT FOR OPERATING THE PUMP SLOWLY ENOUGH

The first fraction, 50 per cent of the whole, was white, had sp. gr. 0.720 (65.0° Bé.), and distilled between 40° and 170° C. The second fraction, 25 per cent of the whole, was yellow in color, sp. gr. 0.771, and distilled between 110° and 210° C. The residue left in the still was deep yellow, sp. gr. 0.804, and distilled between 130° and 250° C.

The transformation distillate used in both cases had not been treated in any way with chemicals to decolorize or otherwise change it. These distillations showed that transformation distillate behaves perfectly normally in the usual gasoline distilling process.

Search was made for aromatic compounds in the transformation distillate by an effort to isolate the xylenes. The method employed was as follows: The fraction of boiling point 130° to 220° obtained in steam-distilling the transformation distillate was fractionated in a copper still-head still and the fractions up to 140° and 140° to 150° collected separately. The residue left in the steam still was subjected to the same process, and the corresponding fractions were mixed. Lots of 1600 cc. each, of these fractions,



were then further fractionated from a 2000 cc. round-bottomed flask provided with a glass 12-bulb pear still-head and an Anschütz normal thermometer. The fractions 135° to 145° were collected and mixed. A total of 1170 cc. were obtained originating from the 24½ gals. transformation distillate. This was again fractionated, as before, collecting this time between 138.5° and 142.5°. Of this last fraction, only 125 cc. were obtained. A little of this was treated with concentrated nitric acid, first cold, finally boiling, but it yielded no nitro compounds. Hence, no xylene is present. Since xylene is absent, it is assumed that no aromatic hydrocarbons are present.

Several distillations were made of the tars obtained in these experiments with the object in view of isolating any viscous hydrocarbons of value as lubricating oils that might be present. This was always done with live open steam, with the simultaneous application of fire heat to the bottom of the still in the manner usual in the petroleum industry. In one case, 30 gals. of tar were subjected to this treatment. It is unnecessary to go into details about these trials, since nothing of value was found. The high heat and great pressure seems not only to have broken down whatever viscous hydrocarbons were originally present, but also to have prevented the formation of others, either by balanced reactions or otherwise. The original tars were all of heavier gravity than the oils from which they were made, of good cold test, and very thin in viscosity. All the residual oils left after steam distillation were similar, but the cold test was not so good; that is to say, there was present sufficient crystallizable paraffine to render the oil more susceptible to cold. All that is said above applies equally to tars derived from light original oils—namely, 300 oil and kerosene, and to those from heavy, waxy original oils—namely, wax distillate, etc. The original crystallizable paraffine, when present, was almost totally destroyed by the heat and pressure and so were all viscous components.

Credit is due to my son, James A. Bjerregaard, for constructing and operating this apparatus. My thanks are due to the Canfield Oil Company, of Cleveland, Ohio, for permission to publish this report.

CLEVELAND, OHIO

### THE TEMPERATURE COEFFICIENT OF EXPANSION OF PETROLEUM RESIDUUMS

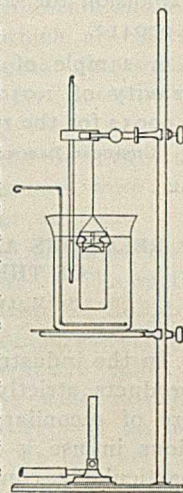
By H. ROSSBACHER

Received March 29, 1915

In the purchase of residuum oil the measurement of volume is usually made at an elevated temperature and the volume is then reduced to some standard temperature, usually 60° F. Engler<sup>1</sup> has shown that this coefficient is not a constant for all ranges of temperature but must be determined for ranges closely approximating those to which it is to be applied. Even for a defined temperature range the value will vary with the consistency of the material and the type of crude petroleum from which it is prepared. A closer attention to this value might prove of commercial advantage in many cases. With this

idea, the following description is given of an easily applied method for determining the temperature coefficient of expansion of a petroleum residuum over any desired temperature range.

**DESCRIPTION**—To consider the most complicated case, it is assumed that the sample is semi-solid at the standard temperature. When the sample is sufficiently fluid to allow the seating of the stopper at this temperature, the following operations and calculations can be somewhat simplified. The specific gravity at the standard temperature is determined in a Hubbard pycnometer.<sup>1</sup> The pycnometer is then filled with the sample, warmed sufficiently to allow the stopper to be seated, and suspended in a wire sling in a glycerine bath, the top of the stopper projecting slightly from the surface of the glycerine. A thermometer is placed in the bath with its bulb opposite the middle of the pycnometer. The bath is heated slowly, with stirring, the stopper being kept firmly seated and wiped clean as the residuum expands. When the desired temperature is reached it is kept constant until the absence of further exudation of the sample from the capillary indicates that the sample has reached the temperature of the bath. The pycnometer is then removed, wiped clean, allowed to cool and weighed.



#### CALCULATION

- Let  $a$  = Weight of pycnometer, empty.  
 $b$  = Weight of pycnometer, + water at standard temperature.  
 $c$  = Weight of pycnometer + sample at standard temperature.  
 $d$  = Weight of pycnometer + sample + water at standard temperature.  
 $e$  = Weight of pycnometer + sample at elevated temperature.  
 $f$  = Coefficient of cubical expansion of pycnometer, assumed 0.0000156 per °F. in this case.<sup>1</sup>

<sup>1</sup> "Chemiker Kalendar," Vol. II (1912), p. 89.

From values  $a$ ,  $b$  and  $c$ , calculate  $W_s$ , the weight of sample in the pycnometer at the standard temperature. The specific gravity of water at  $T_s$  may be taken as unity for the purposes of this calculation. From  $a$  and  $b$  find  $V_s$ , the volume of the pycnometer at the standard temperature. Applying  $f$ , find the volume at the elevated temperature,  $V_e$ , in terms of  $V_s$ .

$$V_e = \frac{1 + 3T_e(f)V_s}{1 + 3T_s(f)}$$

From  $a$  and  $e$  find  $W_e$ , the weight of sample in the pycnometer at  $T_e$ .  $\frac{W_e}{V_e} = W_{es}$ , weight at  $T_e$  for

volume corresponding to  $V_s$ .  $\frac{W_{es} - W_s}{W_s} = I_e$ , the loss in weight of  $V_s$  in increasing  $T_e - T_s$  degrees in temperature.

$\frac{I_e}{T_e - T_s} = m$ , coefficient of expansion in the formula

$$V_e = V_s[1 + m(T_e - T_s)]$$

Some results obtained by this method are of interest in illustrating the effect of temperature range on the coefficient.

<sup>1</sup> "Das Erdoel," Vol. 1, p. 95.

<sup>1</sup> "Dust Preventives and Road Binders," pp. 329-30.



"STANOLITE"		
SPECIFIC GRAVITY	COEFFICIENT OF EXPANSION PER °F.	
60/60° F.	60-212° F.	0.000364
1.0957	60-264° F.	0.000378
77/77° F.	77-212° F.	0.000337
1.0887	77-264° F.	0.000343

By Weiss' method of calculation<sup>1</sup> the coefficient of expansion for the range 60-77° F. on this sample is 0.000412.

A sample of Mexican residuum having a specific gravity of 1.0104 at 77/77° F. gave the coefficient 0.00032 for the range 77-160° F.

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## RELATIONS AMONG THE PHYSICAL CONSTANTS OF THE PETROLEUM DISTILLATES<sup>2</sup>

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In the industrial study of petroleum and petroleum products strictly chemical methods of identification are of secondary importance. The number of reactions in use is limited, and these processes are not particularly convenient and satisfactory. They fail to give the sort of information most needed. For instance, the sulfonation test for olefines gives the same results whether the hydrocarbons have a boiling point of 100° or 300°, and indicates little regarding the commercial use or possibilities of an oil. Likewise a liquid sulfur dioxide extraction does not aid in differentiating a gasoline from a kerosene.

The important information in the study of petroleum distillates is obtained from determinations of

the limits of experimental error no matter what device is employed to secure them.

Viscosity coefficients for crude oils and refined products are commonly determined. Many chemists measure refractive indices, though the use of this valuable method of identification is rather limited. Other physical constants such as surface tension, capillary rise and molecular weight have been determined in only a limited number of cases and their practical applications have not been given extensive consideration by petroleum technologists.

For the purpose of determining possible simple relationships, measurements were made of the following series of constants:

A—Distillation range	E—Surface tension
B—Specific gravity	F—Capillary constant
C—Refractive index	G—Molecular weight
D—Viscosity	H—Ultimate analysis

### SAMPLES AND DETERMINATIONS

As the present work deals with a comparison of constants, rather than oils, it was not considered necessary to secure an absolutely comprehensive series of samples. Representative oils from a number of different fields were obtained, and the selection was made with the view of including crude petroleum of different types.

The list includes five carefully selected samples of California crude oils, five from Oklahoma, four from Pennsylvania, two from Russia and one from Mexico. From the works of Mabery and other investigators, it is known that wide differences exist among the types of hydrocarbons found in oils from the different

TABLE I—SOURCES AND PHYSICAL CONSTANTS OF CRUDE OIL SAMPLES

No.	FIELD	DISTRICT	SAMPLED	LOCATION	STATE	COUNTY	LEASE	WELL No.	PHYSICAL CONSTANTS OF CRUDE PETROLEUMS ARRANGED IN ORDER OF THEIR SPECIFIC GRAVITIES					
									Sp. Gr.	Viscosities	Surf. Tens.	Cap. Const.		
269	Cal.	Piru	12/ 6/07	T3N, R18W	Cal.	Ventura	Union Oil Co.	15						
273	Cal.	Piru	12/ 4/07	T4N, R18W	Cal.	Ventura	Modella, 7, 19, 21, 22, 28, 29							
587	Cal.	Midway	10/ 8/10	T31S, R22E	Cal.	Kern	Manchuria, Midway	1	Sam- ple					
591	Cal.	Midway	10/18/10	T31S, R22E	Cal.	Kern	Bear Creek	3						
Head														
764	Pa.	J. S. Sloan	{9/7/11	Emlenton	Pa.	Venango	Boulder Sand: 1195 ft.	9	815	0.799	1.30	67.5	24.07	6.17
765	Pa.	Farm	{9/7/11	Emlenton	Pa.	Venango	Second Sand: 1050 ft.	3	764	0.800	1.29	67	25.12	6.44
815	Pa.	Branden	{9/21/11	Pleasantville	Pa.		First Sand: 580 ft.	11	816	0.808	1.32	68.5	24.81	6.30
816	Pa.	Farm	{9/21/11	Pleasantville	Pa.		Second Sand: 650 ft.	6	765	0.816	1.40	73	25.44	6.38
1280	Okla.	Collinsville	May/13	T22N, R15E	Okla.		Claremore Pool	1	1336	0.825	1.44	75	24.78	6.15
1281	Okla.	Collinsville	May/13	T22N, R15E	Okla.		Sellers Lease, Claremore Pool	1	1339	0.838	1.71	89	26.19	6.40
1336	Okla.	Collinsville	5/24/13	T14N, R18E	Okla.		G. Callahan Lease, Muskogee Pool	3	1280	0.846	1.70	88.5	25.03	6.06
1339	Okla.	Collinsville	5/24/13	T14N, R18E	Okla.		Stevens Lease, Muskogee Pool	1	Head	0.865	2.77	144	26.59	6.30
									1281	0.870	3.35	174	26.59	6.26
									269	0.876	2.31	120	25.70	6.00
									R. R.	0.876	2.61	136	27.55	6.43
									R. M.	0.878	3.22	167.5	27.82	6.49
									273	0.891	2.11	110	26.08	5.99
									S. M.	0.901	4.92	256	26.13	5.94

S. Maria

R. R. Russian—Provided by the kindness of C. I. Robinson of the Standard Oil Co. of N. J.

R. M. Russian—Provided by the kindness of Prof. C. F. Mabery, The Case School, Cleveland, O.

Mex. Mexican—Provided by the kindness of Dr. D. T. Day, U. S. Bureau of Mines, Washington, D. C.

various physical constants. In view of the convenience with which they can be measured, and the wide utility of these constants, it has been thought desirable to study relations existing among them. The work described in this communication deals with a comprehensive series of measurements and furnishes data which are helpful in indicating how the results of various experiments may be interpreted.

The two processes most universally employed and best understood are distillation and measurement of specific gravity. Distillation figures are more or less relative, depending upon the method used.<sup>3</sup> Gravity measurements are absolute and agree within

fields. Table I gives the sources and physical constants of the oils studied.

VISCOSITIES of the crude oils were measured in the Standard Engler Viscosimeter at a temperature of 20° C. Results are expressed in Engler degrees, which represent ratios of the rates of flow of the oil and water. When expressed in this manner the results indicate specific viscosity. This is in contrast to empirical refinery practice using the Saybolt machine, which shows the time required for a given quantity of oil to pass a given orifice and omits comparison with the standard liquid, water.

The conversion factors from Engler<sup>1</sup> to Redwood and Saybolt are:

$$T_R = 192.2K \left( 1 + \sqrt{1 + \frac{0.01624}{K^2}} \right)$$

<sup>1</sup> Chem. Rev. *Fell-Harz. Ind.*, 19 (30, 33), (44 to 49).

<sup>1</sup> John Morris Weiss, "The Coefficient of Expansion of Tar," *J. Frank. Inst.*, Sept., 1911.

<sup>2</sup> Published with the permission of the Director of the Bureau of Mines.

<sup>3</sup> See Rittman and Dean, *THIS JOURNAL*, 7 (1915), 185.



$$T_s = 228.7K \left( 1 + \sqrt{1 + \frac{0.01309}{K^2}} \right)$$

$$K = 0.08019E - \frac{0.07013}{E}$$

The values calculated from the formulas agree with those actually observed within 4 per cent by Redwood and 2 per cent by Saybolt. By dividing the readings for Redwood and Saybolt instruments by the respective readings for water, comparative accuracy for these instruments is increased.

DISTILLATIONS were conducted according to a method which was designed to give a high degree of separation. In accordance with the results of some recent investigations conducted under the direction of one of the authors,<sup>1</sup> a Hempel column of definite height was provisionally adopted as standard for this set of experiments. The degree of efficiency attained was approximately that of the standard creosote flask<sup>2</sup> of the Forestry Division of the Department of Agriculture. The flasks here used were of the following dimensions:

Initial charge 400 cc. Height from bulb to outlet 6 in.  
Capacity of bulb 500 cc. Height from outlet to top 1 1/2 in.  
Cuts at 50° intervals 100 to 300° C. Diameter of neck of bulb 5/8 in.  
Fractionating column: 5 in. aluminum beads (between 1/4 and 3/8 in.)

The results of distillation, shown in Table II, need no discussion in the present connection. The Kern River and Mexican Oils were emulsified and frothed badly, and to overcome this difficulty it was necessary to apply heat to the neck of the flask, which obviously altered the effect of the fractionating column.

a cut is selected, it will be noted that densities of Pennsylvania products are least and those of California and Russian greatest. This is in accord with observations of other investigators and is a striking evidence of the difference among the hydrocarbons contained in petroleum from different fields. Pennsylvania oils contain paraffins which have a low gravity for a given boiling point: California and Russian oils contain cyclic compounds which are heavier for the same boiling point: Oklahoma oils, containing both types of hydrocarbons, give intermediate gravity values.

REFRACTIVE INDICES were measured by means of a Pulfrich Refractometer. Determinations were made at room temperature, maintained at 20° C.

The use of refractive index as a means of identification of oils is to be recommended. The method is simple, rapid, and only a few drops of liquid are necessary for a determination. Comparatively little has been done in the use of refractive index by petroleum technologists, despite its wide utility in identifying essential oils. The property is an additive one and within certain limits we can assign to each atom in the molecule a certain share in the refractive index of the molecule.

The above property is emphasized by the present experiments. The values increase in the ascending order with increase of specific gravity of a series of oils: this is clearly shown when the oil is graphed against specific gravity and refractive index.

TABLE II—RESULTS OF FRACTIONAL DISTILLATIONS OF PETROLEUM OILS AND CONSTANTS OF VARIOUS DISTILLATION CUTS

Source Sample	Cal. 269	Cal. 273	Cal. 587	Cal. 591	Cal. S. M.	Pa. 764	Pa. 765	Pa. 815	Pa. 816	Okla. 1280	Okla. 1281	Okla. 1336	Okla. 1339	Okla. Heald	R. R.	Russian R. M.	Mexican	
VOLUME—PERCENTAGES																		
To 100°	8.00	5.25	0.38	...	6.75	5.19	6.25	6.25	8.25	3.25	0.31	8.38	5.50	5.00	0.62	1.12	...	
100-150°	10.50	15.50	0.50	...	13.25	7.38	13.75	6.63	14.25	14.25	3.38	12.50	12.25	8.62	11.13	7.38	1.12	
150-200°	8.25	10.25	1.50	...	8.62	6.06	11.50	6.00	12.75	10.38	10.75	11.12	9.50	7.38	11.50	8.62	2.50	
200-250°	11.00	12.63	5.25	...	11.12	6.12	11.50	5.25	11.75	13.88	14.12	11.12	11.75	10.25	13.75	12.75	8.25	
250-300°	11.25	12.00	16.00	...	10.63	6.19	12.50	5.75	11.75	14.88	16.75	12.63	15.00	17.00	15.25	15.62	25.75	
SPECIFIC GRAVITIES																		
To 100°	0.688	0.706	...	...	0.706	0.686	0.682	0.671	0.686	0.705	...	0.680	0.689	0.690	...	0.733	...	
100-150°	0.756	0.762	...	...	0.762	0.736	0.748	0.737	0.740	0.746	...	0.757	0.749	0.752	0.754	0.767	0.759	
150-200°	0.792	0.805	0.820	...	0.826	0.806	0.766	0.780	0.767	0.771	0.781	0.785	0.783	0.785	0.791	0.804	0.806	
200-250°	0.825	0.851	0.858	...	0.860	0.846	0.789	0.799	0.792	0.793	0.814	0.815	0.809	0.812	0.818	0.836	0.836	
250-300°	0.855	0.891	0.887	...	0.890	0.878	0.812	0.818	0.815	0.813	0.839	0.839	0.831	0.836	0.839	0.861	0.861	
INDICES OF REFRACTION																		
To 100°	1.386	1.390	1.423	...	1.392	1.385	1.385	1.375	1.386	1.389	1.409	1.385	1.387	1.388	1.401	1.403	...	
100-150°	1.418	1.419	1.434	...	1.420	1.407	1.416	1.408	1.410	1.413	1.419	1.416	1.417	1.418	1.421	1.423	1.419	
150-200°	1.436	1.440	1.445	...	1.448	1.444	1.425	1.430	1.426	1.427	1.431	1.435	1.432	1.434	1.435	1.439	1.441	
200-250°	1.455	1.465	1.465	...	1.465	1.437	1.443	1.438	1.439	1.449	1.450	1.448	1.448	1.451	1.451	1.457	1.457	
250-300°	1.472	1.493	1.484	...	1.484	1.449	1.452	1.449	1.449	1.464	1.464	1.459	1.461	1.465	1.472	1.474	1.481	
SURFACE TENSIONS																		
To 100°	19.54	18.92	...	...	20.78	18.81	18.87	19.11	19.53	19.99	...	19.85	18.92	19.71	...	21.19	...	
100-150°	22.12	22.33	...	...	22.47	20.95	21.87	21.67	20.98	22.05	...	22.69	22.09	21.53	22.34	22.75	22.80	
150-200°	22.70	24.55	25.25	...	25.36	25.31	23.29	24.00	23.75	22.64	24.25	24.35	24.07	22.91	23.98	24.85	24.93	
200-250°	23.47	26.43	28.62	...	27.22	26.28	25.04	25.29	25.42	23.67	26.13	26.12	25.61	23.91	24.99	26.50	26.71	
250-300°	23.81	28.18	29.51	...	28.03	28.04	26.47	26.84	26.80	24.48	27.48	27.37	27.02	24.45	26.01	27.15	28.01	
CAPILLARY CONSTANTS OR SPECIFIC COHESIONS																		
To 100°	5.84	5.50	...	...	6.04	5.64	5.69	5.86	5.84	5.82	...	6.00	5.64	5.86	...	5.93	...	
100-150°	6.00	6.01	...	...	6.06	5.84	6.13	6.03	5.81	6.06	6.15	6.05	5.88	6.07	6.08	6.08	...	
150-200°	5.87	6.25	6.30	...	6.29	6.44	6.23	6.46	6.35	6.02	6.32	6.36	6.31	5.99	6.21	6.34	6.34	
200-250°	5.82	6.36	6.83	...	6.48	6.36	6.51	6.61	6.58	6.12	6.57	6.56	6.49	6.03	6.26	6.49	6.55	
250-300°	5.71	6.47	6.81	...	6.45	6.54	6.68	6.79	6.73	6.16	6.71	6.68	6.66	5.99	6.34	6.46	6.67	
CRYSCOPIC MOLECULAR WEIGHTS																		
150-200°	133.3	125.8	131.4	...	142.9	125.9	137.6	121.7	139.8	130.3	132.2	138.3	130.6	130.7	127.8	127.6	119.1	
200-250°	166.7	152.7	151.5	...	179.2	140.0	164.5	159.4	167.3	149.0	158.4	170.1	165.9	153.9	159.8	146.4	140.7	
250-300°	191.6	173.2	181.8	...	193.9	179.6	202.6	184.2	205.8	180.9	195.7	212.3	214.3	190.6	192.5	171.3	180.5	

SPECIFIC GRAVITY determinations were made at 15° C. by the use of a special small Westphal Balance with a plummet of 1 cc. displacement.

A study of the specific gravities shown in Table II brings out one fact, which, though well known, is worthy of comment. If for any given temperature

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Dean and Bateman, *Bull.* 112, Forest Service of the U. S. Department of Agriculture.

SURFACE TENSION—Up to the time of beginning this research but little attention has been given to the determination of surface tension and capillary constants of petroleum and its products. This phenomenon is important to the geologist<sup>1</sup> as well as to the chemist.

Surface tension is a direct result of unbalanced inter-molecular forces at the boundary between the liquid and gas phase, and is manifested by the apparent

<sup>1</sup> *Bull. Am. Inst. Min. Eng.*, 1914, p. 2365.



formation of an elastic skin. The familiar experiment of floating a greasy steel needle on water is the simplest and most impressive way of demonstrating the existence of a tension along the surface of a liquid. Two common resulting effects are the tendency of all liquids to form spherical drops whenever possible and the rise in tubes of all liquids which are able to wet the material of which the tube is composed.

Surface tension measurements were made by the use of the Morgan<sup>1</sup> drop weight apparatus. The method evolved by Morgan<sup>2</sup> and his co-workers is simple, rapid and highly accurate. It has in addition the advantage of being particularly adapted to liquids which are mixtures of several constituents of different volatilities—whereas the capillary rise method fails utterly under these conditions.

The method gives directly and accurately the weight of the drop of the liquid. From this the value of surface tension can be calculated by the following relation:<sup>3</sup>

$\gamma$  = Surface Tension (dynes per cm.) = KW  
where K = The constant for the apparatus used and W = Weight of a drop in milligrams.

It will be noted from the results shown in Table II that surface tension is apparently an additive property as far as the distillation cuts of any one oil are concerned, but that additivity vanishes when the relations of different petroleum products are considered. An explanation is not difficult to find, for it has been demonstrated by Morgan<sup>4</sup> that small additions of certain substances influence greatly the surface tension of a solvent. Thus in the presence of 1 per cent of amyl alcohol the surface tension of water decreases 48 per cent, while 1 per cent of phenol<sup>5</sup> in water produces a 17 per cent depression of surface tension.

All this indicates the possible occurrence in crude petroleum of small quantities of substances which have a large influence on surface tension and which are distributed throughout the various cuts of a distillation. On this basis it is easy to understand why the apparent additive nature of this constant vanishes when relations of different original oils are considered. With pure hydrocarbons, of homologous series, surface tension is an additive property.

That phenols, cresols, mercaptans and other sulfur and oxygen compounds exist in crude petroleum has been clearly shown by the work of Markownikoff and Ogloblin,<sup>6</sup> Pebal and Freund,<sup>7</sup> Hall,<sup>8</sup> Thiele,<sup>9</sup> and Mabery.<sup>10</sup>

The above mentioned observations on surface tension have indicated interesting possibilities for research. It is hoped that in the near future investigations along these lines may be conducted and knowledge of more specific character obtained.

<sup>1</sup> J. Am. Chem. Soc., **32** (1911), 349.

<sup>2</sup> Z. physik. Chem., **1915**; Jour. Am. Chem. Soc., **1911-1915** (résumé).

<sup>3</sup> J. Am. Chem. Soc., **33** (1911), 658.

<sup>4</sup> Ibid., **35** (1913), 1860.

<sup>5</sup> Results on phenol not published—Morgan and Egloff.

<sup>6</sup> Ber., **16** (1883), 1873; Chem. Ztg., **1881**, p. 609.

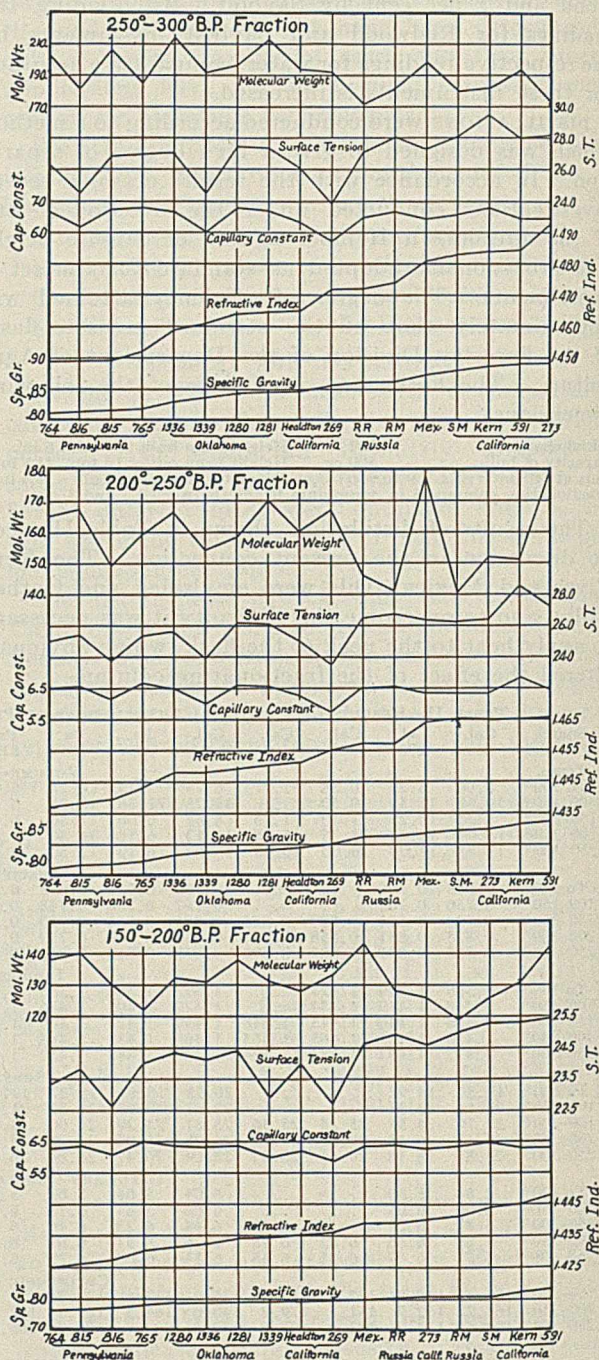
<sup>7</sup> Liebig's Ann., **115** (1860), 19.

<sup>8</sup> J. Soc. Chem. Ind., **1907**, p. 1223.

<sup>9</sup> Chem. Ztg., **175** (1901), 433.

<sup>10</sup> Proc. Am. Acad., **36** (1901), 255; **40** (1904), 348.

CAPILLARY CONSTANT OR SPECIFIC COHESION—The capillary constant is a derived function of surface tension and specific gravity. It has been largely used in the past and many values in the literature are expressed in terms of this constant. For purposes of comparison the surface tension values obtained by the drop weight method have been converted into



RELATIONS AMONG PHYSICAL CONSTANTS OF PETROLEUM DISTILLATES

capillary constants. Transformations were made by the use of the following formula:<sup>1</sup>

$$a^2 = \frac{2\gamma}{9.8d}$$

$a^2$  = Capillary constant     $\gamma$  = Surface Tension  
 $d$  = Specific Gravity

<sup>1</sup> Morgan, "Principles of Physical Chemistry," **1914**, p. 100.



Values of  $d$  for  $20^\circ$  were calculated (see Table II) from those measured at  $15^\circ$  by conversion figures given by Markownikoff-Ogloblin<sup>1</sup> for American oils, and by Mendelejeff<sup>2</sup> for Russian.

CRYOSCOPIC "MOLECULAR WEIGHT"—The average "molecular weights" of the  $50^\circ$  cuts between  $150^\circ$  and  $300^\circ$  were determined by the cryoscopic method, using benzol as a solvent. No measurements were made on fractions boiling below  $150^\circ$  because of the possible presence of benzol in these distillates.

The concentration of solute was kept practically constant and to eliminate possible variations due to association so as to make all determinations comparable. The values of solute were between 0.12 to 0.15 of a gm., whereas the solvent weighed from 13 to 18 gms. The temperature readings were made with a Reichsanstalt certified Beckmann thermometer. The solvent used was Kahlbaum's thiophen-free, recrystallized benzol. The benzol was further purified by

temperature of a cut obtained on distilling a crude oil is lower than the average indicated by the given limits.

ULTIMATE ANALYSIS—Eight samples of distillates of b. p.  $200\text{--}250^\circ$  were analyzed for the carbon and hydrogen content. The results appear in Table III

TABLE III—ULTIMATE ANALYSES OF CERTAIN  $200\text{--}250^\circ$  B. P. FRACTIONS

Sample No.	269	1281	816	Kern S. M.	Mex. R. M.	R. R.	R. M.
Per cent hydrogen...	13.62	13.90	14.57	13.40	13.07	13.34	13.42 13.31
Per cent carbon....	86.36	85.37	84.99	86.27	85.42	85.00	86.34 84.49

and indicate for a number of American oils, practically pure hydrocarbons with small amounts of oxygen, nitrogen or sulfur compounds, whereas one Russian and the Mexican oil show a relatively high per cent of oxygen, nitrogen or sulfur compounds, which might bear out the statement as to small amounts of certain extraneous substances greatly changing the surface tensions of pure hydrocarbons.

The relations existing among the various sets

TABLE IV—PHYSICAL CONSTANTS OF DISTILLATION CUTS IN ORDER OF SPECIFIC GRAVITIES

SAMPLE	FRACTION B. P. UP TO $100^\circ$ C.																
	815	1336	765	764	816	269	1339	Heald	1280	1281	273	S. M.	R. R.	R. M.	587	591	Mex.
Sp. gr.....	0.670	0.680	0.682	0.686	0.686	0.688	0.689	0.690	0.705	..	0.706	0.706	..	0.733	..	..	..
Ref. ind.....	1.375	1.385	1.385	1.385	1.386	1.386	1.387	1.388	1.398	..	1.390	1.392	1.401	1.403	1.423	..	..
Sur. ten.....	19.11	19.85	18.87	18.81	19.53	19.54	18.92	19.71	19.99	..	18.92	20.78	..	21.19	..	..	..
Cap. const.....	5.86	6.00	5.69	5.64	5.84	5.84	5.64	5.86	5.82	..	5.50	6.04	..	5.93	..	..	..
SAMPLE	FRACTION B. P. BETWEEN $100^\circ$ AND $150^\circ$																
	764	815	816	1280	765	1336	1339	Heald	269	1281	Mex.	273	S. M.	R. R.	R. M.	Kern	591
Sp. gr.....	0.736	0.737	0.740	0.746	0.748	0.749	0.752	0.754	0.756	0.757	0.759	0.762	0.762	0.767	0.769	..	..
Ref. ind.....	1.407	1.408	1.410	1.413	1.416	1.416	1.416	1.418	1.418	1.419	1.419	1.419	1.420	1.421	1.423	1.434	..
Sur. ten.....	21.95	21.67	20.98	22.05	21.87	22.09	21.53	22.34	22.12	22.69	..	22.33	22.47	22.75	22.80	..	..
Cap. const.....	5.84	6.03	5.81	6.06	6.13	6.05	5.88	6.07	6.00	6.15	..	6.01	6.06	6.08	6.08	..	..
SAMPLE	FRACTION B. P. BETWEEN $150^\circ$ AND $200^\circ$																
	764	815	816	765	1280	1336	1281	1339	Heald	269	Mex.	R. R.	273	R. M.	S. M.	Kern	591
Sp. gr.....	0.766	0.767	0.771	0.780	0.781	0.783	0.785	0.785	0.791	0.792	0.798	0.804	0.805	0.806	0.806	0.820	0.826
Ref. ind.....	1.425	1.426	1.427	1.430	1.431	1.432	1.434	1.434	1.435	1.436	1.439	1.439	1.440	1.441	1.444	1.445	1.448
Sur. ten.....	23.29	23.75	22.64	24.00	24.25	24.07	24.35	22.91	23.98	22.70	24.62	24.85	24.55	24.93	25.31	25.25	25.36
Cap. const.....	6.23	6.35	6.02	6.46	6.32	6.31	6.36	5.99	6.21	5.87	6.33	6.34	6.25	6.34	6.44	6.30	6.29
Mol. wt.....	138	140	130	122	132	131	138	131	128	133	143	128	126	119	126	131	143
SAMPLE	FRACTION B. P. BETWEEN $200^\circ$ AND $250^\circ$																
	764	815	816	765	1336	1339	1280	1281	Heald	269	R. R.	R. M.	Mex.	S. M.	Kern	591	
Sp. gr.....	0.789	0.792	0.793	0.799	0.809	0.812	0.814	0.815	0.818	0.825	0.836	0.836	0.843	0.846	0.851	0.858	0.860
Ref. ind.....	1.437	1.438	1.439	1.443	1.448	1.448	1.449	1.450	1.451	1.455	1.457	1.457	1.464	1.465	1.465	1.465	1.465
Sur. ten.....	25.04	25.42	23.67	25.29	25.61	23.91	26.13	26.12	24.00	23.47	26.50	26.71	26.36	26.28	26.43	28.62	27.22
Cap. const.....	6.51	6.58	6.12	6.61	6.49	6.03	6.57	6.56	6.26	5.82	6.49	6.55	6.39	6.36	6.36	6.83	6.48
Mol. wt.....	165	167	149	159	166	154	158	170	160	167	146	141	178	140	152	151	179
SAMPLE	FRACTION B. P. BETWEEN $250^\circ$ AND $300^\circ$																
	764	816	815	765	1336	1339	1280	1281	Heald	269	R. R.	R. M.	Mex.	S. M.	Kern	591	273
Sp. gr.....	0.812	0.813	0.815	0.818	0.831	0.836	0.839	0.813	0.839	0.855	0.861	0.861	0.871	0.878	0.887	0.890	0.891
Ref. ind.....	1.449	1.449	1.449	1.452	1.459	1.461	1.464	1.464	1.465	1.472	1.472	1.474	1.481	1.483	1.484	1.484	1.493
Sur. ten.....	26.47	24.48	26.80	26.84	27.02	24.45	27.48	27.37	26.01	23.81	27.15	28.01	27.26	28.04	29.51	28.03	28.18
Cap. const.....	6.68	6.16	6.73	6.79	6.66	5.99	6.71	6.68	6.34	5.71	6.46	6.67	6.41	6.54	6.81	6.45	6.47
Mol. wt.....	203	181	206	184	214	191	196	212	193	192	171	181	198	180	182	194	173

the method advocated by Richards<sup>3</sup> and Shipley for freezing point in thermometry.

Every experimental precaution was taken to eliminate errors due to impurity of solvent, weighing vessels and thermometer. The average "molecular weights" as determined are given in Table II.

It appeared from these experiments that "molecular weights" did not exhibit an agreement with the values for specific gravity and refractive index. Neither was there any agreement between "molecular weights" and surface tension or capillary constant.

It also appeared that "molecular weights" were lower than would be indicated from calculations concerning hydrocarbons boiling between the given temperature limits. This discrepancy is probably due to the fact that the actual average boiling tem-

perature of a cut obtained on distilling a crude oil is lower than the average indicated by the given limits. Table IV represents cuts boiling up to  $100^\circ$ , from  $100\text{--}150^\circ$ , from  $150\text{--}200^\circ$ , from  $200\text{--}250^\circ$ , and from  $250\text{--}300^\circ$ . Table V represents data on combined cuts up to  $150^\circ$ , generally classed by petroleum technologists as "naphtha," and combined cuts from  $150\text{--}300^\circ$ , generally classed as "kerosene."

Comparisons are best made by the use of the accompanying graphs plotted from the values for the last three series in Table IV. These are representative of the results of all the other tables and were selected because they include the most comprehensive lists of constants.

The graphs are plotted using as abscissas equidistant points, each representing a different oil. The oils are arranged in such order as to give an ascending curve for specific gravities. An inspection of the graphs shows that the only constant bearing any clear-cut relation to specific gravity is refractive index.

<sup>1</sup> Ber., 16, 1873.

<sup>2</sup> Rakusin, *Untersuch. d. Erdols.*

<sup>3</sup> *J. Am. Chem. Soc.*, 36 (1914), 1825.



The curve for surface tension is decidedly irregular but shows a tendency to slope upwards. This indicates that among petroleum hydrocarbons surface tension varies in the same direction as specific gravity. This constant is, however, so strongly affected by small variations in chemical composition that it is at present of little value as a means of identification. It is hoped, however, that later these irregularities may be understood well enough to furnish scientific as well as useful industrial information.

Capillary constant curves show the same irregularities as those of surface tension but lack the slope upward. This is to be expected when the method of derivation of this constant is considered.

In considering the "molecular-weight" graph, it appears that the agreement of this constant with

V—Cryoscopic "molecular weights," as measured by the cryoscopic method with benzene as a solvent, are of questionable value in the study of mixtures of petroleum products.

The experimental work connected with the determinations reported in this paper was carried out in the laboratories of the Departments of Physical Chemistry and Industrial Chemistry of Columbia University, New York.

CHEMICAL SECTION OF PETROLEUM DIVISION  
U. S. BUREAU OF MINES, PITTSBURGH

### THE SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME AND ITS DETERMINATION BY A NEW SOLUTION METHOD

By FRANK GOTTSCH  
Received April 21, 1915

The following methods for the chemical analysis of rubber goods are those in use at Mt. Prospect Laboratory, Department of Water Supply, Gas and Electricity, City of New York. These methods contain certain matter original with the author, under the headings of "MINERAL FILLERS," "FOREIGN ALCOHOLIC POTASH EXTRACT," "VULCANIZED RUBBER GUM BY WEIGHT," and "VULCANIZED RUBBER GUM BY VOLUME." The method for "FREE SULFUR" is novel in the application of a well-known method for total sulfur to the free sulfur determination.

#### METHODS OF TEST

**SAMPLES**—Samples shall be taken representative of the lots to be tested.

**BLANKS**—Blanks shall be run and deductions made according to the lots of reagents.

**CHECKS**—In the event of any determination not falling within the limits given in the specifications, a check test shall be made before the report is sent out.

**PREPARATION OF SOFT RUBBER**—Prepare a sample of not less than 25 grams, taking pieces from various parts of the original sample. The backing of fire hose shall be buffed off before grinding; in all other hose, separate samples of tube and cover shall be made, without removing the backing or friction compound. Other rubber goods built up with friction fabric shall have the rubber layers ground up without removal of the adhering rubber friction.

**GRINDING**—The sample shall be cut into small pieces and then run through the grinder, taking for analysis only such material as will pass a standard 20 mesh sieve. Care must be taken to see that the grinder does not become appreciably warm during the grinding. If the nature of the material is such that it gums together so that it will not pass through the sieve, as would be the case with undervulcanized samples, it will be sufficient to pass the material through the grinder twice and accept all the material for the final sample. Crude rubber shall be cut with scissors.

Pass a strong magnet through the sample to remove any metal from the grinders, mix thoroughly, and put in tightly stoppered bottles. Do not expose to sunlight or heat.

**HARD RUBBER**—Samples of this material shall be prepared for analysis by rasping.

**REAGENTS**—Acetone shall be distilled not more than 10 days before use over anhydrous potassium carbonate, using the fraction 56 to 57° C.

Alcoholic potash shall be of normal strength, made by dissolving the required amount of potassium hydroxide in absolute

TABLE V—PHYSICAL CONSTANTS OF "NAPHTHA" AND "KEROSENE" CUTS OF OILS STUDIED

NAPHTHA—B. P. UP TO 150° C.					KEROSENE—B. P. 150° TO 300°				
Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.	Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.
815	0.706	1.392	19.96	5.82	815	0.789	1.437	24.73	6.44
764	0.716	1.398	20.54	5.88	764	0.790	1.438	25.07	6.50
816	0.722	1.400	20.02	5.69	816	0.792	1.439	23.96	6.20
1336	0.726	1.402	20.52	5.79	765	0.795	1.440	24.66	6.43
765	0.731	1.405	19.34	5.57	1336	0.808	1.445	25.59	6.49
269	0.733	1.406	21.12	5.92	1281	0.811	1.448	26.80	6.66
Heald	0.734	1.406	20.38	5.69	1339	0.814	1.449	23.91	6.02
1339	0.736	1.407	19.41	5.41	1280	0.815	1.451	25.04	6.30
1280	0.741	1.410	20.28	5.61	269	0.820	1.452	23.18	5.77
S. M.	0.744	1.410	21.34	5.87	Heald	0.824	1.454	25.27	6.28
273	0.750	1.412	20.74	5.67	R. R.	0.836	1.458	26.34	6.45
R. M.	0.765	1.418	22.37	5.99	R. M.	0.841	1.459	26.57	6.46
					273	0.842	1.463	25.50	6.20
					S. M.	0.849	1.466	26.40	6.37
					Mex.	0.861	1.475	26.96	6.40
					Kern	0.878	1.476	27.79	6.48
					591	0.878	1.476	26.87	6.26

specific gravity, though theoretically to be expected, is conspicuous by its absence. No satisfactory explanation appears except that there is some inherent error in the method here employed for the determination of molecular weights. Present experience indicates that the measurement of this constant by the cryoscopic method with benzol as a solvent is of doubtful value in the identification of petroleum distillates. The experimental values are recorded with a full knowledge of their being "so-called Molecular Weights."

#### CONCLUSIONS

I—The present series of experiments has tended to justify the methods of identification (distillation, specific gravity and refractive index) usually employed in petroleum testing laboratories.

II—Volatility and specific gravity are the two most important constants and a knowledge of these two is generally sufficient for the identification of an oil.

III—Refractive indices vary in the same direction as specific gravities. When only small quantities of distillates are available, determinations of the former are more convenient than measurements of specific gravities.

IV—Surface tension is a constant not yet of value. This is on account of our lack of knowledge regarding variations caused by the probable presence of small quantities of certain substances in crude petroleum. Surface tensions in general seem to increase with specific gravity when relations among petroleum hydrocarbons are considered.



alcohol the day before use, and allowing to settle. Only the clear solution shall be used.

*Barium chloride solution* shall be made by dissolving 100 grams of barium chloride in one liter of distilled water, and adding two or three drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness, the solution shall be heated on the steam bath over night, and filtered through S. & S. 589 blue-ribbon filter paper.

*Turpentine* shall be redistilled.

*All reagents* shall be of C. P. quality.

#### ANALYSIS

**ACETONE EXTRACT**—Place a two gram sample, which has been ground not more than 24 hours before, in an acetone extracted paper thimble, and insert in a glass syphon cup (E. & A. 1913, No. 2846) under a condenser (E. & A. 1913, No. 2848). Dry and weigh, by means of a wire loop, a clean 8 in.  $\times$  1 $\frac{1}{4}$  in. test tube weighing between 20 and 40 grams, pour in 50 cc. acetone, connect the apparatus, and extract continuously for 7 hours in such a manner that the drops of condensed solvent fall directly on to the ground rubber, and the syphon cup fills between 2 $\frac{1}{2}$  and 3 $\frac{1}{2}$  minutes, that the discharge of the syphon cup does not appreciably interrupt the boiling, that the condensed solvent filters rapidly through the paper thimble, and that no fine particles of rubber or fillers are carried over. If the solution in the cup is colored after seven hours' extraction, the extraction shall be continued for four hours the next day. Evaporate off the acetone from the tube in a slanting position over live steam, wipe off the outside with a clean linen cloth, and dry to constant weight in the water oven at 95 to 100° C., or until the weight increases, cooling in a desiccator. Calculate and record as "total acetone extract."

**FREE SULFUR**—Entirely transfer the residue from the tube to a 60 cc. iron or nickel crucible (E. & A. 1913, No. 2366) by acetone, chloroform, or benzol, evaporate off the solvents on the steam bath and add six grams of potassium carbonate and four grams of sodium peroxide. Mix by rotating the crucible, cover, heat at a low temperature over an asbestos shield to avoid sulfur fumes, until the mixture fuses, then bring to quiet fusion for 15 to 20 minutes. Avoid rapid heating and explosions. Rotate the melt while solidifying. When cool, put the crucible and cover into a casserole containing 200 cc. of water, add 5 to 10 cc. of bromine water, and boil until the melt is dissolved. Allow to settle, decant, filter and wash through a thick filter with hot water. Cool, acidify the filtrate with dilute hydrochloric acid, using Congo red paper, make up the volume to 400 cc., and precipitate boiling with 10 cc. of a 10 per cent solution of barium chloride, keeping the beaker covered with a watch glass. Allow the precipitate to stand over night, filter on an asbestos mat in a Gooch crucible, wash with hot water, ignite and weigh, cooling in a desiccator. Calculate to sulfur (factor 0.1372), and record as "free sulfur."

**ORGANIC ACETONE EXTRACT**—When waxy hydrocarbons are not to be determined, subtract the percentage of free sulfur from the percentage of total acetone extract above, and record the difference as "organic acetone extract."

**MINERAL FILLERS**—Extract a one gram sample as under "acetone extract" above for 4 hours and dry the rubber in the water oven at 95 to 100° C. until the odor of acetone is gone. Transfer the sample to a 100 cc. beaker, burn the thimble to ash, and add the residue to the beaker. Add 50 cc. of clear molten salol, and heat the beaker on the hot plate at a temperature of not less than 120° nor more than 150° C., stirring occasionally until the rubber is apparently dissolved. After settling a few minutes, carefully transfer the liquid to a 200 cc. beaker and examine the residue in the bottom of the smaller beaker for particles of undissolved rubber. If found, more salol is added and solution completed. Stir two cc. of a 1 per

cent solution of soluble cotton in amyl acetate into the united warm liquids in the 200 cc. beaker, cool and add redistilled turpentine until a good "flock" has formed, adding at least 75 cc. of turpentine with constant stirring. Allow the liquid to stand until the flock has settled. The supernatant liquid is decanted and filtered by suction through an alundum crucible (Norton R. A. 84—B. P. 5204) placed in the Spencer holder (E. & A. 1913, No. 2384). Wash the flock by decantation with turpentine, filtering the latter, transfer the whole to the crucible, then dissolve carefully in a few cc. of acetone, and wash the fillers with acetone, being careful not to allow the fillers to cover up the sides of the crucible and so cause clogging. Wash thoroughly all beakers and crucible with acetone, using an acetone extracted policeman. Dry to constant weight at 105° to 110° C., cooling in a desiccator. Evaporate all the filtrates and washings, transfer to a weighed porcelain dish, burn off the organic matter, cool in a desiccator and weigh. Add this weight found to the fillers in the crucible, and calculate and record as "mineral fillers."

**TOTAL SULFUR**—Mix a five-tenths (0.5) gram sample with six (6) grams of potassium carbonate and four (4) grams of sodium peroxide and proceed exactly as under "free sulfur." Calculate the results in the same manner and record as "total sulfur."

**FOREIGN ALCOHOLIC POTASH EXTRACT**—When the presence of tar, pitch or asphalt is not indicated, spread out the rubber residue from the acetone extraction and dry in the water oven at 95° to 100° C., until the odor of acetone is no longer apparent. Transfer to a 100 cc. pressure flask (E. & A. 1913, No. 1064), fitted with washers previously extracted with alcoholic potash. Add 50 cc. of alcoholic potash, stopper and heat in an air oven kept between 105° and 110° C. for four hours. Cool the flask, filter and wash the residue with hot absolute alcohol until the washings are no longer colored. Make the filtrate strongly acid with concentrated hydrochloric acid to precipitate potassium chloride, allow to settle, filter and wash with hot chloroform into a small casserole. Place the casserole on the steam bath and evaporate until the odor of hydrochloric acid just disappears. Take up the residue with chloroform, filter and wash with hot chloroform into a beaker, evaporate the chloroform and examine the residue. If the residue is not oily or greasy to the touch, no report shall be made. If the residue is oily or greasy to the touch, it shall be washed with small portions of warm 88° Beaumé naphtha, filtered through a washed plug of cotton into a small weighed beaker, the naphtha evaporated, and the beaker dried in the water oven at 95° to 100° C. in 15-minute periods until the weight is constant, or increases, cooling in a desiccator. Calculate and record as "Foreign Alcoholic Potash Extract."

**FOREIGN CHLOROFORM EXTRACT**—If the compound is light in color, tar, pitch and asphalt shall be considered absent. If the compound is dark or black in color the residue after the acetone extract determination above, without removing the acetone, and before the alcoholic potash extraction is made, is extracted with chloroform for four hours in the same manner and by the same procedure as for the acetone extraction. If the chloroform extract is very dark in color, or the residue is tarry, from its calculated amount shall be subtracted 3 per cent of the weight of vulcanized rubber gum as determined below, and the balance recorded as "Foreign Chloroform Extract."

**PRECAUTIONS**—When the chloroform extraction is made the day after the acetone extraction, the rubber residue shall be covered with acetone over night. When the alcoholic potash extraction is made the day after either the acetone extraction or the chloroform extraction, the dried rubber residue shall be covered with the alcoholic potash over night.

**CARBONACEOUS FOREIGN MATTER**—Heat about a one gram sample with 30 cc. of concentrated nitric acid and 15 cc. water.



A black, insoluble residue indicates the presence of carbon as lampblack, graphite, etc. Examine the ground rubber under the microscope and observe the residue of fillers in the mineral fillers determination. If fibers or carbon are seen except as a trace proceed as follows:

The crucible containing the fillers is washed with hot dilute hydrochloric acid and hot water to decompose carbonates and sulfides, dried to constant weight at 105° to 110° C., and desiccated until cool. The crucible is then gently ignited to constant weight and the loss calculated and recorded as "Carbonaceous Foreign Matter," and shall be subtracted from the per cent of "mineral fillers" recorded above.

**SPECIFIC GRAVITY**—Make the determination on a strip or strips of not less than five grams weight. Weigh to 1 milligram in air, and then thoroughly wet with water, pressing and squeezing with the fingers under water to remove bubbles or films of air. Weigh to 1 milligram in water at 20° C. (taken as 1.00), calculate to 0.001, and record as "Specific Gravity."

#### CALCULATIONS

**VULCANIZED RUBBER GUM BY WEIGHT**—Subtract the sum of the percentages of free sulfur, organic acetone extract, mineral fillers, and corrected foreign matter from 100 per cent and record the balance as "Vulcanized Rubber Gum by Weight."

The correction applied to the foreign chloroform extract reported shall be based on the vulcanized rubber gum calculated as above except that the value for foreign matter shall be taken uncorrected.

**VULCANIZED RUBBER GUM BY VOLUME**—Multiply the percentage by weight of vulcanized rubber gum by the specific gravity, recording the result to 0.01 per cent.

This product shall be that which is specified by the term "Vulcanized Rubber Gum by Volume."

**RATIOS**—Free sulfur, total sulfur, and organic acetone extract shall be separately calculated and recorded as percentages by weight of vulcanized rubber gum present.

#### DISCUSSION

**GENERAL**—Deductions for blanks are always made. The grinder mentioned is a No. 0 Enterprise Coffee Mill, fitted with a ball-bearing washer on the crank end of the shaft.

If the alcoholic potash is made up the day before use, the difficulties concerning aldehyde or decomposition are avoided.

**ACETONE EXTRACT**—The acetone extractions are made on an electric hot plate (Simplex, 110 V., D. C., 4A.) taking a battery of six tubes. These are supported by Forg's brass tool holders bolted to an asbestos cylinder by stove bolts. The tubes rest directly on the plate. The condensers are supplied by independent syphons from a constant water level as shown in the illustration.

The hydraulic head is about six inches. Too great a head of too cold water will cool the distillate in the cup below the boiling point, as well as causing annoying condensation of dew during the summer months.

A great economy of space is secured. The whole arrangement as shown hardly occupies more than one square foot of space. By this apparatus the extractions are made under exactly the same conditions, heated at the same temperature, and cooled by the same volume of water at the same temperature.

The solvent is quickly evaporated from these tubes when placed in a slanting position in a wire frame on the steam bath, without danger of loss by spurting

at the end. When placed nearly horizontal in the water oven, the vapor pours out rapidly and drying is quickly effected and constant or increasing weight always obtained after two half-hour periods.

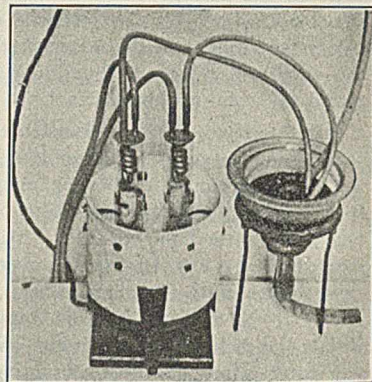
Duplicates show for example 2.99 per cent and 3.03 per cent. The blank approximates one milligram of total acetone extract.

**FREE SULFUR**—Waters and Tuttle<sup>1</sup> have shown that prolonged digestion with nitric acid gives low results in determination of total sulfur. F. W. Hinrichsen has shown that high results are caused by precipitation of barium resins, which we have confirmed in dealing with high organic acetone extracts by nitric acid methods. We have used the following methods:

- |                            |                             |
|----------------------------|-----------------------------|
| 1—Nitric acid alone,       | 3—Nitric acid and chlorate, |
| 2—Nitric acid and bromine, | 4—Bromine and water.        |

All of these we have found have certain disadvantages and tendencies to error, due mainly to occlusion of sulfur with organic matter which has not been completely dissolved or to precipitation of barium resins, when organic matter has been completely dissolved. These errors are sometimes very appreciable.

The method adopted for free sulfur is designed to absolutely remove the influence of organic matter by its complete destruction. Duplicates of free sulfur in a hose tube showed by this method 1.75 and 1.77 per cent as compared with 1.78 per cent obtained by oxidation with bromine and water as recommended by the Bureau of Standards, in Washington. One-tenth of a gram of pure flowers of sulfur gave by the fusion method adopted 0.10006 gram. The blank approximates 2.5 milligrams of sulfur with a nickel crucible and 3.0 with an iron crucible, and is constant for a given crucible and lot of reagents. Nickel crucibles, although more expensive, offer an advantage over iron inasmuch as permanganate is sometimes formed from new iron crucibles.



**MINERAL FILLERS**—In the mineral fillers determination, the rubber compound is extracted with acetone to remove free sulfur and any fatty oils that may be present, both of which would combine with the metallic oxides and thus make the fillers too high and the vulcanized rubber gum by difference too low. Salol will dissolve soft rubber in less than an hour, vulcanite it from two to three hours. Many of the mineral fillers used in rubber compounding are in an extremely fine state of subdivision approaching the order of the wave lengths of light (the so-called "fume pigments" especially) and without a coagulant it is a prolonged operation to filter them off even through an

<sup>1</sup> THIS JOURNAL, 3 (1911), 734.



alundum crucible. Such a coagulant is found in soluble cotton dissolved in amyl acetate. This is added to the warm liquid not only in order to secure thorough mixing but also on account of the fact that the cold, undiluted salol crystallizes on stirring. Cooling is necessary before addition of the turpentine, as the texture of the flock is coarser and the settling more rapid. The flock settles in about fifteen minutes. After washing by decantation and transferring with turpentine the flock is dissolved by carefully adding acetone. About 20 mg. of ash are recovered from the filtrates: the blank approximates 6 mg. Determinations made on compounds of known composition follow:

COMPOUND	PER CENT FILLERS USED	PER CENT FILLERS FOUND
Medium hard valve.....	64.23	63.12
Sheet rubber.....	54.81	55.04
Hard valve.....	61.23	61.40
Medium hard valve.....	52.78	52.20
Hose tube.....	49.00	51.01
Hose tube.....	61.00	61.29

A sample of smoked Ceylon crepe with ash 0.98 per cent gave 1.21 per cent by the Mineral Fillers method. It would seem that any proteid matter present was almost entirely soluble.

For many years many investigators have endeavored to develop a satisfactory and accurate solution method for determination of the amount of rubber gum in rubber compounds. The method of determination by ashing at present in vogue is universally conceded to be inaccurate. Such fillers as carbonates, especially magnesium carbonate, lose carbon dioxide, sulfides such as antimony pentasulfide entirely volatilize, other sulfides change to oxides or sulfates, water of crystallization or of composition is lost. The above errors are avoided by the new method described.

Among the solvents tried by the author and found unsatisfactory before the discovery of the present solvent, *salol*, were the following: nitro-benzol, nitro-naphthalene, gum camphor, camphor oil, kerosene, paraffin and other mineral oils, turpineol, turpenol, terebene, fatty oils and acids such as palm oil, oleic acid, etc., methyl salicylate, thymol, menthol, amyl acetate, amyl alcohol, benzol, xylol, toluol, naphthalene, aniline and many others.

Even after complete solution of the vulcanized rubber gum difficulty was experienced in finding a suitable diluting agent which would not reprecipitate the rubber. Ether, chloroform and turpentine were the only satisfactory ones found among many tried. Of these only turpentine satisfactorily reprecipitates the soluble cotton used to form a flock suitable for filtration. The advent of the alundum crucible and later of the Spencer holder aided in the successful development of the method.

**TOTAL SULFUR**—In the total sulfur determination there is no danger of occlusion of silica in the barium sulfate precipitate if the cold dilute solution is acidified with dilute acid, as recommended by Hillebrand.<sup>1</sup>

**FOREIGN MATTER**—The methods for foreign matter are designed primarily to detect the presence of such

No limiting amounts are fixed on these extracts. The character only of such residues is taken into consideration in determining the presence of foreign material. Most of the tar or asphaltum will be in the acetone extract as well as free fatty oils from substitutes. As the methods of analysis are formulated for specifications to cover compounds made up of rubber, sulfur and mineral fillers only, an excessive organic acetone extract above the limit of the specification as well as the mere presence of foreign matter would condemn the goods. Nevertheless the analyst is expected to report on the amounts of such foreign matter, as well as the amount of vulcanized rubber gum present. However, the determination of the combined total amount of such foreign extracts is necessary in order to find the amount of vulcanized rubber gum present.

The chloroform extraction is not very satisfactory. Soft compounds swell up enormously and the asphaltum is not entirely extracted.

We are now working upon a method for the direct determination of tarry or asphaltic matter.

Saponification under pressure was selected in the method for oily foreign matter to decompose treated oils which are difficult to saponify in the ordinary way. The recovery of the extracted matter by chloroform, as described, is rapid, accurate and clean. The unpleasant, long and dangerous ether method, requiring a special room, is not necessary. A residue of rubber is always obtained due to the solubility of the rubber in alcohol, as previous extractions with absolute alcohol alone have shown. The amount thus extracted depends upon the quality of the new or old rubber used and the method of vulcanizing. This rubber residue is not soluble in 88° B. naphtha, while any fatty acids derived from oil substitutes are dissolved.

When necessary to ignite the alundum crucible containing the undissolved residue of fillers after treatment with hydrochloric acid to determine carbonaceous foreign matter, a loss of combined water in the mineral matter may occur and make the result for foreign matter too high and mineral fillers correspondingly low. This error will rarely amount to more than one per cent of the compound and will not of course affect the result for vulcanized rubber gum present as the sum of carbonaceous foreign matter and mineral fillers is unaltered.

**VULCANIZED RUBBER GUM BY WEIGHT**—Vulcanized rubber gum by weight as calculated by difference represents the pure gum (resin, ash, moisture and air free) plus its combined sulfur. It is this vulcanized rubber gum and not the uncured original rubber that gives rubber goods their specific and desirable properties. It is therefore entirely rational to specify this substance. The amount of resins or organic acetone extract found varies greatly with the kind of rubber used or may consist of added material, and is best reported by itself. Some will question how the results of the analysis will correspond to the materials compounded, especially the rubber, and will say that it

<sup>1</sup> "Analysis of Silicate and Carbonate Rocks," *Bulletin* 305, U. S. Geol. Survey, p. 160, first paragraph, and p. 190, first paragraph.



is better to specify the amount of the original materials.

The experience of two years has shown proper correspondence of analysis to ingredients used, taking into account changes produced by process of manufacture and vulcanization, when adulterants have not been introduced. The manufacturer cannot take chances with materials of unknown composition under our methods.

In specifications reading "It shall contain," the best evidence that certain materials have been used in the compound is to have an inspector at the factory to see them put in. We think we are safe in saying that rubber manufacturers have had enough of this system. We believe that "It shall show" should be specified, that the methods of analysis and tests should be standardized and the specific items defined. This seems by far the better method and offers fewer opportunities for disputes.

**SPECIFICATION OF VULCANIZED RUBBER GUM BY VOLUME**—The physical properties of a rubber compound and the quality are more properly related to the percentage by volume of vulcanized rubber gum present than to the percentage by weight. The large majority of rubber goods are sold by bulk and used by bulk rather than by weight. This volume conception is necessary to an understanding of rubber mixings.

Now the specific gravity of this vulcanized rubber gum (resin-, ash-, and air-free) is very nearly unity. The specific gravity of the purest washed and dried raw rubber is greatly influenced by the mode of preparation in regard to minute air bubbles enclosed in the rubber, and varies from 0.90 to 0.95.

According to Philip E. Young, inventor of Young's Gravimeter, the best value for the pure air-free rubber gum is 0.98. With 30 per cent of combined sulfur without mineral fillers, the specific gravity of the vulcanized rubber gum has been shown to be 1.00. The variation in the specific gravity for various degrees of vulcanization is in any case a small one and for purposes of calculation the specific gravity of all vulcanized rubber gum may be taken as unity. By multiplying the percentage by weight of vulcanized rubber gum present by the specific gravity of the compound a product is obtained which represents the percentage by volume of vulcanized rubber gum present. This volume would be strictly correct if divided by the true specific gravity of the vulcanized rubber gum present. However, it is not intended to determine the true volume, but a factor obtained as specified. As this is very nearly the true volume of vulcanized rubber gum present it has been so called in the methods. No closer method for determining the true volume is possible, or necessary.

It will at once be seen that hard rubbers will show more vulcanized rubber gum by weight than the original rubber put in; and that for soft rubber of good quality that which is taken away and reported as organic acetone extract will about equalize the combined sulfur.

The minimum vulcanized rubber gum by volume

that will give a sound article can hardly be less than 55 per cent if made up of rubber, sulfur and mineral fillers only. Less than this amount needs something to fill the pores between the particles of fillers in the way of resins, oils, waxes or asphaltum. As the percentage of vulcanized rubber gum by volume decreases in a compound made up of rubber, sulfur and mineral fillers only, the liability of decay by oxidation due to porosity becomes greater.

Every manufacturer knows that with a fixed percentage by weight of rubber put into a compound and made into an article with fixed dimensions, like a hose tube or valve, the lighter he can make the specific gravity, the more money he saves. This is due to a reduction in the volume of rubber present. By specifying a minimum percentage by volume of vulcanized rubber gum the choice of fillers is left entirely to the manufacturer, as it should be. Whether he uses light or heavy fillers is immaterial as long as the volume specified is obtained, and the chemical and physical requirements are met. For example, let us suppose a minimum of 75 per cent of vulcanized rubber gum by volume is specified. The manufacturer can meet this by a compound with a specific gravity of 1.22 showing 61.5 per cent vulcanized rubber gum by weight or by a compound with a specific gravity of 2.27 showing 33.0 per cent vulcanized rubber gum by weight, or by various combinations between these extremes. The same result can be obtained by fixing a minimum specific gravity and a minimum percentage by weight of vulcanized rubber gum present but the kind of fillers would then be limited to a few or a mixture of a few having a certain density.

The method specified permits any manufacturer to make as good a compound as he knows how, using good rubber and any fillers he thinks best. He will be on an equal basis of competition with any other manufacturer as far as the quality of the finished article is concerned. He must necessarily also deliver an equal weight of vulcanized rubber gum of quality required to meet the physical tests.

In the few cases where it is advisable to specify total sulfur it is no extra hardship for the manufacturer to specify total sulfur in all forms. It is impracticable to determine sulfur present as barium sulfate, when other forms of barium are present. As a rule, the other chemical and physical tests, including an ageing test, can be made adequate and sufficient to ensure the delivery of goods made up from new rubber. The amounts of sulfur and organic acetone extract are specified as percentages of the weight of vulcanized rubber gum present as they are functions of the amount of rubber present. The specification of fixed limits for these as percentages of the compound does not make due allowance for such corresponding variation of these constituents with the amount of rubber used.

The quality of the rubber used as well as the suitability of the fillers and the proper vulcanization are fixed by physical tests which will be described in an article to follow.



## THE SPECIFIC ABSORPTION OF REAGENTS FOR GAS ANALYSIS

By R. P. ANDERSON

Received February 10, 1915

A knowledge of the absorbing power of the reagents that are commonly used in gas analysis for the gases absorbed by them and for the conditions under which they are ordinarily employed would be of considerable value to the gas analyst. Definite information of this nature is for the most part lacking. Hempel<sup>1</sup> has proposed the term "analytical absorbing power," a suitable expression for this property, but his method of determining it seems open to objection. According to his method, an excess of pure gas was placed in contact with 1 cc. of reagent over mercury and shaken with the reagent as long "als noch schnelle Absorption erfolgte, so dass in Laufe einer Minute mindestens mehrere Kubikzentimeter verschwanden." The decrease in volume thus obtained was divided by four and this value termed the analytical absorbing power. No attempt was made to determine the absolute absorbing power of the reagent, nor was the reagent required to remove the gas completely as it must in actual service. The rapidity with which a reagent absorbs a pure gas that is present in excess is quite different from that with which it completely removes the gas from its mixture with other gases. In the first case, the pressure that is exerted by the gas is presumably that of the atmosphere, while in the second case, the partial pressure of the gas becomes less and less until it equals zero or is so small as to be negligible for technical purposes. In general, as the pressure becomes less, the rapidity of the absorption decreases, the last traces of the gas being absorbed with difficulty, or not at all. It is evident, therefore, that the values that are obtained by Hempel's method have little bearing upon the efficiency of the various reagents for quantitative absorptions, and that they afford the analyst no certainty that his reagents may be used until they have absorbed the quantity of gas indicated by the analytical absorbing power now assigned to them without possibility of the incomplete removal of the constituents.

The determination of the volume of a gas which a certain reagent will absorb up to the point at which the gas is not completely removed from its mixture with other gases is needed by gas analysts. It is here proposed to express this value in cc. of gas per cc. of reagent and term it the *specific absorbing power*, or the *specific absorption*, of the reagent. The statement of the specific absorption of a reagent for a gas must contain the name of the apparatus that is employed, the method of its manipulation, and the temperature of the reagent, since these conditions affect the results. Also the volume of gas that is absorbed at a time may have an effect upon the specific absorption and for this reason the mixture to be employed in the determination of this value should contain an amount of the gas to be removed such as would most frequently be met with, and this amount should be given in stating the specific absorption of a reagent.

For example, the specific absorption at room temperature of a certain solution of alkaline pyrogallol for oxygen, obtained by shaking a mixture of gases containing 21 per cent oxygen with the reagent for 3 minutes in the Hempel double pipette, was found to be 5. By this is meant that successive samples of a gas mixture of the above composition were analyzed for oxygen by pyrogallol in the manner above indicated until the reagent was no longer capable of removing all of the oxygen in the time allotted. The total amount of oxygen absorbed up to that point was found to be 5 times the volume of the reagent that was employed.

Determinations of specific absorption are being made in this laboratory in connection with investigations on the most desirable concentrations of the various reagents and the most desirable conditions for their use. The results on alkaline pyrogallol are given in the following article.

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## REAGENTS FOR USE IN GAS ANALYSIS I. ALKALINE PYROGALLOL

By R. P. ANDERSON

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### HISTORICAL RESUMÉ AND INTRODUCTION

To Döbereiner<sup>1</sup> is attributed the discovery of the absorption of oxygen by an alkaline solution of pyrogallol. Liebig<sup>2</sup> was the first to utilize this reaction for the quantitative removal of oxygen from its mixture with other gases. He employed a solution of potassium hydroxide of 1.4 specific gravity and added to it one-half its volume of a solution of pyrogallol containing 1 g. to 5-6 cc. of water. Much later Weyl and Zeitler<sup>3</sup> studied the effect upon the absorbing power of the reagent of varying the concentration of the alkali. In their work, a definite volume of air was aspirated through a U-tube that contained broken glass and a measured volume of the alkaline solution of pyrogallol. The amount of oxygen that remained in the air after this treatment was determined by titration with a solution of sodium hyposulfite, using indigo as the indicator. Three solutions of potassium hydroxide, of specific gravities 1.025, 1.050 and 1.500, were employed, and the reagent was prepared by adding 0.25 g. of pyrogallol to 10 cc. of one of these solutions. The oxygen that was not absorbed under the arbitrary conditions of the experiments amounted to 1.56, 0.88 and 2.9 per cent for the solutions in which the specific gravity of the alkali was 1.025, 1.050 and 1.500, respectively. From these data the authors conclude that the solution of potassium hydroxide of specific gravity 1.050 gives the reagent with the highest absorbing power and they state also that the pyrogallol probably is quickly destroyed by the solution of potassium hydroxide of specific gravity 1.5. Wehl and Goth<sup>4</sup> performed similar experiments substituting sodium

<sup>1</sup> Gilbert's *Ann.*, **74** (1823), 410.

<sup>2</sup> Liebig's *Ann.*, **77** (1851), 107.

<sup>3</sup> *Ibid.*, **205** (1880), 255.

<sup>4</sup> *Ber.*, **14** (1881), 2659.

<sup>1</sup> "Gasanalytische Methoden," 4th Ed., p. 128.



hydroxide and sodium carbonate for the potassium hydroxide.

Soon after Liebig's experiments, it was found<sup>1</sup> that carbon monoxide was formed under certain conditions on the oxidation of alkaline pyrogallol. Lewes<sup>2</sup> states that a solution prepared by adding 10 g. of pyrogallol to 150 cc. of a 20 per cent solution of sodium hydroxide must not be employed for the absorption of oxygen more than four or five times on account of the formation of carbon monoxide. Clowes<sup>3</sup> studied the behavior of alkaline pyrogallol with especial reference to the formation of carbon monoxide. He found that although a reagent containing 10 g. of pyrogallol and 24 g. of potassium hydroxide to 100 cc. of solution can be used in determining oxygen when it does not exceed 28 per cent of the total volume, carbon monoxide is formed on the analysis of richer mixtures. He recommends that the amount of potassium hydroxide be increased to 120 g. whenever gases that contain more than 28 per cent of oxygen are to be analyzed. An attempt to determine oxygen in a gas mixture containing 90 per cent of it, with the reagent containing only 24 g. of potassium hydroxide to 100 cc. of solution, resulted in the formation of 6 per cent carbon monoxide, while no more than a trace was formed when the stronger solution of alkali was employed. Berthelot<sup>4</sup> found, from a study of the various factors that might affect the formation of carbon monoxide, that alkali in large excess and pyrogallol sufficient to absorb four or five times the amount of oxygen present are necessary in order to prevent the formation of more than a negligible amount of this undesirable product of the reaction. He also investigated the behavior of the reagent when the potassium hydroxide was replaced by sodium hydroxide, barium hydroxide and ammonium hydroxide. The total amount of oxygen that was absorbed by the solution containing sodium hydroxide was found to be practically the same as with the use of potassium hydroxide, while the solution in which barium hydroxide was used gave a smaller absorption, and the one in which ammonium hydroxide was used gave a larger absorption. The effect of these substitutions upon the formation of carbon monoxide was small.

Benedict<sup>5</sup> found, from precise determinations of the oxygen content of the atmosphere, that the results that were obtained depended upon the concentration of the alkali that was employed. The average of 14 determinations made with Haldane's<sup>6</sup> solution containing 1 g. of pyrogallol to 10 cc. of potassium hydroxide, 1.55 specific gravity, was 20.956; the average of similar determinations made with a slightly modified Haldane reagent which contained somewhat less alkali than the original, was 20.938;

and other solutions containing less alkali gave still lower results. Benedict suggests that the discrepancy in the results obtained from the various solutions may be due to the formation of carbon monoxide. Haldane states that the solution prepared according to his directions yields no carbon monoxide on the absorption of oxygen.

An inspection of the proportions of pyrogallol, potassium hydroxide, and water that have been recommended by various gas analysts for the preparation of alkaline pyrogallol shows that there is little uniformity as regards either the composition of the reagents or the terms in which their descriptions are couched. In the accompanying list, for purposes of comparison, an attempt has been made to standardize as far as possible the statement of the composition of the reagent by expressing with sufficient accuracy the amount of pyrogallol and of potassium hydroxide in 100 cc. of the solution:

AUTHOR	Grams per 100 cc. of solution of PYROGALLOL	KOH
Liebig <sup>1</sup> .....	6 to 7	37*
Clowes <sup>3</sup> .....	a 10	24
	b 10	120
Winkler <sup>2</sup> .....	5	22*
Hempel <sup>3</sup> .....	3.5	84
Berthelot <sup>4</sup> .....	15	25
Franzen <sup>5</sup> .....	8	70
Gill <sup>6</sup> .....	a 4.9	43
	b 4.9	81
Haldane <sup>1</sup> .....	9.4	74*
Benedict <sup>1</sup> .....	9.4	66*

<sup>1</sup> *Loc. cit.*

<sup>2</sup> "Lehrbuch der technischen Gasanalyse," 1901 Ed., p. 81.

<sup>3</sup> "Methods of Gas Analysis," 1902 Ed., p. 149. In the fourth edition of this work (1913), Hempel recommends practically the same proportions as are given by Benedict.

<sup>4</sup> "Traité Pratique de L'Analyse des Gas," 1906 Ed., p. 185.

<sup>5</sup> "Gasanalytische Übungen," 1907 Ed., p. 4.

<sup>6</sup> "Gas and Fuel Analysis," 1912 Ed., p. 54.

<sup>7</sup> "The Composition of the Atmosphere," 1913 Ed., p. 80.

Four of the solutions were prepared by using potassium hydroxide of a definite specific gravity. The amount of *water-free* potassium hydroxide is given in these cases and is marked by an asterisk to distinguish it from the amounts used in the other solutions where ordinary potassium hydroxide of unknown water content was employed. The water content of potassium hydroxide that is sold in stick form varies between rather wide limits and the amount of alkali in Haldane's solution would ordinarily be found to exceed that recommended by any other authority with the possible exception of Clowes' stronger solution.

In view of the conflicting results that have been obtained by earlier investigators of alkaline pyrogallol, and because of the apparent lack of any effort to determine what constitutes the most desirable reagent from a consideration of the various determining factors, it was decided to attempt a systematic investigation of the reagent. A study of the effects upon the specific absorption<sup>1</sup> of the reagent of variations in the amounts of potassium hydroxide and pyrogallol was made the starting point of the experimental work and, in order to eliminate as much unnecessary work as possible, an apparatus was constructed in which the specific absorption of various solutions of alkaline pyrogallol could be easily determined.

<sup>1</sup> See Calvert, *Compt. rend.*, **57** (1863), 873; Cloez, *Ibid.*, p. 875; Bous-singault, p. 885; and Poleck, *Z. anal. Chem.*, **8** (1869), 451.

<sup>2</sup> *J. Soc. Chem. Ind.*, **10** (1891), 407.

<sup>3</sup> *Chem. News*, **72** (1895), 288; *J. Soc. Chem. Ind.*, **15** (1896), 170; *Chem. News*, **74** (1896), 199.

<sup>4</sup> *Ann. chim. phys.*, [7] **15** (1898), 294; *Compt. rend.*, **126** (1898), 1066, 1459.

<sup>5</sup> "The Composition of the Atmosphere," p. 113.

<sup>6</sup> "Methods of Air Analysis," 1912 Ed., p. 13.

<sup>7</sup> See preceding article, *THIS JOURNAL*, **7** (1915), 587.



## SPECIAL APPARATUS FOR EXPERIMENTAL WORK

In the apparatus in Fig. 1, artificial mixtures of oxygen and nitrogen were shaken with the alkaline pyrogallol over mercury and the readings were made under constant volume (approximately), *i. e.*, the amount of oxygen absorbed was determined by the change in the pressure that was exerted by the gas as indicated by the change in a manometer reading during the absorption. A new sample was not taken after each determination, nearly the same result being obtained by the addition of oxygen to take the place of that which had been previously absorbed.

The contact between the gas mixture containing oxygen and the alkaline pyrogallol was effected in the pipette *P* which connects by means of a long, enameled rubber tube with the leveling bulb *L*. The pipette is closed at the top by a two-way stopcock, *A*, by means of which connection may be made either

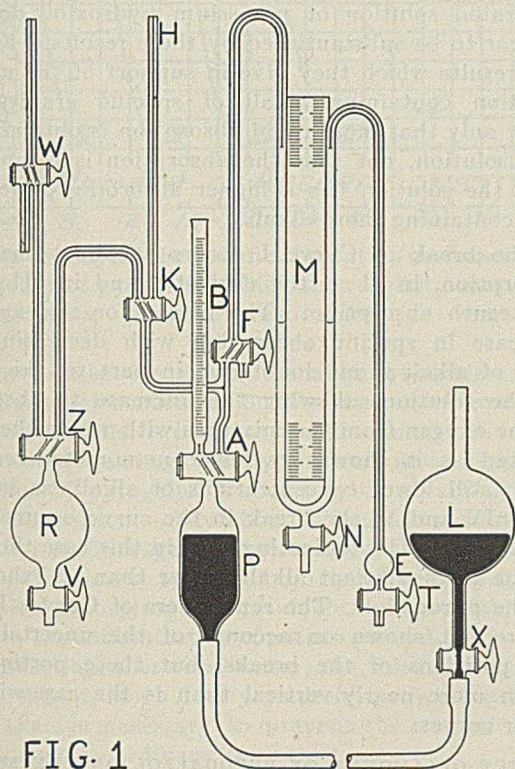


FIG. 1

with the burette *B* or with one arm of manometer *M* through stopcock *F*, and with the oxygen reservoir *R* through stopcocks *K* and *Z*. Reversal of the position of *K* permits connection of the pipette with the atmosphere at *H*. The other arm of the manometer bends downward and terminates in the enlargement<sup>1</sup> *E* and stopcock *T*.

To support the apparatus, a tall, narrow, rectangular iron frame was constructed of iron rods and clamps and the upper and lower ends of the pipette *P* were fastened to horizontal cross pieces near the bottom of the frame. In turn, the frame was suspended at a point about midway between the top and bottom (corresponding approximately to *K* on the apparatus) to a horizontal iron rod in such fashion that the appara-

tus might be rocked back and forth with the rod as an axis by means of a hot-air engine and the proper connections. A glass jar containing water was brought up around the apparatus<sup>1</sup> until *R*, *P* and *E* were covered, in order to maintain a uniform temperature in the separate compartments where gas was confined. The enameled rubber tubing passed from the pipette over the edge of the jar to the leveling bulb which was supported by a separate stand.

The apparatus was prepared for use by pouring mercury, sufficient in amount to fill the pipette *P*, into the leveling bulb *L*, drawing water into the manometer *M* through *N* by lowering *L* with *A* and *F* in the proper positions, and filling the reservoir *R* through *Z* and *W* with oxygen under pressure. The air in *R* was previously displaced by oxygen by opening *V* and allowing the oxygen to bubble through the water in the cell. After these operations were performed, the manipulation of the apparatus was carried out in the following fashion:

## MANIPULATION OF THE APPARATUS

With *F* closed, mercury from the pipette was driven up to *H* by raising the leveling bulb. Connection was made at this point with a capillary tube, also filled with mercury, to a Hempel burette containing nitrogen from a phosphorus pipette, and 20 cc. of this gas was drawn into the pipette, following it with mercury from the burette over to *K*, which was thereupon closed. The proper amounts of solutions of pyrogallol and potassium hydroxide were then introduced separately into the pipette through the burette *B*. This was accomplished without danger of admission of air providing the mercury in the leveling bulb was at a slightly lower level than that in the pipette and care was taken in the manipulation of *A*. Connection with the manometer was next made by turning *A* and *F*, and the leveling bulb was then lowered until the water stood at some definite point on the scale near the upper end of the left-hand arm of the manometer. *X* was thereupon closed. At this point the engine that rocks the pipette back and forth was started in order to obtain a thorough mixture of the solutions of pyrogallol and potassium hydroxide in the pipette and to facilitate the absorption of the small amount of oxygen that was usually present in the space between *A* and the water in the manometer. This absorption of oxygen decreased the pressure in the pipette and necessitated the readjustment of the level of the water in the manometer. Oxygen was next admitted from the reservoir *R* into the pipette until the manometer reading indicated that the desired quantity<sup>2</sup> had been added. Shaking was started at this point and continued for 5 minutes, at the end of which time the motor was stopped, the manometer reading taken, oxygen added to the same manometer reading as before, and the shaking

<sup>1</sup> To make the apparatus more compact, the capillary connections were bent so that *R* and *E* were situated behind *P*.

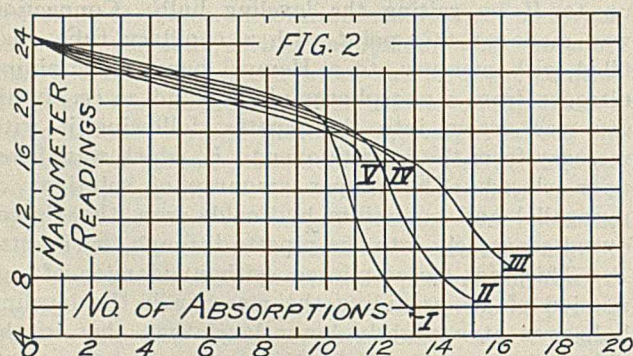
<sup>2</sup> This quantity was usually 5 cc., thus giving an artificial mixture containing 20 per cent of oxygen. The manometer reading that corresponded to the admission of 5 cc. of oxygen was obtained by running in 5 cc. of nitrogen without changing the level of the mercury in the pipette.



continued. This was repeated until the reagent became exhausted.

#### EFFECT OF AMOUNT OF POTASSIUM HYDROXIDE ON THE SPECIFIC ABSORPTION OF THE REAGENT

Five solutions of potassium hydroxide were employed. These consisted of a solution (of specific gravity 1.55) containing about 1.5 parts of potassium hydroxide in stick form to 1 part of water, and four other solutions that were prepared from the first in the proportions of 4 volumes of alkali to 1 volume of water, 3 volumes to 2 volumes, 2 volumes to 3 volumes, and 1 volume to 4 volumes, respectively. The solution of pyrogallol was prepared by dissolving 1 part of pyrogallol in 1.5 parts of water: 0.43 cc. of this solution (containing 0.2 g. of pyrogallol) was employed in each case and to it was added 5 cc. of one of the solutions of alkali. The saturation of each reagent was carried out as previously outlined and the results are shown in Fig. 2 in which manometer readings that were obtained after the absorption of oxygen from its mixture with nitrogen are plotted against the number of samples from which the oxygen had been absorbed. Curve I was obtained from the



solution containing the most alkali, Curve II from the next weaker, etc.

Three or more determinations were made on each of the five solutions. Owing to difficulties in admitting to the pipette exactly the proper amount of reagent and in maintaining a uniform rate of shaking, duplicate manometer readings did not always agree as closely as seemed desirable, but sufficient determinations were made to establish with the necessary accuracy the relative positions of the curves corresponding to the different solutions with the exception of the latter portion of Curves IV and V. The different determinations failed to show definitely the positions of the breaks in these two curves. The break in Curve V falls at the left of the break in Curve IV and both lie between the breaks in Curves I and III. It was not deemed of sufficient importance to locate them more accurately.

The downward slope of the first portion of each of the curves is due to the presence of about one per cent of nitrogen in the oxygen. This caused a gradual decrease in the amount of oxygen that was added at a time, and a corresponding drop in the manometer reading. This fact proved to be of little consequence in the study of the various solutions since it did not obscure the sudden break which was obtained when

the reagent became nearly exhausted, and consequently no effort was made to free the gas from the impurity.

It will be noted that the largest manometer readings were obtained with the solution that contained the most potassium hydroxide; in other words, the greater the amount of alkali, the larger the apparent oxygen content of the gas sample. To determine whether the amount of alkali present in Solution I was sufficient for the removal of all of the oxygen from a mixture of this nature, similar determinations were made with a solution containing still more potassium hydroxide<sup>1</sup> and the same amount of pyrogallol. As far as could be determined from the apparatus that was employed, the curve obtained from this solution occupied practically the same position as Curve I, thus showing that practically complete absorption is obtained with Solution I. The statement of Weyl and Zeitler<sup>2</sup> regarding the effect on pyrogallol of a concentrated solution of potassium hydroxide does not appear to be substantiated by these results. Further, the results which they give in support of the use of a solution containing alkali of specific gravity 1.05 show only that more rapid absorption is obtained with this solution, not that the absorption is complete or that the solution has a higher absorbing power than one containing more alkali.

The break in Curve I occurs at about the ninth absorption, in II at the eleventh, and in III at the thirteenth absorption. The reason for this apparent increase in specific absorption with decreasing content of alkali is no doubt due in part to the failure of the solutions showing this increase to absorb all of the oxygen from the mixtures with which they were treated as is shown by lower manometer readings. With still lower concentrations of alkali, as in Solutions IV and V, the break in the curve occurs before the break in III, indicating that in this case the break is due to insufficient alkali rather than to exhaustion of the pyrogallol. The remainders of Curves IV and V are not shown on account of the uncertainty of the positions of the breaks, but these portions are much more nearly vertical than is the case with the other curves.

#### EFFECT OF AMOUNT OF PYROGALLOL ON THE SPECIFIC ABSORPTION OF THE REAGENT

Five solutions of pyrogallol were employed. These consisted of a solution containing 0.625 g. of pyrogallol per cc., which was obtained by dissolving pyrogallol in an equal weight of water, and four other solutions that were prepared from the first, containing 0.5, 0.375, 0.25, and 0.125 g. of pyrogallol per cc. It was desired to keep the concentration of potassium hydroxide in this series of experiments as high as in Solution I of the previous series<sup>3</sup> and, at the same time, introduce as much as possible of the solution of pyrogallol in order to obtain a wide variation of this constituent. Accordingly, a solution of potas-

<sup>1</sup> The amount of potassium hydroxide was sufficient to place the solution in the zero position in the sequence 0, I, II, III, IV, V.

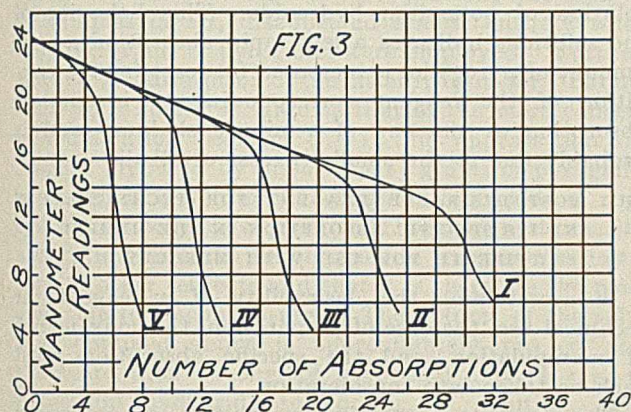
<sup>2</sup> *Loc. cit.*

<sup>3</sup> Solution I contained 5 cc. of a solution of KOH, sp. gr. 1.55 (4 g. KOH), to about 5.4 cc. alkaline pyrogallol.



sium hydroxide was prepared of such strength that 4.45 cc. contained as much potassium hydroxide as 5 cc. of the alkali in Solution I, and was employed in this series of experiments in the proportion of 4.45 cc. of alkali to 1 cc. of one of the solutions of pyrogallol. The curves that were obtained from the treatment of these various solutions in the special apparatus are shown in Fig. 3, Solution I containing the most pyrogallol and Solution V the least.

From these curves it is evident that, within the limits of this series and with the amount of potassium hydroxide



that was employed, the specific absorption increases with the amount of pyrogallol which the reagent contains.

#### THE MAXIMUM SPECIFIC ABSORPTION OF ALKALINE PYROGALLOL

The two series of experiments that have been described show that a high concentration of potassium hydroxide in alkaline pyrogallol is necessary for the quantitative absorption of oxygen in gas-analytical work and a high concentration of pyrogallol is necessary to obtain a high specific absorption. Any effort to increase the specific absorption of the reagent by increasing the concentration of pyrogallol cannot be carried too far without danger of incomplete absorption as a result of the unavoidable decrease in the concentration of potassium hydroxide. In this connection, therefore, water, the third constituent of the reagent, is obviously undesirable in an amount larger than is necessary to prevent the reagent from crystallizing at ordinary temperatures.

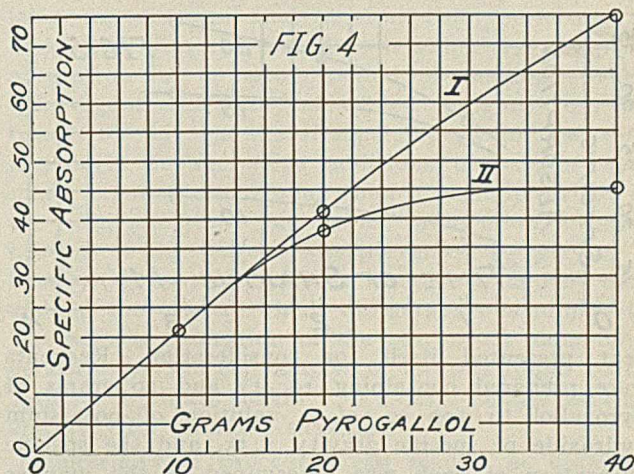
To determine what proportions of pyrogallol, potassium hydroxide, and water give the maximum specific absorption for this reagent, a third series of experiments was performed. One set of solutions was prepared by dissolving 10, 20, 40 and 50 grams of pyrogallol in 100 cc. portions of a solution of potassium hydroxide, specific gravity 1.55, and a similar set was prepared using alkali of specific gravity 1.60, the necessary precautions being taken to prevent their deterioration through contact with the oxygen of the air. A definite amount of reagent (about 25 cc.) was transferred to a Hempel pipette for use with mercury without allowing oxygen to come into contact with it and was treated at room temperature<sup>1</sup>

<sup>1</sup> Hempel has shown that the absorption of oxygen by alkaline pyrogallol is much less rapid at temperatures below 15° C. than at room temperature. It was found that a temperature change from 20° to 24° C. caused little, if any, variation in the specific absorption of the reagent and no analyses were made if the room temperature fell outside these limits. Temperatures below 21° or above 23° were unusual.

with 100 cc. samples of air<sup>1</sup> until the absorption of oxygen was no longer sufficiently complete for technical purposes<sup>2</sup> at the end of three minutes. The absorption was effected by gently rocking the pipette and stand backward and forward at the rate of two or three times a second, using the front edge of the base of the pipette stand as an axis.

The total volume of oxygen that had been absorbed, divided by the volume of the solution, gave the specific absorption of the particular reagent for the conditions under which the determinations were made. The values of the specific absorptions for the various amounts of pyrogallol in 100 cc. of alkali are shown in Fig. 4. Curve I was obtained from the solutions containing the alkali of specific gravity 1.60 and Curve II from those containing alkali of specific gravity 1.55.

In the case of Solution I, the specific absorption is approximately proportional to the amounts of pyrogallol to 100 cc. of alkali, and the lack of strict proportionality may be imputed to two causes. First, owing to the increase in volume that results when pyrogallol dissolves in a solution of potassium hydroxide, the concentration of pyrogallol in the various solutions is not proportional to the amount of pyrogallol that was employed, *e. g.*, the solution that was prepared by dissolving 20 g. of pyrogallol in 100 cc. of potassium hydroxide does not contain twice as much pyrogallol as the one prepared by dissolving 10 g. of pyrogallol in the same amount of alkali, and consequently the value that is obtained for the specific absorption of the stronger solution should be less than twice that of the weaker. Secondly, the concentration of the alkali is gradually lessened by the forma-



tion of carbon dioxide and water<sup>3</sup> during the oxidation of the pyrogallol, thus causing an earlier lack of complete absorption than would be expected from the amount of pyrogallol in the solution. The effect

<sup>1</sup> When it was known that the reagent was still capable of removing the oxygen from many samples of air before becoming exhausted, pure oxygen was added from a burette to lighten the routine work of the experiment. Care was taken that the heat of the reaction between the oxygen and the alkaline pyrogallol did not cause more than a slight rise in the temperature of the reagent.

<sup>2</sup> It was assumed that the absorption was complete as long as the apparent oxygen content of the sample amounted to 20.8 per cent or more.

<sup>3</sup> See Berthelot, *Ann. chim. phys.*, [7] 15 (1898), 294.

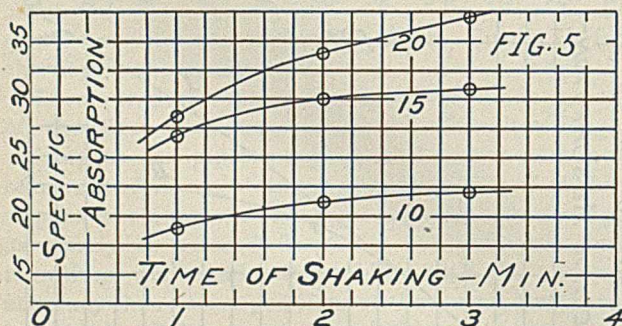


of this gradual diminution in the amount of potassium hydroxide is especially noticeable in Curve II, where the specific absorption of a solution containing 40 g. of pyrogallol to 100 cc. of alkali, specific gravity 1.55, is but little more than that obtained from a solution containing one-half of that amount of pyrogallol.

The highest specific absorption that was obtained from the solutions of these two series is about 75 for the conditions that have already been stated. This probably does not actually represent the maximum specific absorption that might be obtained, but is no doubt a close approximation to it. The solutions that contained 50 g. of pyrogallol to 100 cc. of alkali failed to give an absorption sufficiently complete for technical use, even when new, and thus their specific absorption equals zero. This was no doubt due to the increase in volume which accompanied the solution of the pyrogallol and lowered the concentration of alkali beyond the lower limit for the production of complete absorption. It might be possible to increase the specific absorption by using a higher concentration of pyrogallol in a solution of potassium hydroxide of higher specific gravity or by preparing the solution by adding a minimum of water to a mixture of solid pyrogallol and solid potassium hydroxide; but such reagents would certainly never be actually employed on account of high viscosity and a tendency to foam on shaking, and consequently no attempt was made to determine more accurately the maximum specific absorption.

#### EFFECT OF TIME OF SHAKING UPON THE SPECIFIC ABSORPTION OF THE REAGENT

The question as to the effect of the time of shaking upon the specific absorption of alkaline pyrogallol



next presented itself for consideration. Reagents were prepared containing 10, 15 and 20 grams of pyrogallol to 100 cc. of a solution of potassium hydroxide of specific gravity 1.55, and the specific absorption of each was determined in the manner described under the previous heading except for the time of shaking. This was made one minute for each reagent at the start, lengthened to two minutes when the absorption of oxygen was no longer practically complete for the shorter interval, and finally increased to three minutes for similar lack of complete absorption for the two-minute period. In this fashion, three values of the specific absorption corresponding to the three periods of shaking were obtained for each solution. In Fig. 5 these values are plotted against the time of shaking. The numbers below the curves

represent the amounts of pyrogallol that were used in the preparation of the various solutions.

In the case of the reagent that contains the least amount of pyrogallol, the specific absorption for 1-minute shaking is nearly as large as that for 3-minute shaking, the difference amounting to only 3 units. The specific absorption for 1-minute shaking does not increase as rapidly as the value for 3-minute shaking when the amount of pyrogallol is made larger, as shown by the differences in the shapes of the curves for 10, 15 and 20 grams of pyrogallol to 100 cc. of a solution of potassium hydroxide. This behavior of the solutions indicates a less rapid absorption as the amount of pyrogallol is increased (at least for the condition of the reagent corresponding to incomplete absorption at the end of 1-minute shaking) and is probably due to the smaller excess of alkali.

#### THE MOST DESIRABLE REAGENT FOR TECHNICAL USE AND ITS SPECIFIC ABSORPTION IN THE HEMPEL PIPETTE FOR USE WITH MERCURY

In ascertaining the desirability of a reagent for technical use, the ease of preparation, the convenience of manipulation, and the specific absorption must each be taken into consideration.

The reagents containing a solution of potassium hydroxide of 1.60 specific gravity are less simple to prepare and less convenient to manipulate than those containing alkali of 1.55 specific gravity. The greater difficulty of preparation is caused by the fact that a solution of potassium hydroxide of 1.60 sp. gr. crystallizes at ordinary temperatures (20° C.) and consequently must be heated for the preparation of the reagent.<sup>1</sup> This is not true of the solution of 1.55 specific gravity. The greater difficulty of manipulation is caused by the high viscosity of the solution that contains the greater amount of alkali. In the case of the reagents prepared from alkali of 1.60 specific gravity, the viscosity causes a comparatively thick film of the reagent to remain on the walls of the capillary tubing when a sample of gas is passed into the pipette, the film being of such thickness as to render opaque the bore of the capillary, even with only moderately large amounts of pyrogallol in the reagent. This opaque film makes it difficult to ascertain the position of the reagent in the capillary when the sample is drawn back into the burette.

The reagents that contain a high concentration of pyrogallol show a greater tendency to foam than those of low concentration. This tendency first becomes noticeable in regard to its effect upon the ease of manipulation in the case of those solutions that contain 20 grams of pyrogallol to 100 cc. of alkali and becomes decidedly objectionable in solutions containing twice as much pyrogallol.

Thus it is seen that high concentrations of potassium hydroxide and pyrogallol, the important factors in obtaining a reagent with a high specific absorption, are responsible for undesirable features such as diffi-

<sup>1</sup> The reagent itself is stable in liquid form at ordinary temperatures on account of the increase in volume that accompanies the solution of pyrogallol and also on account of the replacement of a part of the potassium hydroxide by water in the formation of potassium pyrogallate.



culty of preparation and manipulation. To eliminate these undesirable features necessitates limiting the specific gravity of the solution of potassium hydroxide to 1.55 and the amount of pyrogallol to less than 20 g. to 100 cc. of the alkali. This involves a sacrifice in specific absorption of about 40 units (see Fig. 4), but it is felt that the limits that have been mentioned should not be exceeded in choosing the most desirable reagent for technical use.

It was found that foaming, such as was noticed in the solution containing 20 grams of pyrogallol to 100 cc. of alkali of specific gravity 1.55, during the analysis of samples of air, disappeared almost entirely when only 15 grams of pyrogallol were employed. Further, the specific absorption of the latter reagent for 1-minute shaking is nearly as large as that of the more concentrated solution (see Fig. 5). It thus appears that the reagent prepared by dissolving 15 grams of pyrogallol in 100 cc. of a solution of potassium hydroxide of 1.55 specific gravity has practically the highest specific absorption that can be obtained in a solution satisfactory in other respects and that it is therefore the most desirable for technical use.<sup>1</sup> The volume of the solution obtained above is approximately 110 cc. and there are then 13.6 g. of pyrogallol and 71.5 g. of potassium hydroxide to 100 cc. of solution. The specific absorption of this reagent is about 27 when employed at room temperature in 25-cc. portions in a Hempel pipette over mercury and treated with 100-cc. samples of air with 1-minute shaking. The same reagent may be used still further to effect the absorption of oxygen from air if the analyst prefers a longer time of shaking to discarding the old and preparing a new reagent. The specific absorption for 2-minute shaking is about 30, and that for 3-minute shaking about 31. No material increase in the specific absorption of this solution can be effected by increasing the time of shaking beyond three minutes. Experiments have shown that the specific absorption that is obtained with a reagent prepared four months before the time when it was found to be no longer able to give complete absorption is as great as that obtained with one exhausted shortly after it was prepared. It thus appears that the proposed reagent is stable over an indefinite period of time, although conclusive results have not yet been obtained on this point.

The reagent that has been proposed has the disadvantage over using separate solutions of pyrogallol and potassium hydroxide that it must be prepared outside the pipette, thus allowing some oxidation, due to contact with the oxygen of the air, unless special precautions are introduced which would complicate its preparation. However, the specific absorption that may be obtained when pyrogallol is dissolved directly in a solution of potassium hydroxide of 1.55 specific gravity is greater than is possible when separate solutions of the two constituents are employed, and this fact more than offsets the deterioration that cannot readily be avoided in using the former method

<sup>1</sup> At least, in the particular absorbing device in question. Other absorbing devices, with widely different methods of manipulation, might perhaps operate more successfully with a solution prepared in a different fashion.

of preparing the reagent and in transferring it to a pipette.

When the specific absorption 31 has been reached, each molecule of pyrogallol in the reagent has then taken up about 2.3 atoms of oxygen. Berthelot<sup>1</sup> obtains 3 atoms of oxygen for each molecule of pyrogallol for complete saturation of the reagent.

Of the various solutions that have previously been employed for the absorption of oxygen (see Introduction), the one described by Haldane most closely resembles the one that has just been proposed. The specific absorption of a reagent prepared according to Haldane's directions is given on the lower curve of Fig. 5.

#### THE SPECIFIC ABSORPTION OF THE PROPOSED REAGENT IN THE HEMPEL DOUBLE PIPETTE FOR LIQUID REAGENTS

Thirty grams of pyrogallol was weighed into an Erlenmeyer flask of 300 cc. capacity, and was dissolved in 200 cc. of a solution of potassium hydroxide of 1.55 specific gravity: 185 cc. of this solution was then transferred to a Hempel double pipette<sup>2</sup> for liquid reagents. Unnecessary deterioration of the reagent was avoided by stoppering the flask while the process of solution was taking place and by transferring it to the pipette as expeditiously as possible.

During the process of exhausting the reagent and determining the specific absorption of it for various periods of shaking with 100 cc. samples of air, the analysis of air was alternated with the admission of nearly pure oxygen from a calibrated gas holder. In other words, the greater portion of the oxygen necessary to exhaust the reagent was slowly admitted to the reagent from a gas holder in order to save time and labor, an occasional analysis of air being performed to make sure that the reagent was still giving complete absorption for a certain period of shaking. When the reagent was nearly exhausted (judging from the results obtained in the Hempel pipette for use with mercury) the successive additions of oxygen were made small to avoid more than a negligible error in the determinations of specific absorption. Undue heating of the reagent was prevented by playing a blast of air on the outside of the pipette and by controlling the rate at which the oxygen was admitted.<sup>3</sup> The specific absorption of the reagent at room temperature for 100 cc. samples of air was found to be 25.1 for 1-minute shaking, 29.4 for 2-minute shaking and 31.3 for 3-minute shaking.

Uniformity of procedure can readily be obtained with different pipettes except for the amount of reagent that is left in the first bulb of the pipette when the gas sample is introduced. This will vary with the size of the bulb and there is frequently a considerable variation in this particular in different pipettes. It seems likely, however, that any change in the specific

<sup>1</sup> *Loc. cit.*

<sup>2</sup> A modified form was employed. See THIS JOURNAL, 6 (1914), 237.

<sup>3</sup> The effect of the rapid admission of oxygen without proper cooling is taken up in a later section. In each case after the admission of oxygen, the reagent was allowed to cool to room temperature before the analysis of a sample of air was attempted.



absorption of the reagent due to this cause would be so small as to be negligible.

#### THE EFFECT OF HIGH PERCENTAGES OF OXYGEN ON THE SPECIFIC ABSORPTION

The specific absorption of the proposed solution of alkaline pyrogallol was determined for the Hempel pipette for use with mercury and for the Hempel double pipette for liquid reagents, using mixtures containing about 90 per cent oxygen.

In the case of the Hempel pipette for use with mercury, 25 cc. of the proposed solution was employed and this was treated with 100-cc. gas samples containing about 90 per cent oxygen until the absorption failed to be complete for different times of shaking. The specific absorption under these conditions was found to be about 21 for 1-minute shaking and about 24 for 2- and 3-minute shakings. These results are only approximate since the amount of oxygen in each sample represents nearly four times the volume of the reagent.

In the case of the Hempel double pipette for liquid reagents, 185 cc. of the reagent was employed and this was treated with 100-cc. gas samples of a mixture containing about 90 per cent oxygen, alternated with admission of pure oxygen, until the absorption failed to be complete for different times of shaking. The specific absorption under these conditions was found to be zero for 1-minute shaking, 26.9 for 2-minute shaking, 29.9 for 3-minute shaking, 31.1 for 4-minute shaking, and 32.5 for 5-minute shaking.

The striking differences in the specific absorptions for the two forms of apparatus in the case of 1-minute shaking may be due, in a measure at least, to the following causes: (1) The heat of combination of oxygen and pyrogallol would cause a greater elevation of temperature when the volume of the reagent is 25 cc. than when it is 185 cc., which in turn would tend to increase the velocity of the reaction as Hempel has shown. (2) The shaking process would probably result in a more intimate contact of the gas and reagent when a small volume of the reagent is confined over mercury than when the reagent fills the pipette, due to the momentum of the mercury when the direction of its motion is suddenly changed.

#### OTHER CONSIDERATIONS THAT MAY AFFECT THE SPECIFIC ABSORPTION UNDER WORKING CONDITIONS

Conditions which affect the specific absorption of alkaline pyrogallol, such as the composition of the reagent (concentrations of pyrogallol and potassium hydroxide) and the method of its manipulation (the apparatus employed, temperature of the reagent, time and character of shaking, and percentage of oxygen in the sample), have been taken into consideration in the previous discussion. Other factors that may influence the specific absorption under exceptional circumstances are the deleterious action of high temperature on the reagent, and the frequency with which analyses are made.

*The Deleterious Action of High Temperatures*—The effect of the temperature of the reagent upon the speed of absorption of oxygen has already been mentioned.

At temperatures much above that of the room, this effect is also accompanied by a decrease in the specific absorption of the reagent, *i. e.*, the reagent becomes exhausted earlier than one that is employed only at ordinary temperatures.

This decrease in the specific absorption of the reagent was noticed particularly in the case of a reagent which was placed in a Hempel double pipette for liquid reagents and which was treated with oxygen in such fashion that its temperature rose to about 50° C. After the absorption of 1500 cc. of oxygen, this reagent removed the oxygen completely from a sample of air with 1-minute shaking, but after the absorption of an additional 2000 cc., it failed to remove the oxygen completely from a sample of air, even with 3-minute shaking. The total volume of oxygen up to this point would correspond to a specific absorption of about 19 while the specific absorption of another reagent prepared in the same manner and exhausted without allowing the temperature to rise much above that of the room, was, as before stated, 31.3 for 3-minute shaking. It seems probable that this decrease in specific absorption is the result of a change in the character of the reactions that take place between oxygen and pyrogallol as the reagent is heated, rather than the result of the direct action of heat upon the reagent. Whatever may be the cause, the drop in specific absorption caused by heating of the reagent would not be of importance under ordinary conditions unless many samples containing high percentages of oxygen were being analyzed in rapid succession.

*The Frequency with which Analyses Are Made*—It was found that the rapidity of the absorption of oxygen from a given sample depended upon whether or no the reagent had been used a short time before, the absorption taking place more rapidly when the reagent had been just previously used. This state of affairs was found to exist in the analysis of the gas samples containing about 90 per cent oxygen. As has previously been stated, the specific absorption of the proposed reagent in the Hempel double pipette was found to be zero for samples of the above composition for 1-minute shaking. After the reagent had been employed for a few analyses, however, it was found that complete absorption of the oxygen was obtained in one minute and this continued for a few absorptions, after which 2-minute shaking was again necessary for complete absorption. Further, when the reagent had been so far exhausted that 3-minute shaking was necessary for the complete absorption of oxygen from a 100 cc. sample, the reagent was allowed to stand for about 24 hours without being used; when the treatment of the reagent was resumed, it was found that complete absorption was not obtained with 3-minute shaking of the first sample, although it was in the second. This occurred a second time with the same reagent under similar conditions. The cause of this behavior of the reagent may be due to a slight rise in temperature caused by the first analysis or it may be due to the presence of some intermediate product of the reaction which hastens the absorption and which disappears on standing. At any rate, it



is of importance only when the reagent has nearly lost its ability to absorb oxygen completely from a sample under the condition of its use, and then only when it has not been used previously for several hours.

#### THE FORMATION OF CARBON MONOXIDE ON THE OXIDATION OF ALKALINE PYROGALLOL

No systematic study of the conditions that affect the formation of carbon monoxide was attempted. However, samples of air that were placed in contact with the proposed reagent after it was no longer capable of removing the oxygen completely during several minutes' shaking were examined for carbon monoxide and none was found. In each case, shaking the same sample with a solution of alkaline pyrogallol, still in good condition, resulted in the indication of the proper percentage of oxygen, and subsequent treatment with an acid solution of cuprous chloride, freshly prepared, had no effect upon the volume of the sample. It is therefore evident that the formation of carbon monoxide attendant upon the use of the reagent that has been proposed is not sufficient in amount to be objectionable, even when the reagent is almost exhausted.

#### THE USE OF POTASSIUM HYDROXIDE PURIFIED BY ALCOHOL

Hempel<sup>1</sup> has called attention to the fact that potassium hydroxide purified by alcohol should not be employed in the preparation of alkaline pyrogallol, and many authors have mentioned this precaution in their description of the reagent. Hempel did not state wherein the unsuitability of this preparation lay, and in an attempt to explain why its use is undesirable, the following experiment was performed:

Five grams<sup>2</sup> of pyrogallol was dissolved in 50 cc. of a solution of potassium hydroxide purified by alcohol of 1.55 specific gravity; 25 cc. of the resulting reagent was introduced into a Hempel pipette for use with mercury and there treated with 100 cc. samples of air in the manner previously described. It was found that, within the limits of accuracy of the apparatus, the absorption of oxygen was complete, and that the only noticeable difference between this reagent and one prepared by using potassium hydroxide not purified by alcohol is in the specific absorption, which is about 18 in the first case and about 21 in the second.

The apparent discrepancy between the results of this experiment and Hempel's statement may perhaps be explained by the assumption either that the method of manufacture of potassium hydroxide purified by alcohol has been changed in such a manner since the publication of Hempel's results that the objection to the use of this substance no longer holds, or that Hempel's objection was made on the ground of incomplete absorption, apparent in his apparatus for exact analysis, but not noticeable in the use of the Hempel apparatus for technical analysis.

<sup>1</sup> *Ber.*, 20 (1887), 1865.

<sup>2</sup> This experiment was made before the question of the most desirable reagent for technical use had been settled.

#### THE USE OF SODIUM HYDROXIDE IN PLACE OF POTASSIUM HYDROXIDE

From the experiments of Weyl<sup>1</sup> and his co-workers and of Berthelot,<sup>1</sup> it is not clear but what sodium hydroxide might be used to replace potassium hydroxide in the preparation of alkaline pyrogallol, a substitution that would result in a material decrease in the cost of the reagent. Accordingly, a solution was prepared by dissolving 5 g. of pyrogallol in 50 cc. of a solution of sodium hydroxide of 1.475 specific gravity prepared by dissolving 87.5 g. of stick sodium hydroxide in 900 cc. of water: 25 cc. of this reagent was transferred to a Hempel pipette for use with mercury and it was then treated with a 100 cc. sample of air. It was found that the absorption at the end of 3-minute shaking amounted to only 10 per cent, but at the end of 12 minutes absorption was complete. From this experiment it seems that such a reagent would scarcely be satisfactory for general use as an absorbent for oxygen.

#### SUMMARY

I—After a consideration of the various factors that determine the desirability of a solution of alkaline pyrogallol for general use, it was decided that the solution prepared by dissolving 15 g. of pyrogallol in 100 cc. of a solution of potassium hydroxide of specific gravity 1.55 is the most desirable. For the preparation of this solution of alkali there is needed from 1.5 to 2 parts of potassium hydroxide in stick form to 1 part of water, the amount depending upon the water content of the preparation. The volume of reagent that is obtained is about 110 cc. and there are thus 13.6 g. of pyrogallol and 71.5 g. of potassium hydroxide to 100 cc. of solution. If any carbon monoxide is formed, the amount is too small to have any bearing upon the use of the reagent for technical purposes.

II—Different values of the specific absorption of this reagent for different conditions are given in round numbers in the following tabulation. It is understood that the temperature of the reagent was between 20–24° C., that the method of shaking previously described was closely followed, that the initial volume of the gas sample was always 100 cc., and that the volume of the reagent was 25 cc. for the first pipette and 185 for the second.

SPECIFIC ABSORPTION IN HEMPEL PIPETTE FOR USE WITH MERCURY				
No. of Minutes Samples were Shaken.....	1	2	3	4
(a) For gas samples containing 20.9 per cent oxygen.....	27	30	31	...
(b) For gas samples containing about 90.0 per cent oxygen.	21	24	24	...

SPECIFIC ABSORPTION IN HEMPEL DOUBLE PIPETTE FOR LIQUID REAGENTS				
(a) For gas samples containing 20.9 per cent oxygen.....	25	29	31	...
(b) For gas samples containing about 90.0 per cent oxygen	0	27	30	31 32

In the application of these figures to routine gas analyses, the conditions that have been specified should be followed accurately, otherwise proper allowance should be made for any deviation. Probably the greater portion of the samples that are analyzed for oxygen contain less than 20.9 per cent of it, and the specific absorptions for samples of this composition are applicable to all samples containing less oxygen.

<sup>1</sup> *Loc. cit.*



The specific absorption for samples containing 90.0 per cent oxygen are applicable to all samples containing less than this amount of oxygen and probably are applicable, for all practical purposes, to the analysis of nearly pure oxygen. Due allowance should be made in the use of solutions that are nearly exhausted if they are not used frequently, or if they have previously been employed at temperatures considerably above 24° C.

III—The objection to the use of potassium hydroxide purified by alcohol does not appear to be valid.

IV—The substitution of sodium hydroxide for potassium hydroxide is not practicable.

Determinations of the specific absorption of the proposed reagent in some of the other forms of absorbing apparatus are being made at the present time and it is planned to present the results that are obtained as a subsequent article of this series.

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### THE INDICATOR IN PYROLIGNEOUS ACID

By J. M. JOHLIN

Received April 26, 1915

The fact that pyroligneous acid contains its own indicator has long been a well-known fact employed in the wood distillation industries, and was recently referred to in THIS JOURNAL.<sup>1</sup> There seems to be no theory or explanation offered in the literature regarding the nature of the indicator which, when the neutral point is reached, turns pyroligneous acid "a pronounced wine-red."

The author has observed that when milk of lime prepared from chemically pure lime is added to pyroligneous acid this color reaction does not take place. It seemed evident then that this reaction must be due to impurities in the lime as well as in the pyroligneous acid. Trial experiments showed that milk of lime, to which traces of ferric salts had been added, gave with pyroligneous acid the color reactions noted.

The color thus produced is not unlike that caused by the addition of ferric salts to solutions containing tannins. Tests showed that tannins, gallic acid and pyrogallol dissolved in dilute acetic acid produced, with milk of lime containing traces of iron salts, color reactions comparable to those produced between pyroligneous acid and the same sample of milk of lime.

Since tannins are nonvolatile and cannot be distilled it does not seem likely that any of these should be found in pyroligneous acid. Pyrogallol boils close to 300° and is not volatile with steam. It is not probable then that this compound should be present in redistilled pyroligneous acid.

Guaiacol and its homologues, methyl-, ethyl-, and propyl-guaiacol have been found<sup>2</sup> present among the products of destructively distilled wood. Tests made with guaiacol and milk of lime containing iron failed to give any color reactions, though the same sample of milk of lime gave decided color reactions with pyroligneous acid. Guaiacol or its homologues should

not then be held accountable as the indicator present in pyroligneous acid.

The ethers of pyrogallol as well as those of its homologues, methyl-, and propyl-pyrogallol have been found<sup>1</sup> by Hofmann to be present in wood tar. As a rule these are compounds which are readily volatile with steam and give color reactions with ferric salts similar to those referred to. Many of these ethers have been synthetically prepared and similar color reactions were noted. The author has synthetically prepared the dimethyl ether of pyrogallol and found that even minute traces of this ether dissolved in water gave with milk of lime, known to contain iron, color reactions comparable to those obtained with pyroligneous acid.

It seems not at all improbable then that the indicator present in pyroligneous acid consists of the volatile ethers of pyrogallol and its homologues.

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### ON THE KAMBARA EARTH AND ITS BLEACHING ACTION ON OILS

By SEIICHI UENO

Received January 4, 1915

Kambara earth is called "acid earth" or "acid clay" in Japan and is widely used in oil factories as the bleaching and refining agent of mineral and fatty oils. On account of the simplicity of the decolorizing method and the cheapness of the works, this use of the earth has greatly increased. This earth was recently studied by K. Kobayashi<sup>2</sup> but, as far as I know, no reports on the bleaching action of the earth on fatty oils have been published.

#### OCCURRENCE, PRODUCTION, MINING AND PREPARATION

The so-called "Kambara" and similar earths are widely distributed in Japan. Although the acidic earths occur in several localities, the most effective material for the bleaching and refining of oils is found at Kawahigashi village, Kitakambara district, Echigo province. Kawahigashi is an inland village situated 7 miles southeast of the town Shibata.

The strata of the earth mine are brownish orange, light yellow and bluish green. The earth is worked much the same as any clay bank: first about 2 to 3 ft. of the surface must be removed with pick and shovel, then the earth is dug in much the same manner.

The massive earth is brought to a small factory by hand-cars and is crushed into fist-sized lumps that are then dried in a flat, iron pan with direct fire and ground to bean-sized grains, causing the loss of about 40 per cent in weight on account of the evaporation of water. The dried earth is brought to a water-mill barn where it is ground to very fine powder and passed through a silk sieve. The powdered and refined earth is put in a paper sack covered with a straw bag. The weight of a bag is 20 Kwan (165.6 lbs.) and the earth factory can produce 130 bags per day. One bag of earth costs about \$0.50 net.

#### PROPERTIES AND COMPOSITIONS OF THE EARTHS

The factory does not sort the earths according to

<sup>1</sup> THIS JOURNAL, 7 (1915), 47.

<sup>2</sup> Cf. Beilstein, "Organische Chemie."

<sup>1</sup> Cf. Beilstein, "Organische Chemie."

<sup>2</sup> THIS JOURNAL, 4 (1912), 891.



color, so that the commercial Kambara earth is a mixture of the three kinds described above. An acidic earth is also found in the province of Iga. This earth is used to bleach oils in the vicinity, but its bleaching power is not as great as that of the Kambara earth. Analyses of these earths appear in Table I.

TABLE I—ANALYSES OF BLEACHING EARTHS

Per cent	THREE VARIETIES OF KAMBARA EARTH			IGA EARTH
	Bluish green	Brownish orange	Light yellow	
SiO <sub>2</sub> .....	70.99	68.42	63.76	49.90
Fe <sub>2</sub> O <sub>3</sub> .....	2.86	4.48	2.27	4.89
Al <sub>2</sub> O <sub>3</sub> .....	15.76	15.36	14.33	19.83
MnO.....	.....	1.07	.....	.....
CaO.....	1.82	1.27	1.54	0.84
MgO.....	2.38	2.38	2.28	3.08
Na <sub>2</sub> O.....	0.43	0.38	0.29	0.40
K <sub>2</sub> O.....	0.12	0.10	0.14	0.27
Ignition loss.....	5.75	6.57	15.55	20.97
Total.....	100.07	100.03	100.16	100.19

The Kambara earth is an amorphous and slightly plastic substance and gives an acidic reaction to litmus paper. It is useful not only for oil bleaching and refining purposes, but may also be used instead of kieselguhr as a carrier for nickel catalysts in the oil-hardening industry.

BLEACHING ACTION OF THE KAMBARA EARTH

I—EXPERIMENTS ON THE BLEACHING OF FATTY OILS

The method used in treating oils in the following experiments consisted essentially in heating a mixture of oil and earth. The bleaching actions of the various earths were tested by weighing accurately into porcelain basins, 1, 2.5, and 5 g. of each dried earth: 100 g. of crude rape-seed oil (A) were then run into each basin. Each mixture was heated on the sand bath a few

TABLE II—BLEACHING ACTION OF VARIOUS EARTHS

SAMPLE No.	Color of original rape-seed oil (A), red 2.00, yellow 65.10					
	(1)		(2)		(3)	
WEIGHT OF EARTH USED	1 gram		2.5 grams		5 grams	
	Red	Yellow	Red	Yellow	Red	Yellow
Light yellow earth.....	1.05	26.2	0.60	5.20	0.07	1.40
Brownish orange earth....	1.00	12.05	0.70	5.20	0.34	2.50
Pale bluish green earth....	1.65	26.00	0.70	5.50	0.04	1.40
Commercial earth.....	0.52	4.70	0.40	2.30	0.04	1.65

minutes, keeping the mass well stirred. When the decolorization was thought to be complete, the contents were allowed to cool a little and then the oil was immediately poured onto a filter paper, to remove the spent earth. The bleached oils were then compared by means of a J. W. Lovibond Tintometer through a 5 mm. thickness of oil.

From Table II it was concluded that the three colors of the earth could not be distinguished by their bleaching actions; indeed, the three earths when dried and powdered are similar in color and appearance.

When the earth is mixed with oils and warmed, its

TABLE III—COLORS OF SPENT RESIDUAL EARTHS

KIND OF ORIGINAL EARTH	NUMBER (1)		NUMBER (2)		NUMBER (3)	
	Wet state	Dry state	Wet state	Dry state	Wet state	Dry state
Light yellow.....	Dark brown	Light brown	Dark brown	Dark brown	Dark brown	Reddish brown
Brownish orange.....	Black-brown	Dark brown	Black-brown	Dark brown	Black-brown	Black-brown
Pale bluish green.....	Black-brown	Brownish yellow	Black-brown	Brownish brown	Black-brown	Brown
Commercial.....	Dark brown	Light brown	Dark brown	Dark brown	Dark brown	Reddish brown

color is changed from brownish black to deep black, due to the absorption, or adsorption, of the coloring matters of the oils.

The earth which had been used to bleach the oils, was termed "spent residual earth." The spent residual earth was filtered and washed with ether three times and then dried. The colors of these residual earths were compared, with the results shown in Table III.

The color of the spent residual earth is related to the degree of oil-bleaching of the originally used earth, and the more deeply colored earth served as a bleaching agent more effectively than the lighter colored earth. The brownish bleached better than the greenish, so that one can easily foretell the bleaching properties of an unknown earth and also distinguish the end point of the bleaching action.

2—RELATION BETWEEN TIME AND TEMPERATURE OF TREATMENT

Attempts were made to find the general relation between the temperature and time of treatment. When the earth is mixed with rape-seed oil (A), at ordinary temperature, it soon absorbs or adsorbs the color of the oil and becomes dark brown. As a test 40 g. of rape-seed oil (A), mixed with 5 per cent (by weight) of the earth, were gently heated on the sand bath with continuous stirring, kept at 150°-160° C. for the intervals of time noted and compared with the color of the bleached oils, with the results shown in Table IV.

TABLE IV—EFFECT OF TIME ON BLEACHING OF RAPE-SEED OIL

	Red	Yellow
Original rape-seed oil (A).....	2.00	65.10
Heated to 160° C.....	0.04	1.40
After standing 5 minutes.....	0.17	1.90
After standing 10 minutes.....	0.24	2.20
After standing 30 minutes.....	0.40	3.40
After standing 60 minutes.....	0.58	4.80

Also, soya bean oil was mixed and treated as indicated in Table V, with the results there given

TABLE V—EFFECT OF TIME AND TEMPERATURE ON BLEACHING OF SOYA BEAN OIL

Temperature °C.	Time (Min.)	Bleached oil		Spent residual earth (Dry state)
		Red	Yellow	
22	30	1.35	39.66	Light bluish yellow
60	1	1.65	48.20	Brown
85-90	1	0.76	31.50	Light brownish yellow
92	1	1.65	29.00	Dark bluish brown
92-94	60	0.58	6.00	Light brownish yellow
92-94	150	0.52	3.90	Light brownish yellow
110	14	0.84	20.00	Light brownish yellow
110	30	0.70	9.60	Brownish yellow
110	60	0.50	7.00	Brown
130	1	0.52	5.00	Brown
130	60	0.38	3.60	Brown
140	1	0.09	1.65	Brown
150-160	10	0.18	1.95	Brown
150-160	30	0.38	2.60	Brown
170-180	10	0.38	2.45	Dark brown
190-200	10	0.40	3.05	Dark brown
200-210	10	0.70	4.70	Dark brown

which indicate that the oil-bleaching action of the earth increases, with rise of temperature, to a maximum at about 140° C. and then gradually decreases. The bleaching action increased with the time for temperatures under 130° C. but decreased for temperatures above about 150° C. The optimum temperature varied according to the kind of oils and fats; drying

oils, fish oils, etc., were bleached, generally, at lower temperatures than soya bean oil.

3—INFLUENCE OF ATMOSPHERIC GASES

In the apparatus shown in Fig. 1, 100 grams of oil in A were mixed with 5 per cent of the earth and violently agitated; the gas, kept at the required temperature, passed through the oil for about 15 minutes. The results obtained appear in Table VI and show that air,



especially oxygen, injures the color of oil; carbon dioxide affects it but little and hydrogen appears to help the bleaching action. It is easily seen at the same

5 grams of the earth, adding 100 grams of rape oil (B) and treating at 140° C. for a definite number of minutes.

TABLE VI

Temp. °C.	SOYA BEAN OIL—R = 1.95 AND Y = 22.59		R = 1.65 Y = 53.20		RAPE OIL	
	R	Y	Hydrogen	Carbon dioxide	Hydrogen	Y
120	..	..	0.12	1.30	0.30	3.01
140	0.31	1.60	0.12	1.30	0.21	2.60
150	..	..	0.13	1.56	0.15	1.65
160	..	..	0.13	1.56	0.15	1.65
170	..	..	0.15	1.45	0.13	1.43
180	..	..	0.15	1.45	0.13	1.43
190	..	..	0.15	1.55	0.11	1.30
200	..	..	0.15	1.55	0.11	1.30
220	..	..	0.10	1.10	0.13	1.40

time that the bleaching action of the earth is not influenced very much by the factors of time and temperature, in the currents of inactive and reducing gases.

#### 4—BLEACHING ACTION ON VARIOUS OILS

Table VII shows some interesting comparisons of the bleaching action of the earth on various oils. It appears that the degree of the bleaching action of the earth depends upon the properties and compositions of the oils and also upon the impurities in the oils; nitrogenous matter, mucilage, etc., hinder the bleaching action of the earth.

It has been pointed out by others that the earth bleaching method does not give such good results with chrysalis, rice and soy oils,<sup>1</sup> since these oils contain large quantities of impurities, but

they too can be well bleached by the earth method, after the removal of impurities with suitable chemicals.

#### 5—PROPERTIES OF BLEACHED OILS

The well bleached oil is nearly colorless. With regard to the chemical characteristics of the bleached oils, according to a number of my experiments, the values are not essentially different from those of the

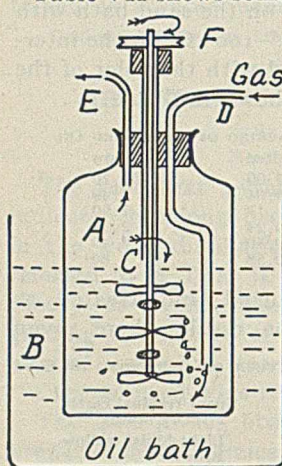


FIG. 1

TABLE VII—ACTION OF 5 PER CENT OF KAMBARA EARTH ON VARIOUS OILS AT 150° C.

KIND OF OIL	Tint of original oil		Tint of bleached oil		Ratio of original color to bleached color		Color of residual earth (wet)
	R	Y	R	Y	R	Y	
Perilla	1.3	16.2	1.05	5.67	1.24	2.86	Black-brown
Linseed	1.0	6.00	0.12	2.50	8.28	2.40	Brownish black
Soya bean	3.20	48.5	0.51	3.00	6.28	16.17	Black-brown
Rape seed (A)	2.00	65.10	0.04	1.40	50.0	46.6	Black-brown
Rape seed (B)	2.60	68.5	0.08	1.50	32.6	45.7	Black-brown
Rape seed (treated at 140° C.)	2.60	68.5	0.04	1.30	65.2	52.6	Black-brown
Apricot kernel	0.38	1.68	0.10	0.07	2.38	24.0	Dark brown
Tsubaki	0.00	0.40	0.00	0.08	..	5.0	Brown
Tsubaki (commercial)	0.10	2.80	0.00	0.20	..	14.0	Brown
Sardine	8.2	39.5	4.7	37.0	1.74	1.65	Black-brown
Machine (mineral)	29.0	12.0	19.0	30.8	1.52	More colored	Brownish black
Engine (2 samples)	..	..	..	..	..	..	Deep black
Crude glycerine	..	..	..	..	..	..	Brownish black
Olein	..	..	..	..	..	..	Brownish black

original oils. On account of their harmless effect on nickel catalyzer, oils bleached by the earth method can be recommended for use as the raw materials in oil-hardening plants.

#### 6—INFLUENCE OF WATER

The influence of water on the bleaching action of Kambara earth was determined by mixing water with

<sup>1</sup> Soy oil is a by-product of Soy making in Japan and is called "Shoyu oil." It is of almost no value.

TABLE VIII—EFFECT OF WATER ON BLEACHING ACTION

Per cent water added	5	10	25	50	100	200
Tint of bleached oil	R: 0.32 Y: 2.80	0.38 2.90	0.50 7.00	1.65 45.70	2.10 49.50	2.10 66.50

Table VIII shows that the presence of water affects the bleaching action of the earth. It was also found that the bleaching power decreased with the moisture content of the earth. It is very important, therefore, in oil bleaching, to have the earth completely dry.

#### 7—INFLUENCE OF ACIDS AND ALKALIES

ACIDS—The effects of hydrochloric, phosphoric and three organic acids on the bleaching action of Kambara earth were studied by means of the experiments outlined in Table IX. From these and previous results it is evident that the presence of strong inorganic acids

TABLE IX—EFFECT OF ACIDS ON BLEACHING OF RAPE OIL (B)

EARTH USED	Treatments of 100 grams of Oil at 140° C. as described in Section I	Bleached oil		Residual earth
		R	Y	
50 grams (a)	HCl (sp. gr. 1.2) (a)	0.58	3.60	..
20 grams	2 cc. HCl (sp. gr. 1.2)	1.35	4.2	..
5 grams	2 cc. H <sub>3</sub> PO <sub>4</sub> (sp. gr. 1.7)	0.34	3.60	..
50 per cent of acid mixed with the earth	Glacial acetic	0.28	1.85	Black brown
	Oxalic	0.26	1.85	Brownish black
	Stearic	0.28	1.95	Brownish black

(a) Fifty grams of the earth and 50 cc. of concentrated hydrochloric acid (sp. gr. 1.2) were mixed, evaporated on the sand bath, powdered, and sieved. Then 50 grams of this prepared earth were added to 100 grams of rape oil (B) and treated at 140° C. as above.

decreases the bleaching action of the earth, but that weak acid, such as phosphoric, does not affect it. The presence of 50 per cent of organic acid in the oil does not affect the bleaching power.

ALKALIES—It has been pointed out by other authors that the bleaching action of fuller's earth is affected by a previous treatment with alkalies, but no statement is found with regard to the action of alkalies on the Kambara earth; this was accordingly tested as follows:

(a) A 5-gram portion of the earth, 10 cc. of N/5 sodium carbonate solution and a suitable quantity of water were mixed into a paste in a porcelain dish. The pasty mass was evaporated on a water bath and the dried earth well sieved.

(b) A second portion of earth was mixed with 2 grams of calcium hydroxide and water and after evaporation, the dried mass was powdered.

(c) A third portion of earth was mixed with a dilute sodium hydroxide solution, boiled and filtered; then washed with hot water, dried on a sand bath and powdered.

Five-gram portions of each of the above specially treated earths were then added to 100-gram portions



of oil and treated at 140° C. The results, given in Table X, show that alkalis decrease the bleaching action of Kambara earth considerably.

TABLE X—ACTION OF ALKALIES ON BLEACHING POWER OF KAMBARA EARTH

Earth treated with	Oil used	Tint of bleached oil	
		R	Y
Na <sub>2</sub> CO <sub>3</sub>	Rape oil (B)	1.00	19.50
Ca(OH) <sub>2</sub>	Rape oil (B)	0.64	9.00
NaOH solution	Soya oil	1.55	30.80
(Original tint of Soya oil)		1.95	22.50

8—EARTH TREATED AT HIGH TEMPERATURE

Portions of Kambara earth were heated to the temperatures indicated in Table XI: 5-gram samples of this heated earth were mixed with 100 grams of rape oil (B) and the bleaching action tested with the results given.

TABLE XI

Temperature to which earth had been heated	Bleached oil	
	R	Y
300° C.	0.34	2.50
400° C.	0.40	2.90
About 600° C.	0.54	3.00
Dull red heat	0.64	3.10
Bright red heat	1.64	21.65
Ordinary earth	0.08	1.50

The earths which were heated to a high temperature, still turned the blue litmus paper to red. On reference to Table XI it will be seen that the earth which was heated to a very high temperature lost its bleaching power considerably, notwithstanding its acidic behavior to litmus paper. According to this fact, the bleaching action may not be derived from the acidic property of the earth. This statement is further corroborated by facts reported below.

9—THE RELATION BETWEEN THE NUMBER OF TREATMENTS AND THE COLOR OF THE BLEACHED OILS

(a) A 100-gram sample of oil was given two treatments with 5-gram portions of earth.

(b) A 100-gram sample of oil was given three successive treatments with 2.5-gram portions of earth and a final 5-gram treatment.

TABLE XII—EFFECT OF NUMBER OF TREATMENTS ON RAPE OIL (B)

Treatment number	Grams of earth used	Bleached oil	
		R	Y
1a	5.0	0.04	1.30
1b	5.0	0.02	1.30
2a	2.5	0.40	2.30
2b	2.5	0.30	2.10
2c	2.5	0.28	1.70
2d	5.0	0.04	1.05

The results of these tests, as given in Table XII, show the ineffectiveness of repeated treatments in comparison with the amount of labor required.

10—PROPERTIES OF SPENT RESIDUAL EARTH

The spent residual earth has an acid reaction to litmus paper: it is a brownish black to black muddy substance in the wet state in oil, and in such condition does not decolorize oil appreciably. For example, 10 grams of the spent residual earth (calculated to the oil-free basis) mixed with 100 grams of rape oil (B) and treated gave an oil reading R 2.60, Y 68.50.

After the oil had been extracted from the spent residual earth with solvent, and the earth dried and powdered, rape oil (B) was bleached by the treatment of 5 per cent of this spent earth to R 1.55, Y 30.63.

Next the following experiments were tried:

(a) Rape oil (B) was bleached by adding 10 per cent of the earth. Result: R 0.10, Y 2.10.

(b) The residual earth of (a) washed with solvent, added to 100 grams of rape oil and treated. Result: R 0.38, Y 2.80.

(c) The residual earth of (b) washed with solvent, added to 100 grams of rape oil and treated. Result: R 0.72, Y 3.90.

It will be seen from the experimental results that the spent residual earth mixed with oil has no bleaching power on oils, but if it is washed with solvent and the absorbed oil removed, the bleaching property is recovered to a considerable extent.

11—FRACTIONAL DIFFUSION OF OILS AND FATTY ACIDS BY TREATING WITH THE EARTH

(a) Experiments were made on linseed oil. Although carried out with care, these experiments gave only negative results.

(b) Experiments on the fatty acids of linseed oil were made by taking up 100 cc. of the mixed fatty acids obtained from linseed oil, into a tap funnel, as shown in Fig. 2, and filtering in a steam oven in a current of hydrogen.

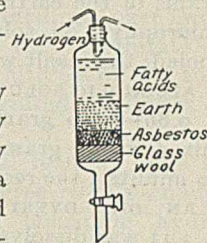


FIG. 2

This experiment, however, was probably not an entirely satisfactory one, since it is difficult to prevent the oxidation and polymerization of higher unsaturated

TABLE XIII

Each 10 cc. of the fractional filtrate were taken and iodine value and refractive index determined.

	Iodine No. (Wijs)	n <sub>D</sub> 20° (Zeiss butyro-refractometer)
1st filtrate	188.73	72
2nd filtrate	189.90	71
3rd filtrate	186.20	71
4th filtrate	180.27	75
Original fatty acids	191.67	70

fatty acids at the somewhat high temperature. But it appears that the fatty acids have been fractionally diffused by treating with the Kambara earth, in some portion.

12—ACTION FOR SOME ORGANIC COLORING MATTERS

METHYL VIOLET—2 grams of the earth were mixed with an alcoholic solution of methyl violet (R 49.5, Y 30.6) shaken, allowed to settle and filtered.

TABLE XIV—EFFECT OF VARIOUS EARTHS ON METHYL VIOLET

KINDS OF EARTH	Solu- tion of filtrate	Color of adsorbed earth washed with alcohol		Color of adsorbed earth washed with alcohol	
		Wet	Dried in air	Dried in a steam oven	
Kambara	20 20.0 10.4	Beautiful purple	Green	Deep green	Beautiful purplish blue
Kambara	10 3.3 3.3				
Sample of Echigo	10 15.0 8.4	Violet	Green	Deep green	Beautiful purplish blue
Iga	10 33.5 14.0				
Bitchu, red	10 36.5 17.0	Violet	Green	Deep green	Beautiful purplish blue
Bitchu, yellow	10 18.5 2.7				

Methyl violet solution is green with inorganic acids and blue with very weak acids. It is a curious thing that the Bitchu and Iga earths which have the weak bleaching power on oil, turn green, and a sample of Echigo earth, which has no acidic property, is similar to the Kambara earth in respect to coloration.

ALKALI-BLUE—The Kambara earth absorbs alkali-blue and turns to violet-blue. The solution is almost decolorized. When the colored earth is washed with alcohol several times the alcohol dissolves some of



the absorbed color. The color of the dry colored earth is not altered by mixing with linseed oil, but the drying property of the oil is decreased.

**METHYL ORANGE**—A dilute solution is almost decolorized by an earth and the earths themselves change color as follows:

Kambara earth Iga, Echigo, Bitchu	Pink Brown to reddish brown.
--------------------------------------	---------------------------------

A concentrated solution changes all the earths to orange-red.

**CRUDE CHLOROPHYLL**—Crude chlorophyll solution is prepared by extracting green leaves with ether and mixing with bleached rape oil (R 0.0, Y 0.42) and the tint of the solution is R 0.74, Y 20.42, B 0.16. Five grams of the earth were mixed with 100 grams of the chlorophyll oil solution, treated at 110° C., filtered, cooled; the result was R 0.70, Y 4.5, B 0.00.

**ALCOHOLIC SOLUTION OF CRUDE CHLOROPHYLL** (Y 2.3, B 0.86)—100 grams of the chlorophyll solution were mixed with 5 grams of the earth and treated at 22° C., 10 minutes; the result was Y 1.75, B 0.16.

**AN OIL DYESTUFF—GREEN CORI BASE** (Y 1.9, B 3.1) was dissolved in bleached rape oil, treated with 5 per cent of the earth at a temperature of 22° C. for 10 minutes: the result was Y 1.75, B 0.10.

It appears that the bleaching action of the earth is not similar in the cases of the oil dyes and the dyestuff solutions tested. Although the earth has an effective bleaching power on a dyestuff solution, it did not bleach the oil so effectively.

### 13—A COLOR REACTION ON COD LIVER OIL

A few grams of the earth were mixed with cod liver oil in a test tube and then shaken: the earth became a beautiful bluish green color. The coloration seems due to the presence of coloring principles in the oil and is a very characteristic one. According to my experiments most other oils have not such a coloration, so that this coloration would seem applicable to the detection of cod liver oil.

### SUMMARY AND CONCLUSIONS

The foregoing investigations seem to have established the following conclusions:

1—The Kambara earth has a remarkable bleaching action on fatty oils.

2—The bleaching action of the earth is affected by the presence of impurities in oils.

3—The bleaching power of the earth on oils varies with the time and temperature of the treatments. At low temperatures the longer treatment is more effective than the shorter. In the case of high temperatures, shorter treatment is better than longer.

4—The presence of air while the oil is under treatment influences the color of the bleached oil.

5—Contact with hydrogen or carbon dioxide while the oil is undergoing treatment does not lessen the bleaching power of the earth.

6—In the current of hydrogen or carbon dioxide gas, the bleached oil is very little affected by time and temperature.

7—The presence of free water with the earth seriously decreases its bleaching power.

8—The presence of strong inorganic acid with the earth lessens the bleaching power, but phosphoric acid does not affect it.

9—The bleaching power of the earth is greatly decreased by the presence of alkalies.

10—Kambara earth heated to dull redness loses some of its bleaching power. Earth heated to a bright red condition loses its bleaching power entirely.

11—The acid value and other chemical characteristics of the bleached oil are not different from those of the original oil.

12—Oil bleached by the earth method is a desirable raw material for the manufacture of hardened oil.

13—The color of the spent residual earth depends upon the degree of bleaching accomplished.

14—Spent residual earths have no bleaching power, but if well washed with solvent, they bleach oil effectively. Well washed spent residual earth has an acidic reaction to litmus paper.

15—When Kambara earth is mixed with cod liver oil, the earth soon assumes a beautiful bluish green color. This coloration appears to be applicable for the detection of cod liver oil.

The author's best thanks are due to Mr. M. Tsujimoto, for kind advice in connection with the work reported in this article.

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### THE DETERMINATION OF SULFATES IN WATER BY BENZIDINE HYDROCHLORIDE

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Benzidine hydrochloride was first used in the determination of sulfates by Raschig<sup>1</sup> who thoroughly developed the technic of the method for its use in coal analysis. Friedham and Nydegger<sup>2</sup> investigated the errors in the method with some thoroughness and concluded that the method was quite as accurate for determining soluble sulfates as the quick precipitation by means of barium chloride. Jacobson,<sup>3</sup> in a search for a rapid method for sulfates in connection with the control of water softening, was the first to use the method in water analysis. His conclusions were that the method was quite accurate enough for rapid boiler water analysis. His data, however, are meager, the results of only six determinations being given with an error of 8 per cent on an average of 135 parts per million of SO<sub>4</sub>. With the idea in mind of further investigating the method and obtaining more data on its use in water analysis, this work was undertaken.

The method consists in precipitating the sulfate by means of benzidine hydrochloride, as benzidine sulfate, which, being insoluble in water, is filtered off suspended in water and titrated in the hot with standard alkali, using phenolphthalein as indicator. This titration is rendered possible by the very weak basic properties of benzidine.

<sup>1</sup> *Z. angew. Chem.*, **1903**, pp. 617, 818.

<sup>2</sup> *Ibid.*, **1907**, p. 9.

<sup>3</sup> *Illinois Water Survey, Bull.* **8** (1911), p. 112.



The method of procedure at first used was the same as that employed by Jacobson. To 250 cc. of the water to be tested, 150 cc. of the benzidine hydrochloride solution (2 grams benzidine per liter) were added. The solution was stirred, allowed to settle, filtered rapidly by means of suction, and washed with about 25 cc. of water. The precipitate was returned to the beaker and water added; the mixture was heated to boiling and titrated with 0.05 *N* NaOH, using phenolphthalein as the indicator. Rapid filtration was best accomplished by filtering on a disc of filter paper (preferably Schleicher-Schüll No. 589) placed in a Gooch crucible and protected by a Witt plate.

The influence of concentration of benzidine hydrochloride was first determined. For this work a 0.10 *N* solution of sodium sulfate was used, being prepared by exactly neutralizing a given quantity of 0.2 *N* sulfuric acid with 0.2 *N* sodium hydroxide. Suitable portions of this solution were diluted with distilled water to give five solutions containing the specified amounts of SO<sub>4</sub>. Using a variable excess of benzidine hydrochloride, a series of sulfate determinations were made on each of the above solutions, 250 cc. being taken for each determination. Table I contains the average of three determinations in each series. Judging from these results, an excess of not less than 25 per cent of benzidine hydrochloride appears satisfactory in obtaining a complete precipitation.

TABLE I—EXCESS OF BENZIDINE HYDROCHLORIDE REQUIRED  
Total volume, 500 cc., benzidine hydrochloride, 2 g. per liter.  
Excess benzidine hydrochloride

Excess benzidine hydrochloride		Parts per million SO <sub>4</sub>			
Per cent		Present			
0	48	96	192	384	480
		Found			
10	26	80	180	300	400
15	38	88	186	375	460
25	48	96	192	384	480
35	48	96	192	384	480
45	48	96	192	384	480
60	48	96	192	384	480

With the idea of reducing the volume of liquid to be filtered, a stronger solution of benzidine hydrochloride (8 g. benzidine per liter) was tried with the results as shown in Table II.

TABLE II—SULFATE IN SODIUM SULFATE BY MEANS OF BENZIDINE HYDROCHLORIDE

Benzidine hydrochloride, 8 g. per l.		30 per cent excess used in each determination.		Total volume, 300 cc.		
Parts per million SO <sub>4</sub>		Parts per million SO <sub>4</sub>		Parts per million SO <sub>4</sub>		
Present	Found	Present	Found	Present	Found	
10	10.0	0.00	100	100.2	+0.20	
30	30.0	0.00	150	150.1	+0.01	
50	50.0	0.00	200	199.8	-0.10	
				300	298.0	-0.70
				350	351.0	+0.30
				400	401.0	+0.25

The results seem to be quite as accurate as those obtained with the weaker solution, so that in all of the subsequent work the stronger solution of benzidine hydrochloride was used.

For the purpose of investigating the adaptability and accuracy of the method in determining sulfates in natural waters, the method was used in parallel with the quick precipitation of sulfates by barium chloride on about 100 waters of varying composition.

The procedure with benzidine hydrochloride was the same as previously outlined with the exception that the strong benzidine hydrochloride solution (8 g. benzidine per liter) was used, and that 10 cc. of a 1 per cent hydroxylamine hydrochloride

solution was added in those waters that contained ferric iron. Ferric iron, as pointed out by Raschig,<sup>1</sup> reacts with the benzidine hydrochloride in such a manner as to give low results. Ferrous iron, however, does not have this disturbing influence. By using hydroxylamine hydrochloride the ferric iron present can be readily reduced to the ferrous condition. The hydroxylamine will not react with the benzidine hydrochloride.<sup>2</sup>

Using barium chloride, the procedure was as follows: 250 cc. of the water to be tested were evaporated to dryness in a casserole. The residue was moistened with 5 cc. of concentrated HCl, diluted with hot water and filtered. The filtrate was made up to 200 cc. and after heating to boiling 10 cc. of barium chloride (50 g. per liter) were added at once with vigorous stirring. After allowing the precipitate to settle over night, the BaSO<sub>4</sub> was filtered off on to a Gooch crucible, dried at 180° C., ignited 5 minutes on a Meker burner and weighed.

Table III contains a few typical results. The results obtained by both methods agree closely enough for all practical purposes. The benzidine hydro-

TABLE III—COMPARISON OF RESULTS OBTAINED WITH BARIUM CHLORIDE AND WITH BENZIDINE

Parts per million SO <sub>4</sub>				Parts per million SO <sub>4</sub>			
Lab. No.	BaCl <sub>2</sub>	Benzidine	Diff.	Lab. No.	BaCl <sub>2</sub>	Benzidine	Diff.
6678	80.6	84.5	+3.9	7084	343.9	341.5	-2.4
6682	76.5	80.6	+4.1	7087	101.2	107.5	+6.3
6723	254.2	257.3	+3.1	7114	51.0	46.0	-5.0
6729	87.6	96.0	+8.4	7128	19.8	15.4	-4.4
6742	68.7	76.8	+8.1	7139	38.8	38.4	-0.4
6804	45.4	40.3	-5.1	7142	24.7	19.2	-5.5
6887	584.7	583.7	-1.0	7144	48.0	46.0	-2.0
6942	62.2	63.4	+1.2	7148	16.2	21.0	+4.8
7081	29.6	32.6	+3.0	7155	26.3	25.0	-1.3
7082	173.2	180.5	+7.3	7156	51.8	63.4	+11.6

chloride method, however, has the advantage, since with it results can be had in 30 minutes while with the barium chloride method 6 hours and more, generally 12, are required.

Table IV contains a complete analysis of the waters used in Table III, and will give some idea of the character of the waters on which the method was used.

TABLE IV—COMPOSITION OF WATER ANALYZED (PARTS PER MILLION)

Lab. No.	City	Total solids	Fe (ic)	Ca	Mg	Na	Cl	HCO <sub>3</sub>	SO <sub>4</sub>	NO <sub>3</sub>
6678	Atchison	342	4.0	47.6	19.8	...	10.0	119.5	80.6	0.5
6682	Arkansas City	800	0.3	116.9	20.3	207	240.0	268.0	76.5	2.0
6723	Waldo	873	...	...	...	...	4.4	307.8	254.2	1.5
6729	Pittsburg	329	5.0	66.5	2.0	141	88.0	330.0	87.6	...
6742	Hutchinson	915	9.5	107.0	31.7	243	406.0	264.0	68.7	0.5
6804	Osborne	464	2.5	109.0	14.4	31	19.0	393.0	45.4	4.0
6887	Washington	1297	15.2	154.7	22.7	...	44.0	266.0	584.7	1.0
6942	St. Marys	582	0.5	58.5	26.8	71	46.0	376.0	62.2	6.0
7081	St. Francis	268	1.4	56.7	9.1	28	30.0	224.5	29.5	1.2
7084	Cimaron	844	...	...	...	...	52.0	244.0	343.9	0.0
7087	Mineral	1005	1.0	61.3	32.2	273	344.0	391.0	101.2	...
7114	Winfield	241	8.4	55.0	10.8	...	20.0	176.0	51.0	0.5
7128	Kanopolis	301	1.0	...	...	...	10.0	187.8	19.8	10.0
7139	Junction City	332	1.2	52.0	19.8	55	34.0	295.5	38.8	0.5
7142	Ellis	373	1.2	78.0	14.6	33	12.0	312.5	24.7	1.0
7144	Turon	803	1.0	...	...	...	320.0	246.5	46.0	1.0
7148	Neodesha	184	1.2	59.0	13.0	...	20.0	214.7	21.0	0.7
7155	Abilene	215	1.2	40.5	9.8	11	14.0	156.0	25.0	1.0
7156	Blue Rapids	394	1.2	37.0	23.0	72	18.0	330.0	63.4	0.7

For ordinary routine water analysis the following procedure is recommended: To 250 cc. of the water (less if the SO<sub>4</sub> content is greater than 500 parts per million) add 10 cc. of a 1 per cent solution of hydroxylamine hydrochloride (more if the iron content of the water is very high) and 20 cc. of benzidine hydrochloride. Stir vigorously and allow the silky white precipitate to settle. Filter on a disc of black ribbon

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Raschig, *Loc. cit.*



filter paper in a Gooch crucible with suction. Wash twice with cold distilled water without allowing the precipitate to become dry. Transfer the precipitate to the original beaker, add water and heat to boiling. Titrate with 0.05*N* NaOH, using phenolphthalein as the indicator.

$9.6 \times \text{cc. } 0.05N \text{ NaOH} = \text{parts per million } \text{SO}_4$ .

The benzidine hydrochloride solution is made up as follows: Place 8 g. of benzidine in an agate mortar and add enough water to make a paste. Wash the paste into a 1 liter flask, add 10 cc. concentrated HCl, and make up to the mark. Filter, if necessary. 1 cc. = 0.0026 g.  $\text{SO}_4$ .

#### CONCLUSIONS

I—The benzidine hydrochloride method is applicable for the determination of sulfates in water.

II—The results with the use of benzidine hydrochloride compare favorably with those obtained with the use of barium chloride.

III—The benzidine hydrochloride method is much more rapid than the barium chloride method, for which reason it is very well adapted to routine water analysis.

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#### EXAMINATION OF TOMATO PULP

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Tomato pulp is prepared in very large quantities for the manufacture of ketchup and pulp. While a considerable amount of pulp used for this purpose is made by the ketchup manufacturers, the preparation of pulp for sale as such has reached considerable proportions. There is also an increasing amount of this product placed on the market in small containers for household use in the preparation of soup.

While the greater part of the pulp placed on the market is made from whole tomatoes, there are a number of plants that manufacture pulp from trimming stock in connection with the canning of tomatoes. Since the latter product is given a lower grade commercially than whole tomato pulp and has a somewhat different composition, it becomes important to be able to distinguish the two by examination in the laboratory.

It is found that the results of the samples examined in this laboratory during the last season afford a basis for this distinction. They also make it possible to simplify the examination which we have heretofore found necessary.

#### COMPOSITION OF WHOLE TOMATO PULP

The results obtained by the examination of 33 samples of whole tomato pulp are given in Table I. The concentration of the samples varies from unconcentrated pulp as it runs from the cyclone, to pulps of very heavy consistency. This table contains the data from which Table III and IV were calculated, although during the season a partial analysis was made of a large number of other samples, and the data secured therefrom were in all respects confirmatory of the relations calculated from Table I.

In addition to the data obtained by the various determinations, Table I gives the relation between the results of the determinations for each individual sample. For instance, the ratio of pulp solids to filtrate solids (pulp solids divided by filtrate solids) varies in the different samples from 1.091 to 1.154, and, with the exception of two samples, it varies from 1.100 to 1.145. The average of the 33 samples was 1.12. The relation of insoluble solids to total solids (expressed as per cent of insoluble solids in total solids) is shown in Table I. Considering the variations in the methods employed by different manufacturers in the preparation of tomato pulp, the per cent of insoluble solids in the total solids as shown by this column is closer than we might expect, varying in most of the samples from 11 to 14 per cent.

The per cent of sugar in the soluble solids, as shown by Table I, varies in most of the samples from 50 to 55 per cent. This figure cannot be expected to be constant in different localities and in different years.

The acid, estimated as citric, constitutes in most of the samples from 9 to 10 per cent of the soluble solids.

Of especial interest is the refractive constant of the filtered liquor, shown in the last column of Table I. The refractive constant of the various samples is much more uniform than might be expected from a product of this nature.

On the whole, Table I is chiefly interesting as affording the data from which Tables III and IV were calculated. The uniformity of the relations shown in Table IV is such that it is usually possible from one determination on the filtrate and the determination of solids in the pulp by drying to distinguish pulp made from whole tomatoes from that made from trimming stock. For instance, if the specific gravity or index of refraction of a filtrate prepared from a pulp of unknown origin, and the per cent of solids in the pulp by drying, do not agree with the relation between these determinations as shown in Table IV, it may be assumed that the sample was not prepared from whole tomatoes, or that some other substance, such as salt, has been added. Moreover, trimming stock pulp rarely conforms to the relations found in whole tomato pulp. For instance, the insoluble solids are usually higher and the acid lower in trimming stock pulp.

#### COMPOSITION OF TRIMMING STOCK PULP

In Table II are given the results of the examination of 21 typical samples of trimming stock pulp prepared at different plants and in different localities. This table is of especial interest in showing that the relations between the results of the various analytical determinations differ from those of whole tomato pulps as given in Table IV. For instance, in No. 1470 the immersion refractometer reading is 45.90, and the per cent of solids is 9.54, whereas, according to Table IV, the per cent of solids in the pulp corresponding to an index of refraction of 45.90 should be 8.57. The specific gravity of the pulp is 1.0373, which, according to Table IV, should correspond to 8.98 instead of 9.54. Of course it cannot be said definitely that a pulp



which on examination is found to conform to all the relations shown in Table IV is necessarily whole tomato pulp. It is entirely possible for an occasional sample of trimming stock pulp to conform to all the relations shown in that table; moreover, the extent to which different samples of trimming stock pulp will vary from the relations shown in Table IV differs with the manner of preparation. For instance, if a portion of the juice is discarded in the manufacture of trimming stock pulp, as is still the practice of some manufacturers, the variation from whole tomato pulp will be greater than otherwise and the variation will increase with the amount of juice discarded.

METHODS OF ANALYSIS

The methods given may also be applied to the examination of raw tomatoes and canned tomatoes. In applying the relations given below to the results obtained by the examination of tomato pulp

or cup for the determination of specific gravity, air bubbles are introduced which it is found impossible to remove without the aid of a centrifuge. These can be completely removed by whirling the specific gravity flask in a centrifuge for about one minute at a speed of about 1000 r. p. m. A hand Babcock milk tester is satisfactory for this purpose. This causes the pulp to settle into the flask, because of the elimination of the air bubbles. The flask is again filled and centrifuged; this is continued until the surface of the pulp remains at the top of the flask. A few drops of pulp are added to bring the contents above the top of the flask and the pulp is then "struck off" with a straight edge, the outside of the flask washed and dried and the flask and contents weighed.

A table can be constructed readily giving in parallel columns the weight of flask and contents and the specific gravity of the pulp. For the use of Table IV, the

TABLE I—COMPOSITION OF WHOLE TOMATO PULPS

SAMPLE NO.	COMPOSITION OF PULPS			FILTRATE FROM PULPS							Refractive constant of filtered liquor (f)			
	Sp. gr. at 20° C.	Per cent total solids(a)	Per cent insoluble solids	Sp. gr. at 20° C.	Per cent solids(a)	Per cent sugar(d)	Per cent acid as citric	Immersion refractometer 17.5° C.	Ratio of pulp solids to filtrate solids	Per cent insoluble solids in total solids		SOLIDS OF FILTRATE		
											Percentages	Ratio sugar to acid		
1290	1.0252	5.94	0.66	1.0233	5.24	2.41	0.58	36.24	1.133	11.1	46.0	11.1	4.1	0.20556
1291	1.0273	6.54	0.78	1.0252	5.71	3.10	0.53	37.80	1.145	11.9	54.3	9.4	5.8	0.20550
1292	1.0234	5.50	0.80	1.0211	4.88	2.48	0.49	34.51	1.127	14.6	50.8	10.1	5.0	0.20564
1293	1.0293	7.02	0.74	1.0276	6.28	3.35	0.61	40.04	1.118	10.5	53.4	9.7	5.5	0.20548
1294	1.0272	6.48	0.69	1.0256	5.82	3.20	0.55	38.27	1.113	10.6	55.0	9.5	5.8	0.20525
1295	1.0361	8.67	0.95	1.0340	7.69	4.36	0.67	46.03	1.127	11.0	56.8	8.7	6.5	0.20534
1296	1.0380	9.00	1.06	.....	8.05	4.47	0.66	46.86	1.117	11.8	55.5	8.2	6.8	.....
1297	1.0465	11.20	1.19	1.0446	10.27	5.61	0.89	56.70	1.091	10.6	54.6	8.9	6.3	0.20544
1299	1.0417	10.07	1.23	1.0394	9.09	4.96	0.81	51.75	1.108	12.2	54.6	8.9	6.1	0.20550
1300	1.0322	7.70	0.93	1.0304	6.88	3.55	0.67	42.84	1.119	12.1	51.6	9.7	5.3	0.20546
1301	1.0312	7.36	0.91	.....	6.68	3.27	0.69	41.56	1.102	12.4	48.9	10.3	4.8	.....
1302	1.0310	7.45	0.91	1.0293	6.61	3.43	0.64	41.76	1.127	12.2	51.9	9.7	5.4	0.20551
1303	1.0340	8.17	0.91	1.0323	7.29	3.77	0.71	44.65	1.120	11.1	51.7	9.7	5.3	0.20549
1304	1.0292	6.88	0.88	1.0274	6.20	3.03	0.64	39.74	1.110	12.8	48.9	10.4	4.7	0.20546
1305	1.0371	9.03	1.19	.....	7.98	4.14	0.82	47.30	1.132	13.2	51.9	10.3	5.0	.....
1306	1.0370	8.95	0.98	.....	8.01	4.71	0.69	47.60	1.117	11.0	58.8	8.7	6.8	.....
1307(b)	1.0328	7.86	1.01	1.0308	6.97	3.79	0.66	43.15	1.126	12.9	54.4	9.5	5.7	0.20544
1481	1.0449	10.82	.....	1.0421	9.64	5.15	0.99	54.20	1.123	.....	53.4	10.3	5.2	0.20545
1482	1.0444	10.83	.....	1.0422	9.86	5.62	0.94	54.75	1.100	.....	57.0	9.6	6.0	0.20554
1483	1.0464	11.21	.....	1.0441	10.19	5.67	0.98	56.45	1.100	.....	55.6	9.6	5.8	0.20550
1484	1.0423	10.27	.....	1.0396	9.23	5.42	0.81	52.10	1.114	.....	58.7	8.8	6.7	0.20544
1485	1.0347	8.55	.....	1.0332	7.73	4.35	0.72	45.85	1.106	.....	56.3	9.3	6.0	0.20529
1477(c)	1.0610	13.86	.....	1.0579	12.75	6.55	0.97	67.15	1.111(e)	.....	51.4	7.7	6.7	.....
1479	1.0411	10.00	1.21	1.0386	8.96	.....	.....	51.57	1.116	.....	9.8	.....	.....	0.20554
1486	1.0169	4.34	0.62	1.0158	3.76	.....	.....	.....	1.154	14.3	.....	.....	.....	.....
1491	1.0198	4.97	0.63	1.0188	4.40	.....	.....	32.67	1.128	12.7	.....	.....	.....	0.20565
1496	1.0341	8.27	1.15	1.0318	7.31	.....	.....	44.86	1.131	13.9	.....	.....	.....	0.20554
1515	1.0352	8.56	1.15	1.0331	7.61	.....	.....	46.20	1.125	13.5	.....	.....	.....	0.20556
1529	1.0209	5.11	0.89	1.0195	4.54	.....	.....	32.96	1.125	17.4	.....	.....	.....	0.20556
1530	1.0252	6.21	0.98	1.0231	5.42	.....	.....	36.31	1.145	15.8	.....	.....	.....	0.20553
1531	1.0291	7.17	1.08	1.0273	6.27	.....	.....	40.09	1.143	15.1	.....	.....	.....	0.20547
1224(c)	1.0486	11.22	0.91	1.0468	10.33	.....	.....	57.62	1.124(e)	11.8	.....	.....	.....	.....
1325	1.0327	7.86	0.93	.....	6.99	.....	.....	43.80	1.123	.....	.....	.....	.....	.....

(a) Determined by drying *in vacuo* at 70° C.  
 (b) Composite of 1290 to 1306 inclusive.

(c) This sample contained salt.  
 (d) Expressed as invert.

(e) Salt-free ratio.  
 (f) Calculated by formula of Lorentz-Lorenz,  $\frac{n^2 - 1}{(n^2 + 2)}$

or canned tomatoes, it is assumed that no substance such as sugar or salt has been added. If sodium chloride is found to be present in excess of the amount normal to tomatoes (from 0.05 to 0.1 per cent), it is necessary to determine the amount of salt and make correction therefor before applying the relations given below.

In examining raw tomatoes, care must be taken to secure a representative sample of the juice. This cannot be done by applying pressure directly, as the juice of the seed receptacles is of different composition from that of the fleshy part of the tomato. It is necessary, therefore, to crush the sample and thoroughly cook it in a flask surrounded by boiling water and connected with a reflux condenser.

DETERMINATION OF SPECIFIC GRAVITY

In pouring the sample of tomato pulp into a flask

specific gravity should be determined at 20° C. If the temperature varies from this, the specific gravity may be corrected by the correction table for Brix hydrometers, changing the Brix degrees in that table to the corresponding specific gravity, and also allowing for the fact that the correction table mentioned is based on 17½° instead of 20° C.

DETERMINATION OF SOLIDS

I. BY THE EXAMINATION OF THE PULP—The total solids in tomato pulp may be determined by drying *in vacuo* at 70° C.; by drying at atmospheric pressure at the temperature of boiling water; by calculation from the specific gravity of the pulp; or from the percent of solids, specific gravity or index of refraction of the filtrate. The solids obtained by different methods on 31 samples of pulp are given in Table III.

(a). BY DRYING—By drying either *in vacuo* or at



atmospheric pressure, it is our experience that after the sample has reached apparent dryness, four hours' drying gives complete results. From 2 to 4 grams should be taken for the determination, and enough water added to distribute the sample uniformly over the bottom of the flat-bottomed dish.

The solids as determined by drying *in vacuo* at 70° C. are about 108.5 per cent of the result obtained by drying at the temperature of boiling water at atmospheric

only one case did it exceed 0.20 per cent. The results obtained by the subsequent examination of a considerable number of other samples confirm this relation.

(b). BY CALCULATION FROM THE SPECIFIC GRAVITY OF THE PULP—There is a very exact relation between the specific gravity of pulp (determined by the method given above) and the per cent of total solids as determined by drying. The solids corresponding to

TABLE II—COMPOSITION OF TRIMMING STOCK PULPS

SAMPLE No.	COMPOSITION OF PULPS			COMPOSITION OF LIQUOR		OBTAINED BY FILTERING PULPS			Ratio of pulp solids to filtrate solids	Per cent insoluble solids in total solids	Per cent sugar in solids of liquor	Per cent acid in solids of liquor	Ratio of solids acid to sugar
	Specific gravity at 20° C.	Per cent total solids(a)	Per cent insoluble solids	Specific gravity at 20° C.	Per cent solids(a)	Per cent sugar(c)	Per cent acid as citric	refractometer at 17.5° C.					
1470.....	1.0373	9.54	.....	1.0337	7.68	4.11	0.58	45.90	1.241	.....	53.5	7.6	7.0
1471.....	1.0385	9.40	.....	1.0334	7.62	4.05	0.59	45.75	1.233	.....	53.2	7.7	6.9
1470-1.....	1.0349	8.56	.....	1.0302	7.11	.....	.....	42.87	1.203	.....	.....	.....	.....
1470-2.....	1.0316	7.88	.....	1.0279	6.55	.....	.....	40.75	1.203	.....	.....	.....	.....
1470-3.....	1.0284	7.00	.....	.....	5.83	.....	.....	37.80	1.201	.....	.....	.....	.....
1470-4.....	1.0258	6.62	.....	1.0232	5.53	.....	.....	36.40	1.197	.....	.....	.....	.....
1471-1.....	1.0334	8.12	.....	1.0288	6.86	.....	.....	41.60	1.184	.....	.....	.....	.....
1471-2.....	1.0258	6.41	.....	1.0227	5.41	.....	.....	36.10	1.184	.....	.....	.....	.....
1471-3.....	1.0299	7.48	.....	1.0275	6.14	.....	.....	39.25	1.218	.....	.....	.....	.....
1471-4.....	1.0191	4.74	.....	1.0168	3.94	.....	.....	30.35	1.203	.....	.....	.....	.....
1572.....	1.0424	10.28	.....	1.0400	9.28	.....	.....	52.47	1.109	.....	.....	.....	.....
1573.....	1.0392	9.53	1.22	1.0369	8.53	.....	.....	49.33	1.117	12.8	.....	.....	.....
1574.....	1.0427	10.29	1.17	1.0401	9.29	.....	.....	52.40	1.109	11.4	.....	.....	.....
1575.....	1.0386	9.73	1.29	1.0369	8.28	.....	.....	49.37	1.175	13.3	.....	.....	.....
1662(b).....	1.0204	4.85	0.18	1.0201	4.65	.....	.....	33.27	1.042	3.7	.....	.....	.....
1664(c).....	1.0577	13.2	0.62	1.0566	12.70	.....	.....	66.92	1.040	4.7	.....	.....	.....
1665.....	1.0331	7.74	1.10	1.0304	6.89	.....	.....	42.65	1.123	14.3	.....	.....	.....
701.....	1.0200	4.89	0.72	1.0184	4.29	2.35	0.30	32.09	1.140	14.7	54.8	7.0	7.8
703(d).....	1.0180	4.24	0.10	1.0178	4.15	2.32	0.29	32.09	1.022	2.4	55.9	7.0	8.0
705.....	1.0388	9.85	1.83	1.0359	8.08	4.07	0.51	47.85	1.220	18.6	50.4	6.2	8.0
706.....	1.0333	8.35	0.98	.....	7.29	3.51	0.46	44.69	1.145	11.7	48.3	6.3	7.6

(a) Determined by drying *in vacuo* at 70° C.

(b) Unconcentrated tomato juice from peeling table.

(c) No. 1662 concentrated.

(d) Clear liquor separated from unconcentrated pulp on standing.

(e) Expressed as invert.

pressure. This figure is the average of the results obtained by the examination of 20 samples of pulp, in all of which the per cent of solids obtained by drying *in vacuo* agree quite closely with the per cent

pulps of various specific gravities are given in Table IV, or may be obtained from the following formula which is derived from the same table:

Per cent SOLIDS

$$= 228 (\text{sp. gr. of pulp} - 1.000) + 19.1 (\text{sp. gr. of pulp} - 1.015).$$

2. BY THE EXAMINATION OF THE FILTRATE—

If a sample of pulp of considerable size be thrown on a folded filter, a filtrate is obtained whose composition has a definite relation to that of the whole pulp.

(a). BY DRYING—The per cent of solids in the filtrate may be determined by drying *in vacuo* at 70° C., or under atmospheric pressure at the temperature of boiling water.

As in the case of the drying of pulp, a constant relation is found to exist between the per cent of solids as determined by drying *in vacuo* at 70° C., and the per cent of solids as determined by drying at atmospheric pressure at the temperature of boiling water. The per cent of solids in the filtrate obtained by drying at atmospheric pressure, multiplied by 1.125, gives the per cent of solids obtained by drying *in vacuo*. This relation is shown in detail in Table IV.

The per cent of solids in the filtered liquor obtained by drying *in vacuo*, multiplied by 1.12, gives the per cent of solids in the original pulp obtained by drying *in vacuo*. This relationship is shown in Table I, in the column headed "Ratio of pulp solids to filtrate solids," and also in Table IV.

Of the 33 samples shown in Table I, the result obtained by multiplying the per cent of solids in the filtrate (obtained by drying *in vacuo*) by the factor 1.12 is very nearly identical with the per cent of solids in the pulp (obtained by drying *in vacuo*). In 22 of the 33 samples the difference between these two figures is less than 0.1 per cent. In 17 samples it

TABLE III—COMPARISON OF METHODS FOR THE DETERMINATION AND CALCULATION OF SOLIDS IN WHOLE TOMATO PULP

SAMPLE No.	PER CENT SOLIDS IN LIQUOR FROM FILTERED PULP			PER CENT SOLIDS IN PULP CALCULATED FROM			By drying <i>in vacuo</i> at 70° C.	Refr. in Table	Specific gravity of Filtered Pulp in liquor in Table	Filtered in liquor See (b)
	Drying <i>in vacuo</i> at 70° C.	Refr. ind. Table	Sp. gr. Table	By drying <i>in vacuo</i> at 70° C.	Refr. ind. Table	Sp. gr. Table				
1290	5.24	5.31	5.35	5.35	5.94	5.95	6.00	5.97	5.99	6.50
1291	5.71	5.67	5.78	5.80	6.54	6.36	6.48	6.47	6.50	7.11
1292	4.88	4.87	4.85	4.85	5.50	5.47	5.44	5.52	5.43	6.00
1293	6.28	6.21	6.33	6.35	7.02	6.96	7.10	6.98	7.11	7.60
1294	5.82	5.79	5.87	5.89	6.48	6.49	6.58	6.45	6.60	7.11
1295	7.69	7.67	7.82	7.82	8.67	8.59	8.77	8.63	8.76	9.11
1296	8.05	7.88	.....	.....	9.00	8.83	.....	9.11	.....	11.49
1297	10.27	10.27	10.25	10.26	11.20	11.50	11.47	11.20	11.49	10.15
1299	9.09	9.06	9.05	9.06	10.07	10.15	10.14	10.02	10.15	7.83
1300	6.88	6.91	6.98	6.99	7.70	7.75	7.82	7.68	7.83	7.43
1301	6.68	6.59	.....	.....	7.36	7.38	.....	7.43	.....	7.55
1302	6.61	6.64	6.73	6.74	7.45	7.44	7.54	7.40	7.55	8.32
1303	7.29	7.34	7.42	7.43	8.17	8.23	8.33	8.12	8.32	7.06
1304	6.20	6.16	6.30	6.30	6.88	6.90	7.06	6.95	7.06	.....
1305	7.98	7.98	.....	.....	9.03	8.94	.....	8.88	.....	.....
1306	8.01	8.05	.....	.....	8.95	9.02	.....	8.86	.....	7.93
1307	6.97	6.96	7.08	7.08	7.86	7.81	7.93	7.83	7.93	10.84
1481	9.64	9.67	9.68	9.68	10.82	10.83	10.84	10.80	10.84	10.88
1482	9.86	9.81	9.70	9.71	10.83	10.98	10.86	10.70	10.88	11.36
1483	10.19	10.21	10.15	10.14	11.21	11.43	11.36	11.17	11.36	10.20
1484	9.23	9.15	9.10	9.11	10.27	10.25	10.19	10.17	10.20	8.56
1485	7.73	7.64	7.63	7.64	8.55	8.56	8.55	8.30	8.56	9.85
1479	8.96	9.03	8.87	8.88	10.00	10.10	9.94	9.88	9.85	4.07
1486	3.76	.....	3.62	3.63	4.34	.....	4.05	3.90	4.07	8.24
1491	4.40	4.44	4.30	4.32	4.97	4.97	4.82	4.62	4.84	5.03
1496	7.31	7.39	7.30	7.31	8.27	8.28	8.18	8.15	8.29	5.03
1515	7.61	7.70	7.60	7.61	8.56	8.63	8.52	8.40	8.52	7.95
1529	4.54	4.52	4.47	4.49	5.11	5.06	5.01	4.90	5.03	5.03
1530	5.42	5.32	5.30	5.31	6.21	5.97	5.94	5.97	5.95	7.03
1531	6.27	6.25	6.27	6.28	7.17	7.01	7.04	6.92	7.03	.....
1325	6.99	7.13	.....	.....	7.86	7.99	.....	7.81	.....	.....

(a) The solution factor of O'Sullivan (*J. Chem. Soc.*, 1876, p. 129) was employed with slight modification. The formula employed was  $\frac{1000(d - 1.000)}{4.35}$  = per cent solids. In this formula  $d$  = specific gravity of solution at 20° C.

(b) For the figures in this column the formula given in footnote (a) was employed and the results multiplied by 1.12.

obtained by drying at atmospheric pressure multiplied by 1.085. In 15 of the 20 samples examined, the difference did not exceed 0.10 per cent, and in



is less than 0.06 per cent, and in 13 samples it is less than 0.05 per cent. In only two samples does it exceed 0.17 per cent.

(b). BY CALCULATION FROM THE SPECIFIC GRAVITY OF THE FILTRATE—The specific gravity of the filtered liquor may be determined by means of an ordinary pycnometer. From the specific gravity at 20° C., the per cent of solids in the filtrate as determined by drying *in vacuo* at 70° C., may be obtained from

It is of interest to note that the table suggested by Windisch for the determination of extract in wine (Bureau of Chemistry, U. S. Dept. Agr., *Bull.* 107, revised, Table V) may be employed to determine solids in tomato pulp from the specific gravity of the filtered liquor from the same. If the specific gravity of the liquor be determined at 20° C., the figures in the adjoining column, under "Extract," correspond very closely to the per cent of total solids in the orig-

TABLE IV—TOMATO PULP AND FILTERED LIQUOR

FILTRATE FROM PULP				TOMATO PULP				FILTRATE FROM PULP				TOMATO PULP			
% solids, 70° C. <i>in vacuo</i>	% solids, 100° C. <i>in vacuo</i>	Immersion refractometer at 17.5° C.	Sp. gr. at 20° C.	% solids, 70° C. <i>in vacuo</i>	% solids, 100° C. <i>in vacuo</i>	Specific gravity at 20° C.		% solids, 70° C. <i>in vacuo</i>	% solids, 100° C. <i>in vacuo</i>	Immersion refractometer at 17.5° C.	Sp. gr. at 20° C.	% solids, 70° C. <i>in vacuo</i>	% solids, 100° C. <i>in vacuo</i>	Immersion refractometer at 17.5° C.	Sp. gr. at 20° C.
3.05	2.71	26.9	1.0133	3.42	3.15	1.0150		6.30	5.60	40.3	1.0274	7.06	6.51	1.0297	
3.10	2.75	27.1	1.0136	3.47	3.20	1.0152		6.35	5.64	40.6	1.0277	7.12	6.56	1.0299	
3.15	2.80	27.3	1.0138	3.53	3.25	1.0155		6.40	5.69	40.8	1.0279	7.17	6.61	1.0301	
3.20	2.85	27.5	1.0140	3.58	3.30	1.0157		6.45	5.73	41.0	1.0281	7.23	6.66	1.0304	
3.25	2.89	27.7	1.0142	3.64	3.35	1.0159		6.50	5.78	41.2	1.0283	7.28	6.71	1.0306	
3.30	2.93	27.9	1.0144	3.70	3.41	1.0161		6.55	5.82	41.4	1.0285	7.34	6.76	1.0308	
3.35	2.97	28.1	1.0146	3.76	3.46	1.0163		6.60	5.86	41.6	1.0287	7.40	6.82	1.0310	
3.40	3.02	28.3	1.0149	3.81	3.51	1.0166		6.65	5.91	41.8	1.0290	7.45	6.87	1.0313	
3.45	3.07	28.6	1.0151	3.87	3.56	1.0168		6.70	5.95	42.0	1.0292	7.51	6.92	1.0315	
3.50	3.11	28.8	1.0153	3.92	3.61	1.0170		6.75	6.00	42.2	1.0294	7.56	6.97	1.0317	
3.55	3.15	29.0	1.0155	3.98	3.67	1.0172		6.80	6.04	42.4	1.0296	7.62	7.02	1.0320	
3.60	3.20	29.2	1.0157	4.03	3.72	1.0174		6.85	6.09	42.6	1.0298	7.68	7.08	1.0322	
3.65	3.24	29.4	1.0160	4.09	3.77	1.0177		6.90	6.14	42.8	1.0300	7.74	7.13	1.0324	
3.70	3.28	29.6	1.0162	4.15	3.82	1.0179		6.95	6.18	43.1	1.0303	7.79	7.18	1.0326	
3.75	3.33	29.8	1.0164	4.20	3.87	1.0181		7.00	6.22	43.3	1.0305	7.85	7.23	1.0329	
3.80	3.38	30.0	1.0166	4.26	3.93	1.0183		7.05	6.26	43.5	1.0307	7.90	7.28	1.0331	
3.85	3.42	30.3	1.0168	4.31	3.98	1.0185		7.10	6.31	43.7	1.0309	7.96	7.33	1.0333	
3.90	3.46	30.5	1.0170	4.37	4.03	1.0188		7.15	6.36	43.9	1.0311	8.02	7.38	1.0336	
3.95	3.51	30.7	1.0173	4.43	4.08	1.0190		7.20	6.40	44.1	1.0313	8.07	7.43	1.0338	
4.00	3.55	30.9	1.0175	4.48	4.13	1.0192		7.25	6.44	44.3	1.0315	8.12	7.48	1.0340	
4.05	3.60	31.1	1.0177	4.54	4.18	1.0194		7.30	6.48	44.5	1.0318	8.18	7.54	1.0342	
4.10	3.64	31.3	1.0179	4.59	4.23	1.0197		7.35	6.53	44.7	1.0320	8.24	7.59	1.0345	
4.15	3.69	31.5	1.0181	4.65	4.28	1.0199		7.40	6.58	44.9	1.0322	8.30	7.64	1.0347	
4.20	3.73	31.7	1.0183	4.71	4.33	1.0201		7.45	6.62	45.1	1.0324	8.35	7.69	1.0349	
4.25	3.78	31.9	1.0185	4.76	4.38	1.0203		7.50	6.66	45.3	1.0326	8.40	7.74	1.0352	
4.30	3.82	32.1	1.0188	4.82	4.44	1.0205		7.55	6.71	45.5	1.0328	8.46	7.79	1.0354	
4.35	3.86	32.3	1.0190	4.87	4.49	1.0208		7.60	6.76	45.7	1.0331	8.52	7.84	1.0356	
4.40	3.91	32.5	1.0192	4.93	4.54	1.0210		7.65	6.80	45.9	1.0333	8.57	7.89	1.0358	
4.45	3.95	32.7	1.0194	4.99	4.59	1.0212		7.70	6.84	46.2	1.0335	8.63	7.95	1.0361	
4.50	4.00	32.9	1.0196	5.04	4.64	1.0215		7.75	6.89	46.4	1.0337	8.68	8.00	1.0363	
4.55	4.04	33.1	1.0198	5.10	4.70	1.0217		7.80	6.93	46.6	1.0339	8.74	8.05	1.0365	
4.60	4.09	33.3	1.0200	5.16	4.75	1.0219		7.85	6.98	46.8	1.0341	8.80	8.11	1.0367	
4.65	4.13	33.6	1.0203	5.21	4.80	1.0222		7.90	7.02	47.0	1.0344	8.86	8.16	1.0370	
4.70	4.18	33.8	1.0205	5.27	4.85	1.0224		7.95	7.07	47.2	1.0346	8.91	8.21	1.0372	
4.75	4.22	34.0	1.0207	5.33	4.90	1.0226		8.00	7.11	47.4	1.0348	8.96	8.26	1.0374	
4.80	4.26	34.2	1.0209	5.38	4.96	1.0228		8.05	7.16	47.6	1.0350	9.02	8.31	1.0377	
4.85	4.31	34.4	1.0211	5.44	5.01	1.0230		8.10	7.20	47.8	1.0352	9.08	8.36	1.0379	
4.90	4.36	34.6	1.0213	5.49	5.06	1.0233		8.15	7.24	48.0	1.0354	9.14	8.41	1.0381	
4.95	4.40	34.8	1.0216	5.55	5.11	1.0235		8.20	7.28	48.2	1.0357	9.19	8.46	1.0383	
5.00	4.44	35.0	1.0218	5.60	5.16	1.0237		8.25	7.33	48.4	1.0359	9.25	8.51	1.0386	
5.05	4.49	35.2	1.0220	5.66	5.21	1.0240		8.30	7.38	48.6	1.0361	9.30	8.57	1.0388	
5.10	4.53	35.4	1.0223	5.72	5.26	1.0242		8.35	7.42	48.8	1.0363	9.36	8.62	1.0390	
5.15	4.58	35.6	1.0225	5.77	5.31	1.0244		8.40	7.46	49.0	1.0366	9.42	8.67	1.0393	
5.20	4.62	35.8	1.0227	5.83	5.36	1.0247		8.45	7.51	49.2	1.0368	9.47	8.72	1.0395	
5.25	4.66	36.0	1.0229	5.88	5.41	1.0249		8.50	7.55	49.4	1.0370	9.53	8.77	1.0397	
5.30	4.71	36.2	1.0231	5.94	5.47	1.0251		8.55	7.60	49.6	1.0372	9.58	8.83	1.0400	
5.35	4.75	36.4	1.0233	6.00	5.52	1.0253		8.60	7.64	49.8	1.0374	9.64	8.88	1.0402	
5.40	4.80	36.6	1.0235	6.05	5.57	1.0256		8.65	7.68	50.0	1.0376	9.70	8.93	1.0404	
5.45	4.84	36.8	1.0238	6.11	5.62	1.0258		8.70	7.73	50.2	1.0379	9.75	8.98	1.0406	
5.50	4.89	37.1	1.0240	6.16	5.67	1.0260		8.75	7.78	50.4	1.0381	9.80	9.03	1.0408	
5.55	4.93	37.3	1.0242	6.22	5.73	1.0263		8.80	7.82	50.7	1.0383	9.86	9.09	1.0410	
5.60	4.98	37.5	1.0244	6.28	5.78	1.0265		8.85	7.86	50.9	1.0385	9.92	9.14	1.0413	
5.65	5.02	37.7	1.0246	6.33	5.83	1.0267		8.90	7.91	51.1	1.0387	9.97	9.19	1.0415	
5.70	5.06	37.9	1.0249	6.39	5.88	1.0270		8.95	7.95	51.3	1.0389	10.02	9.24	1.0417	
5.75	5.11	38.1	1.0251	6.45	5.93	1.0272		9.00	8.00	51.5	1.0392	10.08	9.29	1.0419	
5.80	5.15	38.3	1.0253	6.50	5.99	1.0274		9.05	8.05	51.7	1.0394	10.14	9.35	1.0421	
5.85	5.20	38.5	1.0255	6.56	6.04	1.0276		9.10	8.09	51.9	1.0396	10.19	9.40	1.0424	
5.90	5.24	38.7	1.0257	6.61	6.09	1.0279		9.15	8.13	52.1	1.0398	10.25	9.45	1.0426	
5.95	5.29	38.9	1.0259	6.67	6.14	1.0281		9.20	8.18	52.3	1.0400	10.30	9.50	1.0428	
6.00	5.33	39.1	1.0261	6.72	6.19	1.0283		9.25	8.22	52.5	1.0402	10.35	9.55	1.0430	
6.05	5.38	39.3	1.0263	6.78	6.24	1.0285									
6.10	5.42	39.5	1.0266	6.84	6.29	1.0288									
6.15	5.46	39.7	1.0268	6.89	6.35	1.0290									
6.20	5.51	39.9	1.0270	6.95	6.41	1.0292									
6.25	5.56	40.1	1.0272	7.01	6.46	1.0294									

Table IV. It may also be calculated by the following formula, which was derived from the same table:

$$\text{Per cent SOLIDS IN FILTRATE} = 230 (\text{sp. gr. of filtrate} - 1.000).$$

The per cent of solids in the pulp may also be ascertained from the specific gravity of the filtrate at 20° C., from Table IV. The same results may be obtained from the following formula, which was derived from Table III:

$$\text{Per cent SOLIDS IN PULP} = 257.5 (\text{sp. gr. of filtrate at } 20^\circ \text{ C.} - 1.000).$$

inal pulp. A still closer agreement is obtained if the figure 0.05 be deducted from the percentage of extract given in the table.

(c). BY CALCULATION FROM THE INDEX OF REFRACTION OF THE FILTRATES—The index of refraction of the liquor obtained by filtering tomato pulp may be determined by means of either the Zeiss-Abbé refractometer, or the immersion refractometer at the temperature of 17.5° C. The latter is preferable as



it permits of much greater accuracy. The corresponding percentage of solids in the filtrate and the percentage of solids in the pulp from which it is prepared may be ascertained from the index of refraction by Table IV. The per cent of solids in the filtrate may also be calculated from the scale reading of the immersion refractometer at 17.5° C., by the following formula, which is derived from Table IV:

$$\text{Per cent SOLIDS IN FILTRATE} \\ = 0.258 (\text{scale reading} - 15) - 0.0165 (\text{scale reading} - 26.4).$$

If the index of refraction has been determined by means of an Abbé refractometer, the per cent of solids in the filtrate may be calculated by the following formula:

$$\text{Per cent SOLIDS IN FILTRATE} = 666 (n_D - 1.3332) - 20.7 (n_D - 1.3376).$$

The per cent of total solids in tomato pulp may also be ascertained from the index of refraction of the liquor prepared by filtering the pulp as shown in Table IV; or, it may be calculated from the immersion refractometer reading by the following formula, which is derived from Table IV:

$$\text{Per cent SOLIDS IN PULP} \\ = 0.289 (\text{scale reading of filtrate} - 15) - 0.0185 (\text{scale reading} - 26.4).$$

If the index of refraction of the filtrate has been determined by means of an Abbé refractometer, the per cent of solids in the pulp may be calculated by the following formula:

$$\text{Per cent SOLIDS IN PULP} = 748 (n_D - 1.3332) - 25.5 (n_D - 1.3376).$$

It is of interest to note that the relation between the index of refraction of the liquor obtained by filtering tomato pulp and the per cent of solids in that liquid is very similar to the relation between the index of refraction and dissolved solids in beer and wine extract, as shown in the table prepared by Wagner.<sup>1</sup>

In the formula given above, as well as in Table IV, it is assumed that salt is absent. If it be desired to calculate the percentage of solids in a sample containing salt from the index of refraction of the filtrate, it is necessary first to determine the amount of salt present and make correction therefor. For this purpose the table of Wagner<sup>2</sup> may be employed.

This correction is necessary, however, if the percentage of solids be determined by drying, or calculated from specific gravity.

#### DETERMINATION OF INSOLUBLE SOLIDS

Transfer 20 grams of the pulp to an eight-ounce nursing bottle, nearly filled with hot water, mix by shaking, and centrifuge until the insoluble matter is collected in a cake in the bottom of the bottle. Transfer the supernatant liquor onto a double, tared filter paper covering the bottom of a Büchner funnel, using suction to facilitate filtration.

Again fill the nursing bottle with hot water, stir the cake of insoluble solids so that it is thoroughly mixed with the water, centrifuge, and decant the supernatant liquor on the filter. Repeat the centrifuging and the filtration of the supernatant liquor once more, and then finally transfer the insoluble solids to the filter paper and thoroughly wash with hot water. Dry the paper and insoluble solids, and weigh. The insoluble solids are quite hydroscopic and the weight must be taken quickly.

<sup>1</sup> "Ueber quantitative Bestimmungen wässriger Lösungen mit dem Zeiss-schen Eintauchrefraktometer," Table XVII.

<sup>2</sup> *Ibid.*, Table I.

#### DETERMINATION OF SUGAR

The sugar of tomatoes is probably always present as invert sugar. If cane sugar is ever present in the raw product it is doubtless inverted during the concentration of pulp. The per cent of sugar given in Tables I and II was determined by the method of Munson and Walker.<sup>1</sup>

#### DETERMINATION OF ACIDITY

Accurate results cannot be obtained by the titration of tomato products in the presence of the insoluble solids. If it be desired to determine the acidity in the entire sample of tomatoes or tomato pulp rather than in the expressed juice, the insoluble solids should first be removed by the method given in the determination of insoluble solids. The per cent of acid given in Tables I and II was obtained by titrating the liquor obtained by filtering the pulp. In products of this nature, the addition of an alkali causes a brownish color which has a tendency to obscure the end point shown by the indicator. To obviate this, the sample should be diluted to at least 200 cc. and a larger amount of indicator employed than is necessary with a clear solution. The following details are suggested:

Dilute 20 grams of the filtrate under examination with over 200 cc. of water. Add at least 1/2 cc. of phenolphthalein solution (prepared by dissolving 1 gram of phenolphthalein in 100 cc. of 95 per cent alcohol) and titrate with sodium hydroxide until the end point is obtained. Add 1 cc. of tenth-normal hydrochloric acid, heat the solution quickly to boiling and boil one minute to expel carbon dioxide. Cool the solution quickly to about room temperature, and then add tenth-normal sodium hydroxide until the end point is obtained. The volume of hydrochloric acid added must, of course, be taken into consideration in the final result.

NATIONAL CANNERS' ASSOCIATION, WASHINGTON, D. C.

#### A CONCISE GROUP METHOD FOR THE DETECTION OF GELATINIZING AGENTS, PASTY MATERIAL AND THICKENERS, USED IN FOOD PRODUCTS

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The extreme difficulty of detecting various gelatinizing agents, pasty material and thickeners used in food products, has led the writer to work out a group method, by which these substances can be identified even if the unknown contains one or all of the common substances used for gelatinizing agents, etc., such as starch, dextrin, gelatine, acacia, agar-agar, tragacanth, albumen and pectin bodies of the fruit juices. The use of these substances has been quite general in recent years. Hence a study of these materials and their detection in food products is important to the chemist. Thickeners, pasty materials, and gelatinizing agents frequently are used to cheapen the genuine articles of food. In this class may be mentioned agar-agar, which has been found in imitation lemon slices; starch, agar-agar, and gelatine in imitation jelly; dextrin in imitation cocoa cubes. These materials are also used to cover up inferiority. In this class might be mentioned albumen, or white

<sup>1</sup> Bureau of Chemistry, U. S. Dept. Agr., *Bull.* 107, revised.



TABLE I

GROUPS	GROUP REAGENTS	REACTIONS WITH WATER-SOLUBLE SOLUTIONS OF THE GELATINIZING AGENTS PASTY MATERIALS AND THICKENERS
Group I.....	Iodine solution	Blue coloration indicates <i>starch</i> . (Sometimes green apples made into jelly will give traces of starch.) Purple coloration indicates <i>Amylo-dextrin</i> . Red coloration indicates <i>Erythro-dextrin</i> . No coloration may indicate neither starch nor dextrin, but may be <i>Achro-dextrin</i> .
Group II.....	Millon's or Stokes' reagent (acid nitrate of mercury)	Mixture, after shaking substance in solution with reagent is cloudy. Yellow precipitate with picric acid solution indicates <i>Gelatine</i> . Drop of this reagent. Gelatinous precipitate, soluble in excess of this reagent, indicates <i>Acacia</i> . A slight white cloudy precipitate may indicate either <i>Agar-agar</i> or <i>Tragacanth</i> or both (test for tragacanth as in Group IV).
Group III.....	Concentrated solution of sodium borate	A white gelatinous precipitate indicates either <i>Agar-agar</i> or <i>Acacia</i> or both. C. T. <i>Acacia</i> will give a gelatinous, opaque white precipitate with solution basic lead acetate.
Group IV.....	Solution of sodium hydrate	<i>Acacia</i> may be further tested for as in Group II or Group IV or by adding a solution of tannin which gives a bluish black coloration.
Group V.....	Solution of mercuric chloride	A brownish yellow color on heating indicates <i>Tragacanth</i> . A white cloudy precipitate indicates <i>Acacia</i> .
Group VI.....	Schweitzer's reagent (solution of cupra-ammonia)	A slight turbidity may indicate <i>Dextrin</i> . A white precipitate may indicate <i>Albumen</i> and <i>Gelatine</i> . If a concentrated water solution of the unknown is treated with this reagent and placed on glass slide under microscope, a delicate framework of cupric pectate is evident, showing a <i>Pectin</i> of fruit or vegetable origin present.

of egg, which is sometimes used to glaze coffee beans to make them appear better than they really are. Again the thickeners, etc., are used in such products as ice cream and custards, primarily to add bulk to the product, and to give the material in which they are used a frothy appearance. They are also used in this connection to make the ice cream and custards "stand up." A great many ice cream manufacturers use a so-called "ice cream powder." These "ice cream powders" vary in composition, but generally contain one or more of the following: dextrin, acacia, tragacanth, gelatine, albumen, and starch.

This paper deals more specifically with the detection of these gelatinizing agents, pasty materials, and thickeners in food products by a group method.

The above table, prepared and worked out by the writer on actual experiments in the laboratory, places the above-mentioned materials in six groups: I—the iodine solution group; II—the acid nitrate of mercury group; III—the concentrated solution of sodium borate group; IV—the solution of sodium hydrate group; V—the solution of mercuric chloride group; VI—the solution of cupra-ammonia group. A careful study of this group method shows that a new means for testing agar-agar has been discovered. This test is based on Groups II, III and IV. The characteristic reactions for agar-agar depend on a new test for acacia in Group II, that is, one drop of acid nitrate of mercury plus the unknown water solution, which test yields a stringy gelatinous precipitate, *soluble in excess of the reagent*. Since the reagent in Group III precipitates only agar-agar and acacia, it is simply a test to prove whether one or both are present in the unknown water-soluble mixture. The reagent in Group IV does not precipitate agar-agar, and hence if no precipitate is obtained here, agar-agar is present in Group III; if a white, cloudy precipitate occurs, the unknown is acacia, and if a brownish yellow color occurs on heating, the unknown is tragacanth. Acacia may be further tested for with a solution of soluble basic lead acetate, which gives a whitish gelatinous precipitate and again tested for by the acid nitrate of mercury test in Group II as already indica-

ted. The remaining tests in the other groups given in the table are rather well known, but the writer thinks that this group method will be helpful to those interested in food chemistry.

DIVISION OF FOOD AND DRUGS  
KANSAS STATE BOARD OF HEALTH, TOPEKA

### TAMARIND SYRUP

By W. C. TABER<sup>1</sup>

Received March 25, 1915

A syrup prepared from the pulp of tamarinds with added sugar has come into use in the United States as a summer beverage that is highly esteemed by Italians. After dilution with water this syrup forms a refreshing drink. The making of this syrup apparently originated in Italy some years ago. The districts of Lombardy and Piedmont are the Italian sections most prominently identified with the making of this product.

The tamarinds used in this country are practically all imported. They are the fruit of a leguminous tree, *Tamarindus indica*, which grows in tropical and semi-tropical countries. A native probably of Africa, it was early introduced into the East Indies, West Indies, Brazil, Mexico and most of the tropical countries. The fruit is a large, flat pod from 4 to 8 in. long, filled with an acid pulp, seeds and a stringy, fibrous matter. In the samples examined in this laboratory the pulp constituted about sixty per cent of the whole fresh fruit as removed from the pod.

The reported analyses of tamarinds are not uniform. The statements in regard to the presence of citric and malic acids are quite conflicting.

Vauquelin,<sup>2</sup> who published one of the earliest analyses of tamarind, reported a large amount of citric acid as one of the constituents. This report can have little weight as the method of identification was faulty. After concentration, the addition of calcium carbonate produced a precipitate, which, on decomposition, gave an acid precipitate with lime water. This would not be sufficient to distinguish between tartaric acid and citric acid.

<sup>1</sup> Assistant Chemist, Bureau of Chemistry.

<sup>2</sup> *Ann. de Chim.*, [1] 5 (1790), 92.



Schmey<sup>1</sup> quotes Nevinney, who found 1.5 to 6 per cent of tartaric acid and up to 9.4 per cent of citric. The methods of analyses used, however, are not given.

Mueller<sup>2</sup> reports the examination of nine samples of tamarind pulp freed from seeds. He found an average of 2.2 per cent of citric acid, which figure included the malic acid which may have been present.

Neumann<sup>3</sup> found on the average from ten East Indian, mostly Calcutta, and one West Indian variety 7.062 per cent of free tartaric acid, 3.05 per cent of citric acid, and 0.969 per cent of malic acid.

Adams<sup>4</sup> reports no citric acid in the pulp.

Octave Remeaud,<sup>5</sup> one of the more recent analysts, reports the results from the pulp of a known sample of the fruit and from two commercial samples. His analyses show a total acidity as tartaric of 11.7 per cent on the known sample, largely due to tartaric acid, with a small amount of undetermined acid. His result on invert sugar is high, 42.30 per cent.

Brunner<sup>6</sup> analyzed twenty-one samples of whole tamarinds from Calcutta, and one from the West Indies, and found on the average 1.76 per cent of citric acid, with possible traces of malic in two cases.

From analyses made by Chace, Tolman and Munson<sup>7</sup> some years ago, it was seen again that the fruit in its natural state is remarkable for its large amount of sugar, over 30 per cent, which is mainly reducing sugar, and for its high degree of acidity which they found to be approximately 10 per cent. It has been stated by Pratt and del Rosario<sup>8</sup> that the tamarind contains more acid and more sugar than any other naturally occurring food. These authors<sup>9</sup> recently report the analysis of Philippine tamarinds in which the total sugar as invert is 41.20 per cent, with less than 1 per cent of sucrose, and with an acidity of 15.33 per cent as tartaric.

Other references to the literature on tamarinds may be found in the article by Brunner,<sup>10</sup> but they are of little importance.

The published analyses agree fairly well as to the amount of tartaric acid present, which is the characteristic acid of the fruit. The sum of the potassium tartrate and tartaric acid was found by Brunner and Neumann to be on the average 11.5 per cent. Mueller obtained a slightly higher figure on the pulp freed from seeds.

The fruit examined in this laboratory, which was purchased in the New York market, had an acidity of about 10 per cent, calculated as tartaric. A large part of the acidity was due to tartaric acid, as found by the quantitative precipitation, and the rest to undetermined acids. No citric acid was found in the syrups made from this fruit, and volatile acids only in very small amounts. In view of the method

used in making the syrups as outlined below, it may be doubted whether a sufficient amount of citric acid would be extracted from the tamarinds to give a test, taking it for granted that it was present in the original fruit to the extent of 2 or 3 per cent.

The fact that the acidity was lower than that found by some analysts mentioned above may have been due to incomplete ripeness. Geerligs<sup>1</sup> has shown that the composition of the pulp varies with the different stages of ripening. In a typical case the tartaric acid content increased from 3.25 to 15.8 per cent during sixteen days of ripening, and the sugars from 0.73 to 15.2 per cent.

The manufacturing process employed in making commercial tamarind syrups consists simply in making a water extract of the tamarinds by adding water to the fruit, heating the mixture for a few hours, filtering it, and adding sugar until a solid content of approximately 60 per cent is obtained. There are, however, on the market artificial or imitation tamarind syrups which are prepared from citric or tartaric acids and colored with caramel to give the product the appearance of a syrup containing a large amount of tamarind, and sometimes a small amount of the tamarind may be added, varying from 1 to 5 per cent. Glucose is also added in some cases and other fruit juices such as prune or raspberry.

The formulae used for making the true tamarind syrup vary somewhat in the amount of fruit used, some manufacturers using as much as 30 to 35 per cent. In the opinion of makers of high-class goods, tamarind syrup should be a preparation containing a sufficient amount of the extract of tamarind to impart to it the desired acidity and flavor. They apparently agree that at least 2 pounds of the whole tamarind to the gallon of the finished product, or approximately 20 per cent, is necessary to impart the distinctive flavor and the degree of acidity desired.

Six syrups of tamarinds were prepared in the laboratory in the following manner:

The pulp, separated from the seeds and other extraneous matter, was used in making the extract. The amount of whole fruit was calculated from the pulp, which in this sample was 60 per cent of the whole fruit. The pulp was covered with water, placed on the steam bath for several hours, allowed to stand over night, filtered through a linen filter, and washed with hot water. Sugar was added until the percentage of solids was between 50 and 60, and the solution finally filtered for analysis. The large amounts of invert sugar present in Samples 5 and 6 may be accounted for by the fact that they were evaporated on the steam bath after the addition of sugar.

The table shows plainly the gradual increase with increasing amounts of fruit of the non-sugar solids, solids other than sugar and acids, acidity, total acid as tartaric, ash, alkalinity of ash, phosphoric acid, and color. The color in Samples 5 and 6 was increased by the evaporation of the syrup on the steam bath, which resulted in caramelization. A subsequent sample of the same concentration as Sample 6 showed a

<sup>1</sup> *Allg. Med. Centr. Ztg.*, 65 (1896), 635.

<sup>2</sup> *Pharm. Centralhalle*, 23 (1882), 593.

<sup>3</sup> *Pharmaceut.*, (1891), p. 15.

<sup>4</sup> *Zts. allg. Oesterreich. apoth. Verein*, Aug., 1905.

<sup>5</sup> *J. pharm. chim.*, 23 (1906), 424.

<sup>6</sup> *Apoth. Ztg.*, 6 (1891), 53.

<sup>7</sup> U. S. Dept. Agr., Bur. of Chem., *Bull.* 87 (1904), 15.

<sup>8</sup> *Phil. J. Sci.*, 8 (1913), Sec. A, No. 1.

<sup>9</sup> *Ibid.*

<sup>10</sup> *Loc. cit.*

<sup>1</sup> *Intern. Sugar J.*, 10 (1908), 372.



color value less than one-half as much. The test of Denigès<sup>1</sup> reagent in the above samples did not indicate citric acid. While it may be questionable whether

ANALYSIS OF TAMARIND SYRUPS PREPARED IN THE LABORATORY

DETERMINATION	Sample					
	1	2	3	4	5	6
Amount of whole fruit (per cent).....	2.0	4.1	8.0	12.1	16.0	24.0
Total solids by refractometer (per cent).....	50.9	50.6	53.3	52.0	56.8	56.7
Reducing sugar before inversion (per cent).....	4.1	9.6	9.7	14.4	42.3	43.8
Sucrose, by copper (per cent).....	45.6	38.8	41.3	35.4	11.5	8.8
Total sugar (per cent).....	49.7	48.4	51.0	49.8	53.8	56.5
Non-sugar solids (per cent).....	1.2	2.2	2.3	2.2	3.0	4.1
Solids other than sugar and acid (per cent).....	1.08	1.79	1.86	1.60	2.18	2.99
Total acidity calculated as tartaric (per cent).....	0.12	0.21	0.44	0.60	0.82	1.11
Acidity (cc. N/10 per 100 g.).....	16.3	28.2	59.3	80.5	109.2	147.9
Tartaric acid, by wine method (per cent).....			0.31	0.34	0.51	0.58
Ash (per cent).....	0.04	0.10	0.15	0.19	0.23	0.33
Alkalinity of ash (cc. N/10 per 100 g.).....	6.8	10.4	17.6	23.5	30.3	43.0
Phosphoric acid (per cent).....	Trace	0.004	0.008	0.01	0.016	0.018
Color in 1/2 in. cell (degrees Brewer's scale)...	1.5	3.0	6.0	8.0	28.0	54.0
Citric acid.....	None	None	None	None	None	None

there is citric acid present in tamarinds either ripe or unripe, there is at least apparently not a large amount.

Organoleptic tests on the samples gave the following results:

The sample containing 2 per cent of fruit has no perceptible taste other than that due to sugar. The sample containing 4 per cent of the fruit did not differ perceptibly from the first syrup. In the syrup with 8 per cent of fruit some acidity was noticeable, while in the 12 per cent product there was a marked acidity, as well as a slight trace of the characteristic flavor, although not enough for a good product. In the syrup containing 16 per cent of fruit the liquor more nearly approached in general qualities the standard of a good tamarind syrup. The last syrup, having a concentration of 24 per cent, formed the most satisfactory product of the series. These tests agree closely with the opinions of the best manufacturers, that 2 pounds of whole tamarinds to the gallon, or nearly 20 per cent of fruit, are necessary to produce the distinctive flavor and desirable degree of acidity.

The interpretation of analytical results on commercial samples, when added substances are present, is not so simple a matter. The results given above may, however, be of value in some cases, in forming an opinion as to the amount of tamarind fruit used in a syrup, and possibly in regard to its adulteration.

BUREAU OF CHEMISTRY  
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WASHINGTON, D. C.

### THE HYDROLYSIS OF SUGAR SOLUTIONS UNDER PRESSURE<sup>2</sup>

By W. S. HUBBARD AND W. L. MITCHEL  
Received March 22, 1915

In the past few years there have come on the market several syrups under various trade names for the use of the manufacturer of fountain supplies, canned

<sup>1</sup> *Ann. chim. phys.*, **18** (1899), 415.

<sup>2</sup> This title might better be "The Hydrolysis of Sugar Solutions at Elevated Temperatures," but to the manufacturer the present title better conveys the idea of the process used.—AUTHORS.

fruit and similar lines requiring a heavy syrup. It is claimed for these syrups that they are better than ordinary sugar syrup in that they will not crystallize out and some even claim that they are sweeter. It is quite well known, however, that these syrups are invert sugar and when they have been correctly prepared will not crystallize out and do make a superior article to use in many food products.

Tartaric acid is used in the preparation of at least one of these syrups on the market, and there is no reason why acetic acid should not be used, for it could be gotten rid of easily. The syrup in which tartaric acid had been used, however, crystallized out into a solid mass after standing two or three months. One in which we were unable to detect any catalytic agent was at the end of six months in as good condition as at the beginning. The latter contained about 46 per cent invert sugar while the former had about 75 per cent.

That bacteria, enzymes, acids, salts, elevated temperatures<sup>1</sup> and carbon dioxide<sup>2</sup> bring about hydrolysis of sugar solutions is known. Ordinary heating brings about hydrolysis, but according to Lund<sup>3</sup> if the air is excluded or the carbon dioxide in the air eliminated, no inversion occurs even on heating 24 hours at 100° C. Lippman<sup>4</sup> and Sheibler<sup>5</sup> found that it was necessary to have moisture present with the carbon dioxide. They report that by raising the temperature and increasing the pressure a complete inversion could be brought about. Follenenius<sup>6</sup> claims to have obtained a very pure invert sugar by injecting a boiling sugar solution into a vessel of carbon dioxide at a pressure of 1.25 to 1.5 atmospheres; others,<sup>6</sup> however, were not able to achieve such good results. When sugar solutions are hydrolyzed by heat alone or by superheated steam<sup>6</sup> a certain amount of color<sup>7</sup> develops which, of course, is objectionable in a commercial article. This investigation was taken up with the idea of finding under what conditions hydrolysis can be successfully carried on without caramelization. Unfortunately, however, we have not been able to carry the work to the point we should desire before publishing, but due to the fact that both of us have since engaged in other fields and see no very immediate prospects of completing the work, we have decided to publish our results. We consider our data of sufficient importance and value to many manufacturers who have been paying a high price for a trade name, to warrant publication.

An autoclave in the bacteriological laboratory was used for obtaining the elevated temperatures and pressure: 250 cc. Erlenmeyer flasks of Jena glass of as near the same shape and age as possible, were employed. They were stoppered with cotton. It was desired to have a glass as insoluble as possible and free from imperfections to avoid introducing outside factors: our final results may have justified this. In the first

<sup>1</sup> Lippman, "Chemie der Zuckerarten," **2**, 1225-1226.

<sup>2</sup> Lippman, *Ibid.*, **2**, 1240.

<sup>3</sup> Lund, *Ber.*, **9**, 277.

<sup>4</sup> Lippman, *Ibid.*, **13**, 1823.

<sup>5</sup> Lippman, *Ibid.*, **2**, 1240.

<sup>6</sup> O. Loew, *Zischr. Chem.*, **1867**, p. 510.

<sup>7</sup> Eckleben, Lippman, "Chemie der Zuckerarten," **2**, 1225.



set of experiments ordinary distilled water was used having a conductivity of about  $6 \times 10^{-6}$ . The invert sugar was determined by titration with Fehling's solution which had been standardized against chemically pure dextrose. The results of the experiments are given in Table I.

The pressures are expressed in kilograms per square centimeter above atmospheric pressure.

TABLE I—EXPERIMENTAL RESULTS

PRESSURE Above atmospheric Kg. per sq. cm.	TEMP. ° C.	TIME Hrs.	CONCENTRATION		PER CENT INVERSION	
			G. Sugar	Cc. Water	Beet Sugar	Cane Sugar
1	120	1	50	50	0.78	1.33
1	120	2	50	50	3.40	10.25
1	120	3	50	50	12.38	31.98
1.25	123.5	1	150	150	5.97	....
1.25	123.5	1	100	200	8.46	....
1.25	123.5	2	75	50	38.76	....
1.25	123.5	2	50	200	42.18	....
1.5	127	1	25	25	9.65	15.29
1.5	127	2	25	25	54.40	75.72
1.5	127	3	25	25	91.02	93.72

An analysis of the results in Table I leads one to believe that the cane sugar solutions hydrolyze more readily than beet sugar, but from another series of experiments which we ran we would say that it depends upon the purity of the sugar used. Cane sugar is perhaps more likely to be pure, and, therefore, less likely to contain negative catalyzers. Of course, if beet sugar contains impurities, one might expect it to contain a catalyzer, but such does not seem to be the case, at any rate with the samples we examined. It will be noticed that by increasing the temperature and pressure the inversion increases and by lengthening the time sufficiently 100 per cent could be produced. From the 123.5° runs it seems evident that concentration plays a part and within certain limits it might be said that the more dilute the greater the hydrolysis.

We also ran a set of experiments in which the temperature was 124° C. and the pressure 1.375 kg. We used cane sugar, beet sugar, and rock candy. To dissolve the sugar, ordinary tap water which was slightly alkaline, the distilled water already mentioned and distilled water which had been recently boiled, were used. Here we found that in each case where the tap water was used that the hydrolysis had been retarded very considerably and the resulting solution was brown, showing considerable caramelization; this was not shown in any of the other runs. The beet sugar showed the same amount of inversion as the cane (both of these samples were different from the material used in the first set of experiments), and the rock candy showed considerably greater inversion in every case. This would seem to indicate that the purer the sugar the greater the inversion.

The inversion is undoubtedly due to the hydrogen ion concentration of the solutions and we had hoped to make such measurements. Kullgren<sup>1</sup> states that the inversion of a sugar solution may be almost completely accounted for by the degree of dissociation of water and sugar with the rise of temperature.

We believe that a concentration of 1 sugar : 5 water will give the most satisfactory results when a pressure of 1.375 kg. and a temperature of 124° C. is used; the time can be adjusted to suit the needs. Since a syrup containing 85 sugar : 100 water is

usually needed in preserving and the amount of invert sugar in the syrups on the market is about 50 per cent then a more dilute solution might be started with, the inversion run to 90 per cent or more if desired and the necessary sugar to bring it up to the proper concentration added later. It is necessary to avoid too great concentration when inverting and also too great a temperature and pressure or there will be some caramelization, a thing which, of course, must be avoided. It is obvious that the manufacturer in making these invert sugar solutions must choose sugar and water with considerable care.

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### REDUCTION OF COPPER OXIDE IN ALCOHOL VAPOR IN REDUCING SUGAR DETERMINATIONS AND COPPER ANALYSIS

By A. WEDDERBURN

Received January 14, 1915

In the usual gravimetric invert sugar determination, the reduced copper is weighed as  $\text{Cu}_2\text{O}$  or after ignition as  $\text{CuO}$ . In weighing either oxide there is always some doubt as to the accuracy of the result. It is difficult to dry the cuprous oxide with certainty that some oxidation does not occur and further the oxide is liable to be contaminated with organic matter, giving a high result. If ignited to the higher oxide, great care is necessary that the oxidation be complete and that the crucible be not held in the reducing flame, the action of which would cause a partial reduction. Even if the cuprous oxide is heated in a muffle furnace considerable time and care are necessary to insure a complete oxidation to  $\text{CuO}$ . The hygroscopic nature of cupric oxide makes it difficult to weigh with accuracy. In the hands of the ordinary laboratory assistant I have found a difference of as high as 12 mgs. after careful re-ignition of the weighed cupric oxide.

The ideal method is to weigh the copper in the metallic state. In accurate work the metal is obtained by the electrolytic method or by reducing the oxide in hydrogen. Both of these methods require considerable manipulation and time, also special apparatus not available in most sugar-house laboratories.

With the purpose of simplifying the electrolytic method and avoiding the use of expensive platinum cathodes, I made some experiments in electrolytically depositing the copper directly from alundum crucibles on copper cathodes, with partial success. I found some difficulty in cleaning the copper cathodes perfectly, prior to weighing. Mr. G. L. Spencer<sup>1</sup> advised that the copper could be readily cleaned by heating to redness and immersing in strong alcohol. This suggestion led to the reduction method described below.

The cleaning action of the alcohol is merely the reduction of the film of oxide to metallic copper and it interested me to know to what extent a precipitate of copper oxide could be reduced by the same means. A precipitate of cuprous oxide was collected on an

<sup>1</sup> Z. physik. Chem., 41, 415.

<sup>1</sup> Chief Chemist of the Cuban-American Sugar Company.



alundum crucible, washed with hot water, the crucible heated to redness and immersed in 95 per cent alcohol. The reduction was complete, the deposit of metallic copper adhering very firmly to the walls of the crucible. A number of trials with solutions of known strength gave very accurate results, but the shock to the crucibles was too great, many of them cracking after being used two or three times.

To avoid the breakage of crucibles the reduction was next tried in the vapor of alcohol and with entire success. The details of the method follow.

Collect the suboxide of copper on an alundum filtering crucible, using Spencer's filtering funnels with suction. Thoroughly wash with hot water followed by alcohol. Heat the crucible to redness a sufficient time to burn off any organic matter that may accompany the copper oxide. Allow the crucible to cool until the redness just begins to disappear and then immerse it in an atmosphere of alcohol vapor as follows:

Bend the wire ends of a small pipe stem or silica covered triangle so as to form a tripod support for the crucible and set the tripod on the bottom of a 400 cc. beaker, preferably of metal. Put into the beaker sufficient strong alcohol (denatured alcohol will answer) to cover the bottom to the depth of about 1 cm. and cover the beaker with a watch glass. Heat the alcohol to boiling and continue heating until the vapors begin to condense on the under side of the cover glass, then place the hot crucible on the support above the alcohol and replace the cover glass. If the crucible is too hot the alcohol may take fire but the flame may be readily extinguished by blowing directly on top of the cover glass, and no harm is done. Allow the alcohol to continue to boil a moment after putting in the crucible, then remove the beaker from the source of heat. The heat radiated from the crucible will prevent any further condensation of alcohol on the cover glass. The crucible should remain in the covered beaker until cooled to a temperature a little above that of the alcohol vapor to prevent oxidation of the copper. About 3 or 4 minutes is sufficient. It may then be taken from the beaker and the cooling be finished in a desiccator, preliminary to weighing. If the crucible is quite cold when taken from the beaker it should be moistened with a little pure alcohol and this be burned, holding the crucible in an upright position. After the alcohol burns off the crucible is ready for cooling in the desiccator. A porcelain Gooch may be used if preferred.

The reduction to metallic copper is almost instantaneous and is complete. The results are identical with those by reduction in hydrogen, closely approximating the electrolytic method.

This method may be used in copper analysis, the separations being made in the usual way and the copper collected in any form readily burned to the oxide. If in form of copper sulfide the precipitate forms in clots and is burned to the oxide with difficulty. It is preferable to dry the sulfide, roast it gently, and then with a glass rod flattened at one end, crush it to a powder. The rod should be wiped off with a piece of ashless filter paper and the paper burned

in the crucible. The heating may then be continued to drive off all sulfur and the oxide reduced in alcohol vapor.

THE CUBAN-AMERICAN SUGAR COMPANY  
CENTRAL "TINGUARO," PERICO, CUBA

#### THE DETERMINATION OF LINT IN COTTONSEED-MEAL

By R. N. BRACKETT  
Received January 7, 1915

While at first sight it might appear an easy matter to determine the amount of lint in cottonseed-meal by purely mechanical means, it has been found impracticable to do so with any degree of accuracy. The following chemical method of estimating the lint was worked out and found to give very satisfactory results:

As preliminary to the work it was first ascertained that alkali and acid of 1.25 per cent strength, as used for crude fiber<sup>1</sup> determinations, was practically without action on lint.

A sufficient amount of cottonseed was then freed from lint by first picking and finally singeing the last portions carefully to avoid injury to the seed. The seeds were then cut open and the meats removed completely from the hulls.

Crude fiber<sup>2</sup> was prepared from both the hulls and the meats, by the method above referred to. The crude fiber thus prepared was treated, in 0.2-gram portions side by side with the same weight of lint, on a boiling water bath, with 25 cc. of a solution of zinc chloride for three minutes, the time required to dissolve the lint. In this way the action of the zinc chloride<sup>3</sup> solution on the crude fiber was determined, and the necessary correction made in carrying out a determination of lint in ordinary cottonseed-meal. The zinc chloride solution was prepared by dissolving metallic zinc in concentrated hydrochloric acid, concentrating until the solution solidified on cooling, and then adding twice the weight of 40 per cent hydrochloric acid. On treating the crude fiber and lint with the zinc solution, the contents of the beakers were stirred vigorously during the three minutes necessary to dissolve the lint, and filtered hot through weighed porcelain Gooch crucibles with asbestos mats; the residues in the case of the fibers were washed with 25 cc. of the zinc solution, then with water and finally with a little 95 per cent alcohol dried and weighed.

EXAMPLE—On treating 0.2-gm. portions of (a) crude fiber from hulls, (b) crude fiber from meats, and (c) "crude fiber" from a cottonseed-meal, with 25 cc. of a zinc chloride solution for three minutes, the amount dissolved was as follows: (a) 0.0687 g., (b) 0.0678 g. and (c) 0.1000 g. The correction was, therefore, 0.06825 gram. Hence the amount of lint in the "crude fiber" from the cottonseed-meal was 0.1000 — 0.06825 = 0.03175 gram. But the

<sup>1</sup> Methods of Analysis, A. O. A. C., *Bull.* 107, revised, p. 56.

<sup>2</sup> This crude fiber includes ash ingredients of the fiber. The ash is, however, so small in amount as to be negligible, unless a large proportion of hulls is contained in the cottonseed-meal. Only in the latter case would it be necessary to take the ash of the fiber into account in calculating the amount of lint in the meal.

<sup>3</sup> "Cross-Bevan's Method for Cellulose"—Cohn's "Tests and Reagents," p. 52.



meal, on analysis, gave 10 per cent of "crude fiber," which gives 1.5875 as the per cent of lint in the cottonseed-meal, since 2 grams of the cottonseed-meal contained 0.03175 gram lint.

To further test the method the following mixtures were made:

(a) 1 gm. of cottonseed-meal with 0.1 gram of lint.

(b) 1 gm. of cottonseed-meal with 0.2 gram of lint.

The crude fiber and lint amounted in (a) to 0.2001 gram and in (b) to 0.3032 gram. The factor for a new zinc chloride solution based on the use of 50 cc. for three minutes was 0.05125 gram.

	(a)	(b)
Crude fiber and lint.....	0.2001 g.	0.3032 g.
Crude fiber residue.....	0.0393	0.0323
	0.1608	0.2709
Correction.....	0.05125	0.05125
Lint.....	0.10955	0.21965
Hence, per cent lint in mixture.....	9.96	18.30
Calculated per cent lint in mixture.....	10.53	17.99

The method as given was worked out under the immediate direction of Assistant Professor J. H. Mitchell by two students of the last senior class, as a thesis. With more careful work and experience, no doubt much more accurate results could be obtained.

At the commencement of the work Schweitzer's reagent (an ammoniacal solution of copper hydroxide) was tried, but the solution as prepared by the students failed to dissolve lint.

Acknowledgments are due Mr. Mitchell for supervising the work, and to Messrs. J. M. McIntosh and E. R. Gilmore, the two students, for their careful and faithful prosecution of the work.

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## SOME IMPORTANT CONSTITUENTS IN THE FRUIT OF THE OSAGE ORANGE

By J. S. MCHARGUE

Received February 8, 1915

The Osage orange (*Maclura pomiferum*) is a small tree which, when first discovered, was growing wild in the southwestern portion of the United States between the Arkansas and Missouri rivers. This particular section of the country was for many years the home and hunting grounds of the Osage Indians. To them this tree was of economic importance for two reasons—from the trunk they made bows which possessed superior elasticity, and from its fruit they obtained a juice which possessed all the necessary adhesive properties for making their war paint. On account of this association with this tribe of Indians and from the resemblance of the fruit to that of the true orange, the tree has received the popular name of Osage orange, although there is no botanical relation between the two plants.

The chief source of value of this plant to the white man has been, first, for growing rural hedges, and secondly, for a crude yellow dye which is obtained from the roots. Owing to its adaptability to the climatic conditions existing in the Mississippi valley it may be found growing in almost any part of this area today, although its use as a hedge is being abandoned.

Through Central Kentucky many farmers have

allowed their hedges to go untrimmed or permitted the plant to grow in out-of-the-way nooks until no small area is covered with this tree. The young tree grows rapidly on good land and the female trees begin bearing large quantities of fruit at from six to ten years of age.

At maturity the fruit has a greenish yellow color, an average diameter of 3½ inches and an average weight of one to one and a half pounds. The fruit, or hedge balls, as they are commonly called, consists of a dense pear-shaped core at the center from which radiate rather long, irregular sized cells that terminate in an enlarged or club form, thus making an irregular surface. The cells are made up of two parts, the milk sacks and the seed sacks. The milk sacks form about two-thirds of the entire length of the cell and extend to the surface. The seed sacks lie beneath the milk sacks and are attached to the core at their base. The milk sacks contain a milky, mucilaginous fluid which in the ripe fruit is neutral to litmus, reacts only slightly with a tincture of guaiacum for oxidases, has an insipid taste and an odor similar to that emitted by the crushed twigs of cedar.

In 1912 considerable interest was aroused through newspaper dispatches emanating from Professors Emerson and Roess of the University of Kansas, who stated that they had discovered in the fruit of the Osage orange a new and cheap source of India rubber. This announcement, according to Fox,<sup>1</sup> created considerable interest among the rubber factories generally and perhaps more in particular among those at Akron, Ohio. Accordingly, Fox read a report of his previous investigations on the Osage orange before The Eighth International Congress of Applied Chemistry, at New York, in 1912. His investigations show that the Osage orange does not contain rubber of any commercial importance.

So far as the literature shows, the above summarizes the work that has thus far been done on the Osage orange from any standpoint.

Recently there appeared, in one of our leading farm journals, an inquiry as to the chemical composition of the Osage orange. This paper also stated that certain farmers in Illinois had been feeding the oranges to their stock and found that they ate them with considerable relish.

In order to find out more definitely concerning the composition of this fruit, a number of oranges were collected in November of 1914 and analyzed (see Tables I and II).

The oranges were prepared for analysis as follows: the outside milky cells were pared off to the seeds; the part containing the seeds was pared off to the core, and each portion dried and kept separately. After drying, the milky portion was ground fine for analysis.

The acetone extract is a brownish, semi-solid resin, at ordinary temperature.

The oranges contain a rather large amount of oval-shaped seeds, the kernels of which are approximately ⅜ in. long and 1/8 in. thick. They are easily separated from the hulls when dry. Kernels were separated from the hulls and dried at 100° C.

<sup>1</sup> Orig. Comm. 8th Inter. Cong. App. Chem., Appendix, pp. 593-597.



The oil from the kernels has a viscosity slightly less than that of either refined cottonseed oil or linseed oil. It absorbs its maximum amount of oxygen in

TABLE I—ANALYSIS OF THE OSAGE ORANGE (PERCENTAGES)

H <sub>2</sub> O in ripe fruit.....	80.00
Gums and resins in dry pulp (acetone extr.).....	29.30
Nitrogen in dry pulp.....	2.81
Protein in dry pulp (N × 6.25).....	17.56
N in pulp after acetone extraction.....	3.42
Protein in pulp after acetone extraction (N × 6.25).....	21.34
Oil in seed (ether extr.).....	42.04
N in oil-free meal.....	10.80
Protein in oil-free meal (N × 6.25).....	67.50

MINERAL CONSTITUENTS	Dry pulp	Dry pulp after extracting with acetone	Oil-free meal
CaO.....	0.16	0.23	0.24
MgO.....	0.20	0.28	0.73
K <sub>2</sub> O.....	3.82	5.40	1.32
Na <sub>2</sub> O.....	0.13	0.18	0.19
P <sub>2</sub> O <sub>5</sub> .....	0.67	0.94	0.60
Ash (crude).....	6.60	9.33	4.60

from fifteen to twenty hours, at 100° C. and thickens to a resin-like mass. Data obtained by analysis are given in Table II with those of oils having similar specific gravity, iodine numbers and saponification values as given in Allen's "Commercial Organic Analysis."

TABLE II—ANALYSES OF OSAGE ORANGE SEED OIL AND SIMILAR OILS

	Specific gravity	Iodine number	Saponification value	Saponification cation equivalent
Osage orange seed oil.....	0.929	134-136	192	....
Linseed oil.....	0.931-0.941	175-201	190-201	....
Sunflower seed.....	0.924-0.926	123-136	188-193	....
Cottonseed oil.....	0.922-0.925	108-110	191-196	....
Peanut oil.....	0.917-0.921	85-103	190-197	291.97

From the analyses in Tables I and II it may be seen that the pulp and seed of the Osage orange contain valuable feed, fertilizer, oil, and resin constituents. The dried pulp of this fruit contains 29.30 per cent resins and gums and in addition, more nitrogen and more than twice as much potash as wheat bran.

From the seed a new oil is obtained which has not been previously described. This oil has a light lemon color, a viscosity below that of refined cottonseed and linseed oils, a very pleasant odor and an insipid, oily taste. Its physical properties, such as specific gravity, iodine number, saponification value and oxygen absorption rate, etc., show that it is a semi-drying oil belonging to the linseed oil class. The yield of this oil is equal to that of linseed and peanut, and 1.7 times that of cottonseed.

The analysis of the oil-free cake shows that it contains 10.80 per cent of nitrogen, which is equivalent to 67.50 per cent of protein. This is 1.8 and 1.5 times more nitrogen than is contained in linseed and cottonseed meal, respectively. Meat scrap contains about 1 per cent more nitrogen than the oil-free cake of Osage orange seed.

It is also well known that the wood of the Osage orange possesses excellent properties of elasticity, durability and fineness of grain. These valuable properties, in connection with that of the fruit, should make this tree a possible economic factor in the reforestation of abandoned farm lands. It is also quite likely that the foliage of this tree would possess an additional fertilizing value with respect to nitrogen and potassium over many of our common forest trees.

This tree, under favorable conditions, produces a trunk two feet in diameter, and grows to a height of sixty feet; during its period of growth the female

tree produces many tons of fruit. Therefore, it is quite probable that with due care and intelligence this tree could be made the source of a profitable industry through the utilization of its timber and the different products of its fruit.

KENTUCKY AGRICULTURAL EXPERIMENT STATION  
LEXINGTON

## ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT OF FEED-STUFFS

By J. B. RATHER<sup>1</sup>

Received October 27, 1914

It has long been known that the extraction of dried samples of plant and animal products with ether for 16 hours, as in the determination of fat, does not completely remove ether-soluble material. The extraction has, however, been considered complete enough for practical purposes. Any ether-soluble matter in excess of that obtained from the usual ether extract, after deducting any possible nitrogenous matter and ash, would fall within the group known to agricultural chemists as "Nitrogen-free extract."

Browne<sup>2</sup> states that upon pepsin digestion of steer feces and water digestion of molasses feeds, etc., considerable material is rendered soluble in ether, in excess of the ordinary ether extract.

Fraps and Rather<sup>3</sup> show that chloroform extracts from hays and fodders, previously extracted with ether, more or less material which is soluble in ether. Generally this is considerably less than the previous ether extract of the same samples.

### EXPERIMENTAL

Twelve samples of concentrated feeding-stuffs and twelve samples of hays and sheep excrements from them were studied.

### AMOUNT OF ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT

The determinations listed below were made and the results recorded in Table I.

1. ETHER EXTRACT—The material soluble in ether, the "crude fat," was determined by the official method<sup>4</sup> of the A. O. A. C.

2. ETHER-SOLUBLE MATTER IN ALCOHOLIC SODA EXTRACT—This is the sum of the unsaponifiable matter, fatty acids, and saponified residue, of the alcoholic soda extract of these samples determined by the alcoholic soda method.<sup>5</sup>

3. ETHER-SOLUBLE MATTER NOT DIRECTLY EXTRACTED BY ETHER—This is the remainder obtained by subtracting the results by (1) from (2).

4. ETHER-SOLUBLE NITROGEN × 6.25—The samples were extracted with ether and the ether-soluble matter obtained in the residue, by the alcoholic soda method. Nitrogen was determined in this by the Kjeldahl method. The factor 6.25 was used because that is the factor with the aid of which the ordinary nitrogen-free extract is obtained, and not because any of the

<sup>1</sup> Under the general direction of G. S. Fraps, chemist. Abstracted by the author from Texas Experiment Station, Bull. 169.

<sup>2</sup> Proc. 20th Conv. A. O. A. C.

<sup>3</sup> Texas Experiment Station, Bull. 162.

<sup>4</sup> (U. S. D. A., Bureau Chemistry, Bull. 107, revised.)

<sup>5</sup> THIS JOURNAL, 7 (1915), 218.



nitrogen was thought to be present in the form of protein.

5. NITROGEN-FREE EXTRACT—The percentage of nitrogen-free extract was obtained in the usual manner by subtracting the sum of the percentages of protein, ether extract, crude fiber, water and ash from 100 per cent. The analyses were furnished through the courtesy of Dr. G. S. Fraps.

6. ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT—This represents the difference between the results by (3) and (4) above, calculated in percentage of nitrogen-free extract.

TABLE I—PERCENTAGE ETHER-SOLUBLE MATTER IN FEED-STUFFS BY VARIOUS METHODS

No.	MATERIALS TESTED	Ether extr.	ETHER SOLUBLE			N-FREE EXTRACT	
			in alc. soda extr.	not directly extracted by ether	N X 6.25	Amt. found by diff.	Ether-soluble matter in
1	Wheat shorts	3.79	5.38	1.59	..	57.65	2.76
2	Corn chops	4.31	4.79	0.48	..	68.01	0.71
3	Cottonseed-meal	15.23	15.15	0.00	..	52.00	0.00
4	Rice bran	7.75	9.66	1.91	..	49.70	3.84
5	Milo maize chops	3.22	3.32	0.10	..	68.70	0.15
6	Cold-pressed cottonseed	7.26	7.81	0.55	..	31.70	1.74
7	Kafir chops	3.20	3.68	0.48	..	68.74	0.70
8	Corn bran	8.59	9.06	0.47	..	61.23	0.77
9	Red rice	1.64	2.36	0.72	..	67.30	1.07
10	Wheat bran	4.10	5.67	1.57	..	51.07	3.07
11	Wheat bran	2.65	3.38	0.73	..	64.22	1.14
12	Rice polish	10.38	11.49	1.11	..	57.76	1.92
13	Tobasa grass	0.92	2.62	1.70	0.19	46.18	3.27
14	Excrement from 13	1.06	3.50	2.14	0.22	43.04	4.46
15	Prairie hay	2.30	3.89	1.59	0.24	47.82	2.82
16	Sudan grass	1.46	3.23	1.17	0.16	48.15	3.34
17	Excrement from 15	2.83	6.25	3.42	0.24	43.28	7.35
18	Excrement from 16	1.90	5.73	3.83	0.21	47.40	7.64
19	Sudan straw	1.44	3.69	2.25	0.24	47.12	4.77
20	Sorghum hay	1.83	3.32	1.50	0.24	46.25	2.72
21	Excrement from 19	1.71	5.37	3.66	0.24	43.81	7.81
22	Moth bean hay	1.55	3.98	2.43	0.28	34.85	6.17
23	Excrement from 20	1.78	5.82	4.04	0.74	43.50	8.74
24	Excrement from 22	3.03	7.01	3.98	0.37	29.14	12.39
	Average for concentrates	6.01	6.81	0.80	..	58.17	1.49
	Average for hays and excrements	1.82	4.53	2.71	0.24	42.96	5.97

The ether-soluble matter in the alcoholic soda extract in excess of that in the ether extract, varies in the concentrates from zero in cottonseed-meal to 1.91 per cent in rice bran, and averages 0.80 per cent. In the hays and excrements from them, it varies from 1.50 per cent in sorghum hay to 4.04 per cent in excrement from sorghum hay, and averages 2.71 per cent, about 150 per cent of the average for the ether extracts of the same samples (see Table I, column 1).

In calculating the ether-soluble matter of the nitrogen-free extract, we have assumed that the ether-soluble matter of the concentrates in column 3 in the table contained no nitrogen. The material may not be completely nitrogen-free, but if it had as much nitrogen, relatively, as the extracts of the hays, which derive their nitrogen in part at least from chlorophyll, the average nitrogen content would be only 0.07 per cent calculated as protein.

The ether-soluble matter in the nitrogen-free extract of the concentrates varies from zero in cottonseed-meal to 3.84 per cent in rice bran and averages 1.49 per cent. The ether-soluble matter in the nitrogen-free extract of hays and excrements from them varies from 27.2 per cent in sorghum hay to 12.39 per cent in excrements from moth bean hay, and averages 5.97 per cent.

#### THE NATURE OF THE ETHER-SOLUBLE MATTER IN THE NITROGEN-FREE EXTRACT

By subtracting the percentages of the various

constituents of the ether extract from those of the ether-soluble portion of the alcoholic soda extract (results are given in a preceding article) and calculating the remainder in percentage of nitrogen-free extract, the general nature of the ether-soluble portion of the nitrogen-free extracts of these samples may be determined. This has been done and the averaged results are shown in Table II:

TABLE II—PERCENTAGE COMPOSITION OF ETHER-SOLUBLE CONSTITUENTS OF THE NITROGEN-FREE EXTRACT

DETERMINATION	CONCENTRATES			HAYS AND EXCREMENTS		
	Max.	Min.	Av.	Max.	Min.	Av.
Unaponifiable	22	0	2	15	0	3
Total fatty acids	100	71	98	44	17	30
Saponified residue	49	0	0	80	40	67

While the minimum figure is given in Table II as zero, in fact some of the results were negative. The averages shown were obtained from the algebraic sums of these differences.

In the concentrates the ether-soluble matter in the nitrogen-free extract consists on an average almost entirely of fatty acids. The variations are considerable in case of the saponified residue and the unaponified matter.

In the hays, and excrements from them, the principal constituents of the ether-soluble matter in the nitrogen-free extract consist of saponified residue (including chlorophyll products) with some fatty acids and a little unaponifiable matter, probably wax alcohols.

#### THE UTILIZATION VALUES OF THE ETHER-SOLUBLE MATTER OF NITROGEN-FREE EXTRACT

Digestion experiments on the six hays studied above were made with sheep.<sup>1</sup> The results are shown in Table III:

TABLE III—PERCENTAGE UTILIZATION VALUES OF SOME ETHER-SOLUBLE CONSTITUENTS OF THE NITROGEN-FREE EXTRACT

	Maximum	Minimum	Average
Fatty acids	36.7	0.0	11.2
Saponified residue	37.8	12.6	21.7
Ether extract	59.5	19.3	35.5

In the hays examined the fatty acids had a utilization value of zero in four cases, and averaged only 11.2 per cent available. The saponified residue was utilized to a greater extent, with an average of 21.7 per cent. These figures are considerably lower than the average for the utilization of the ether extract ("crude fat") of the same hays (35.5 per cent). The fatty acids in the nitrogen-free extract of the hays examined were only slightly available to sheep, and the saponified residue was utilized only about 60 per cent as well as the ether extract of these hays.

#### SUMMARY

The nitrogen-free extract of twelve concentrated feeding-stuffs contained from 0 to 3.84 per cent of ether-soluble material, and averaged 1.49 per cent. The nitrogen-free extract of six hays and six excrements from them contained from 2.72 per cent to 12.39 per cent of ether-soluble material, and averaged 5.97 per cent.

In the concentrates examined, this ether-soluble material consisted on an average of 2 per cent un-

<sup>1</sup> For the method of conducting the experiments see Texas Experiment Station, *Bull.* 147.



saponified and 98 per cent fatty acids. In the hay and excrements from them it consisted on an average of 3 per cent unsaponified, 30 per cent fatty acids, and 67 per cent saponified residue.

The fatty acids in the nitrogen-free extract of six hays were utilized by sheep, 11.2 per cent on an average, and the non-fat organic acids 21.7 per cent. Of the same hays 35.5 per cent of the ether extract ("crude fat") were utilized.

TEXAS EXPERIMENT STATION  
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COMPOSITION OF CERTAIN FISH FERTILIZERS FROM THE PACIFIC COAST AND THE FERTILIZER VALUE OF DECREASED FISH SCRAP

By JOHN R. LINDEMUTH<sup>1</sup>  
Received February 4, 1915

The availability of the fish waste of the Pacific Coast as a fertilizer is one of the investigations now being carried on by this Bureau in its search for possible sources of fertilizer material under the direction of Dr. F. K. Cameron. In this connection Dr. J. W. Turrentine, during the summer of 1913, visited the fishing and fish-canning industries along the coast of California, Oregon, Washington, and Alaska. The results of his investigations appeared as a bulletin of this Department. In conjunction with this work a number of samples of fish scrap prepared from various fish were collected and sent to this laboratory for analysis.

The list comprises samples of the raw cuttings from Humpback salmon, the prepared scrap from Humpback, Chinook salmon, Sardine, Tuna, Whale, and Dogfish. The Humpback cuttings from Alaska were made up of the raw heads, fins, tails and roe. They were shipped in a sealed tin box which was broken open in transit. Formaldehyde had been added to prevent decomposition but some pieces of the scrap were badly decomposed, while others were in a fairly good state of preservation. The altered pieces were separated as far as possible and discarded.

TABLE I—ANALYSES OF SAMPLES OF THE RAW MATERIAL PRODUCED AS WASTE IN THE MECHANICAL DRESSING OF "HUMPBACK" SALMON  
Material Taken from the Floor of the Cannery of the Pure Food Fish Co., Ketchikan, Alaska, July, 1913

	PER CENT CALCULATED TO BASIS OF WET SCRAP					PER CENT CALCULATED TO MOISTURE-FREE BASIS				
	Moisture	Nitrogen N	Phosphoric acid P <sub>2</sub> O <sub>5</sub>	Bone phosphate Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Oil	GALLONS OIL PER TON	Nitrogen N	Phosphoric acid P <sub>2</sub> O <sub>5</sub>	Bone phosphate Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Oil
Roe (1/2 male and 1/2 female)...	68.7	3.68	1.08	2.35	3.18	8.24	11.76	3.44	7.50	10.16
Heads.....	63.2	2.65	1.54	3.36	13.70	35.51	7.20	4.18	9.13	37.22
Fins and tails.....	63.26	3.11	2.20	4.80	11.16	28.94	8.46	5.98	13.06	30.37
AVERAGE.....	64.6	3.02	1.59	3.46	10.43	27.05	8.65	4.44	9.70	28.74

The samples of dry scrap were collected from the respective manufactories and were shipped in canvas sample sacks. Methods of preparation of fish scrap are described in *Bulletin 2* of this Department.<sup>2</sup>

METHODS OF ANALYSIS—The methods of analysis in the main were the same as described by the author in a joint article with E. G. Parker, of the Bureau staff, on the subject, "Some Analyses of Fish Scrap."<sup>3</sup> Before analysis the samples were ground to a powder that would pass a sieve of 16 apertures per linear

inch. Samples of 2 grams each were then dried for about 5 hours or more, according to the kind of fish, in a vacuum oven at a temperature ranging between 75° and 85°. Some types of fish require longer drying than others to remove all the moisture and secure a constant weight. The loss in weight was recorded as moisture. In the case of the sample of raw Humpback cuttings, moisture was determined before grinding by drying to a constant weight in a water-oven. In this operation it is probable that some of the lower volatile oils were lost. In fact, the point where all the moisture is removed without any loss of oil has been very hard to establish, and further work on this subject, together with a study of extraction agents, is expected to be done in the near future by the author. Oil was determined by extracting with ether a 2 gram sample which had been previously dried to constant weight. Nitrogen was determined according to the official method by Mr. T. C. Trescott, of the Bureau of Chemistry. Phosphoric acid was determined by the official gravimetric method. The results appear in Tables I and II.

On the basis of the analysis reported in Table I the value of the raw cannery waste is derived below.

The percentage of nitrogen, 3.02, is equivalent to 3.67 per cent ammonia, NH<sub>3</sub>. This, in the retail market, may be expected to bring \$3.20 per unit; bone phosphate is valued at 10 cents per unit, and oil at 30 cents per gallon. Then:

3.67 per cent NH <sub>3</sub> at \$3.20 per unit.....	\$11.74
3.46 per cent bone phosphate at 10 c. per unit.....	0.35
27.05 gallons oil at 30 c. per gallon.....	8.12
<b>TOTAL VALUE PER RAW TON.....</b>	<b>\$20.21</b>

By present methods in vogue, the manufacturers of fertilizer and oil from this material expect to recover about \$15.00 in values. Present methods, then, can be considered as only 75 per cent efficient. In further substantiation of this conclusion are the results published by Thomas<sup>1</sup> quoted below:

"The averages of all experiments show the following facts: Each ton of salmon offal treated produced 800 lbs. of mixed

oil and fertilizer. Of this amount 200 lbs. was salmon oil and 600 lbs. oil-free fertilizer. The average analysis of the fertilizer thus produced was:

Ammonia..... 14.3 per cent      Bone phosphate... 13.0 per cent

"Estimating the 200 lbs. of oil as being 25 gal., at a price of \$0.32, which seems a fair average, we have then for each ton of offal treated an oil value of \$8, and, estimating the value of a unit of ammonia at \$3.20 and bone phosphate at 10 cents per unit, we have a fertilizer value at:

14.3 per cent ammonia at \$3.20.....	\$45.76	} TOTAL
13 per cent bone phosphate at \$0.10.....	1.30	
		\$47.06 per ton

"Then at 600 lbs. of fertilizer of this quality to the short ton of offal treated, we have \$47.06 × 0.3 = \$14.12, the fertilizer

<sup>1</sup> A. M. Thomas, "Waste in Salmon Canning Industry," *Pacific Fisherman*, [2] 12 (1914), 26.

<sup>1</sup> Scientist in Fertilizer Investigations, Bureau of Soils, U. S. Dept. of Agriculture.

<sup>2</sup> *Bull. 2*, Bureau of Soils, U. S. Dept. Agr.

<sup>3</sup> THIS JOURNAL, 5 (1913), 388.



value of one ton of offal, which gives an available value for one ton of offal of:

Fertilizer..... \$14.12 Oil..... \$8.00 TOTAL VALUE... \$22.12."

In Table I the averages are calculated by doubling the percentages given under heads, since the heads constitute approximately twice as much of the bulk of the scrap as either the roe or the fins and tails. The number of gallons of oil per ton of wet scrap was computed from the percentages of oil, using 0.925 as the sp. gr. of fish oil.

Table II gives the analyses of the samples of prepared scrap. Samples 6 to 10 are of the most important fish, outside of salmon, used in the fertilizer industry on the Pacific Coast. The whale scrap results compare favorably with those given by H. T. Offerdahl-Tarvik<sup>1</sup> of a general whale fertilizer containing 10 to 12 per cent nitrogen and 14 to 15 per cent phosphoric acid, and also with the results given by Stockhardt.<sup>2</sup> Analyses of dog fish were made by the Pacific Products Company of Port Townsend, Washington, on some scrap taken a few days later from the same bin as Sample 10. The results reported by them compare favorably with those of the author and are as follows in percentages:

NH<sub>3</sub>, 15      P<sub>2</sub>O<sub>5</sub>, 3.6      Moisture, 8      Oil, 6.8

The two samples of an English product were examined for comparative purposes. The quantity of the samples, however, was inadequate for complete analysis, and the percentages are low because the samples

scrap, Table III is reprinted from the analyses appearing in "Some Analyses of Fish Scrap."<sup>1</sup>

The salmon scrap has a lighter color and a more pleasant odor than the menhaden scrap. This, again, possibly does not concern the fertilizing value, though there is a possibility that it may affect its demand in the trade. It is said that some agriculturists appraise the value of fertilizer materials by the disagreeableness and strength of their odor. On the contrary, it is a better established fact that considerable prejudice exists against fish scrap on the part of common carriers and the public in general because of its odor. Since nothing is to be lost and something is to be gained by reducing the disagreeable odors of fish fertilizers, the point mentioned is favorable to the salmon scrap. The better smell of the latter is due most probably in greatest measure to the fact that it is dried at moderate temperatures and is not scorched, as inevitably must happen in the hot air driers as now operated on the Atlantic Coast. It is also true that the menhaden scrap is dried in a stream of hot gases generated in a soft-coal fire; the soot from this undoubtedly contributes likewise to the dark color of the product.

Another point of difference between the salmon and menhaden scrap is introduced by the occasional acidulation of the latter. The addition of sulfuric acid to the scrap is practiced most generally to disinfect the undried but freshly cooked and warm "pomace,"

TABLE II—PERCENTAGE ANALYSES OF PREPARED FISH SCRAP

No.	LOCATION AND COMPANY	DESCRIPTION	N	P <sub>2</sub> O <sub>5</sub>	Moisture	Oils(a)
1	Klawack, Alaska: North Pacific Fishing and Trading Co.	Sample from trial run with steam drier	9.39	5.32	5.36	14.96
2	Anacortes, Wash.: Robinson Fisheries Co.	Dry scrap from steam drier	8.26	7.91	5.21	17.36
3	Anacortes, Wash.: Russia Cement Co.	Dry scrap from hot-air drier	9.49	9.26	5.26	8.32
4	Seattle, Wash.: Brandel Chemical Co.	Dry scrap from steam drier	8.76	7.00	3.91	20.02
5	Astoria, Ore.: DeForce Oil Works	Dry scrap from hot-air drier	7.63	12.08	5.11	10.96
6	Monterey, Cal.: Monterey Packing Co.	Sardine scrap	7.97	7.11	5.57	8.42
7	Victoria, B. C.: Canadian North Pacific Fisheries, Ltd.	Whale meal	11.59	0.94	5.41	12.70
8	Victoria, B. C.: Canadian North Pacific Fisheries, Ltd.	Whale bone-meal	3.01	26.08	2.53	Trace
9	San Pedro, Cal.: San Pedro Fertilizer Co.	Tuna scrap	8.54	7.25	4.21	13.27
10	Port Townsend, Wash.: Pacific Products Co.	Dog-fish scrap	12.15(b)	3.59	6.35	7.89
11	London, E. C.: H. Wiskemann Wool Exchange	Fish meal	6.54	4.78	....	....
12	London, E. C.: H. Wiskemann Wool Exchange	Meat meal	8.57	4.56	....	....
13	Key West, Florida	Shark waste	9.34	1.99	13.83	Trace

(a) More accurately, ether extract. This consists principally of oils.

(b) Equivalent to 14.77 per cent ammonia, NH<sub>3</sub>.

contained a large quantity of sand or crushed quartz. Similarly a sample of unedible shark from the Atlantic Coast was examined. In this case the livers alone are used for their oil and the remainder thrown away.

**CHARACTER OF PRODUCT**—The scrap produced from salmon waste is of a very high quality, and is open to criticism, from a fertilizer point, only on the fact of its high content of oil. This amount of oil does have a marked influence on the fertilizing properties of the scrap as is shown in the following pot experiment work. It is further disadvantageous in that it is so much inert material of no fertilizer value. However, the fact that the oil, of high value if extracted, here plays the rôle of a worthless diluent of a less valuable product, has not as much bearing on the value of the scrap as a fertilizer as it has on the economy of the process by which the material is prepared.

**COMPARISON WITH MENHADEN SCRAP**—For the sake of comparison between the salmon and menhaden

and to render it unfit as a breeding place for flies. This is resorted to, as a rule, only when the scrap is being produced at a rate greater than that at which it can be dried. The acidulation frequently is followed by drying. The addition of sulfuric acid to the scrap is supposed to be beneficial in that it "fixes the ammonia" and renders soluble the phosphoric acid of the calcium phosphate constituting the bones. While it induces a disintegration and pulverization of the scrap, and enables the producer to sell the bone phosphate present as soluble phosphoric acid, at the same time it acts as a diluent of slight (if any) fertilizer value, with no rating on a fertilizer basis.

In the foregoing comparison of scrap from salmon and menhaden, respectively, it is not intended that the idea shall be conveyed that the menhaden scrap for fertilizer purposes is inferior to that from the salmon. It is believed that the ammonia and phosphate of the one is as valuable as that of the other.

FISH SCRAP AS CATTLE AND POULTRY FEED—To

<sup>1</sup> Ber. d. deutsch Pharm. Ges., 23 (1913), 558-559.

<sup>2</sup> Chem. Ackermann, 16 (1870), 52.

<sup>1</sup> Loc. cit.



discuss fish scrap from any point of view other than that of fertilizer perhaps is beyond the province of this paper. It should be pointed out here, however, that in connection with such fertilizer materials as dried blood, abattoir tankage of high-grade, cottonseed-meal, and fish scrap, it is better agricultural practice to feed these to stock, provided, of course, that all barn-yard manures be conserved carefully, than to apply them directly to the soil. It can be taken as thoroughly well established that both the nitrogen and the phosphoric acid, after performing their rôle in the life processes of the adult animal, are eliminated. Then the high food value of these rich foods is utilized and at the same time the fertilizing elements are still available for use on the growing crops. From the point of view of cattle and poultry feed, the salmon scrap must be considered superior to the menhaden. In the first place the acidulated scrap is totally unfit for feeding purposes. Its use in that manner undoubtedly would result in disaster. And in smaller degree, the greater care expended in drying the salmon scrap makes it a more desirable article of food. In fact, when the nature of the raw materials and the sanitary conditions under which it is treated, obtaining in certain manufactories, are considered, it might also be regarded as fit for man's consump-

salmon oil. The amount actually produced, 286,000 gallons, is too small to give it very great importance in the industries. It is rated, however, as a high-grade fish oil. The market price, 30 cents per gallon, against 23 cents for menhaden oil as quoted in 1912, is sufficient evidence of that fact. There is no reason to doubt that it is destined to play an important part as an animal oil when the salmon scrap industry is fully developed and there is enough oil available to make its study and exploitation profitable.

In the absence of more detailed information concerning the physical and chemical properties of salmon oil, it must suffice to say that it is merely a high-grade fish oil. The crude salmon oil is lighter in color than, perhaps, the refined menhaden. Its properties, as now understood, adapt it to the uses to which menhaden oil has been successfully applied, conspicuous among which is its utilization as a lubricant, and especially in the paint and enamel industries.<sup>1</sup>

GLUE—Fish glue made from salmon is regarded as low-grade and of proportionately slight value. In this particular it differs markedly from that prepared from cod skins. It is applied, with success, to the preparation of "sizings" and allied materials.

POT EXPERIMENTS—Series of pot and plot experiments were undertaken by J. J. Skinner, of this

TABLE III—MENHADEN SCRAP  
DESCRIPTION

No.	LOCATION AND COMPANY	DESCRIPTION	Per cent			
			N	P <sub>2</sub> O <sub>5</sub>	Moisture	Oils
1	Kilmarnock, Va.: Eubanks Tankard Co.	Dry scrap (from 6 sacks)	8.93	6.17	6.48	5.91
2	Taft, Va.: Taft Fish Co.	Dry scrap (sample from 525 tons)	8.96	7.75	6.18	6.81
3	Irvington, Va.: Carter's Creek Fish Guano Co.	Dry scrap, dried in hot air and steam driers (from one sack) Fall product	7.70	5.22	11.68	6.62
4	Cape Charles, Va.: Atlantic Fish & Oil Co.	Dry scrap, ground (from 3 sacks)	9.29	6.12	7.86	5.38
5	Cape Charles, Va.: Atlantic Fish & Oil Co.	Dust from grinders	8.80	5.21	7.17	7.55
6	Beaufort, N. C.: Beaufort Fish Scrap & Oil Co.	Dry scrap, hydraulic presses, sample from heap	8.22	5.95	6.13	8.57
7	Morehead City, N. C.: R. W. Taylor	Dry scrap from open heap	8.49	5.95	9.12	8.23
8	Morehead City, N. C.: Chas. S. Wallace	Scrap, dry, from hydraulic presses	7.76	9.65	8.15	7.56
9	Lenoxville, N. C.: C. P. Dey	Ground scrap, sun-dried, hydraulic presses. Sample from heap	7.81	5.85	7.46	7.89
10	Lenoxville, N. C.: C. P. Dey	Scrap, dry, ground, hydraulic presses. Sample from heap	8.29	9.00	7.00	5.40
AVERAGES.....			8.43	6.69	7.72	6.99

tion. It would be interesting to learn whether the oil remaining in the salmon scrap is not of a more digestible nature than that in the menhaden scrap. No experimental data is at hand in substantiation of such a belief; but such appears plausible when it is recalled that the salmon oil is light and sweet and partakes more nearly of the nature of the edible oils, while that from menhaden is dark, heavy and viscous and has a disagreeable odor. There are no differences in the methods of rendering sufficiently great to account for the difference in the natures of the respective oils; their differences must be regarded as inherent.

The subject of the suitability of fish scrap for cattle and poultry feed and the experiments performed relating thereto have been discussed in an earlier publication of this Department and therefore will not be repeated here. In all of the experiments, records of which have come to the attention of the writer, the results have been affirmative and of such a nature as to justify the further exploitation of this food material for that purpose. The reader interested in this phase of the subject is referred to *Bulletin 2*, U. S. Department of Agriculture, "The Menhaden Fish Fertilizer Industry of the Atlantic Coast."

OIL—The literature contains little having to do with

Bureau, to determine whether the residual oil in the fish scrap had an injurious effect on the fertilizer value, and the preliminary results are so very interesting from several standpoints that he has been kind enough to allow me to publish them in part. Fish scrap is undoubtedly an efficient fertilizer as shown by the accompanying photographs and green weights. In every case where scrap was applied there was a decided increase in growth and when oil-free scrap was added a still greater growth was noticeable. This residual oil appears to have a large influence on the fertilizer properties and surely warrants further study and a consequent investigation of the efficiency of present methods of removing the oil.

The effect of these fish scrap fertilizers in soils was tested by growing wheat plants in the treated soil in paraffined wire pots. The plants grew from May 5th to 28th. The paraffined wire pot method is described in *Circular 18* of this Bureau. Fish scrap was added at the rate of 700 lbs. per acre and duplicates were made in every case. There were two types of soil used, the one a loam and the other a sandy loam. The analyses of the fish scrap samples used are given in Table IV.

<sup>1</sup> For a brief discussion of menhaden oil see U. S. Dept. Agr., *Bull. 2*, p. 46, et seq.



The green weights of the plants are given in Table V. It will be noticed that the Hagerstown loam was the better producing soil. The tuna scrap was not

TABLE IV—PER CENT ANALYSES OF SAMPLES USED IN POT EXPERIMENTS

FISH	N	P <sub>2</sub> O <sub>5</sub>	Moisture	Oil
Salmon	9.39	5.32	5.36	14.96
Sardine	7.97	7.11	5.57	8.42
Tuna	8.54	7.25	4.21	13.27
Menhaden	8.22	5.95	6.13	8.57

very effective in the case of the Orangeburg sandy loam but shows much better results when added to the Hagerstown loam.

TABLE V—GREEN WEIGHTS (GRAMS) OF WHEAT PLANTS

LOAM USED	Hagerstown	Orangeburg sandy
Soil untreated	2.45	1.65
Soil + Salmon fish scrap—oil-free	4.00	3.15
Soil + Salmon fish scrap	3.05	2.05
Soil + Sardine fish scrap—oil-free	3.25	3.04
Soil + Sardine fish scrap	2.55	2.70
Soil + Tuna fish scrap—oil-free	3.52	2.00
Soil + Tuna fish scrap	3.25	1.90
Soil + Menhaden fish scrap—oil-free	3.60	2.70
Soil + Menhaden fish scrap	3.10	2.50

REMOVAL OF RESIDUAL OIL—The recovery of the residual oil can undoubtedly be accomplished by an extraction with gasoline, similar to the process now in vogue in the degreasing of garbage tankage. In this process the tankage is put in a large cylindrical tank and washed with gasoline until the gasoline drawn off is colorless. The residual gasoline is driven off by

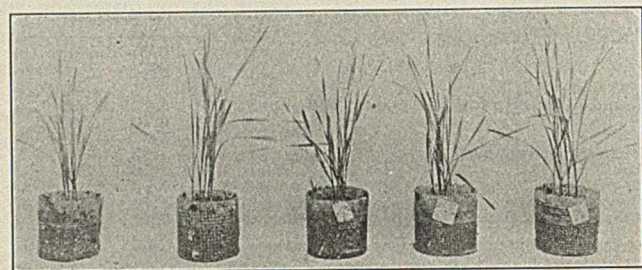


FIG. I—HAGERSTOWN LOAM AND OIL-FREE FISH SCRAP  
 1—Untreated Soil  
 2—Soil + Oil-free Salmon Scrap  
 3—Soil + Oil-free Sardine Scrap  
 4—Soil + Oil-free Tuna Scrap  
 5—Soil + Oil-free Menhaden Scrap

steam, and the gasoline and oil separated by distillation. The equipment consists of one rotary percolator or washing tank, one condenser, one still for distilling the gasoline from the oil, one oil-finishing tank, two separating tanks for separating the solvent from water, one heater for heating solvent, three pumps, the necessary storing tanks for storing the finished oil and gasoline, two conveyors (one for delivering the material to the percolator and the other for removing the same), boilers, motors, piping, etc.

The removal of the residual oil in fish scrap will not only increase to a great extent its value as a fertilizer, as shown in the preceding experiments, but will seemingly also more than pay for itself in the oil recovered.

The following estimates of the cost of degreasing menhaden scrap have been made. Consideration has been given to the oil recovered only and not to the enhanced value of the fish scrap. These figures are based on works data obtained in the degreasing of garbage tankage. The data have been secured through the kindness of Mr. T. D. Banks, of the Municipal Reduction Plant of Columbus, Ohio, and Mr.

W. J. Springborn, of the New Bedford Extractor Company, of New Bedford, Mass. Both estimate the outlay for buildings and equipment to be \$25,000 for a plant with a capacity of about 10 tons per day. To house the degreasing plant a fire-proof

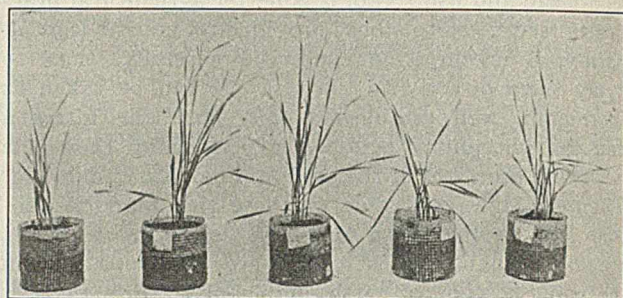


FIG. II—ORANGEBURG SANDY LOAM AND OIL-FREE FISH SCRAP  
 1—Untreated  
 2—Soil + Oil-free Salmon Scrap  
 3—Soil + Oil-free Sardine Scrap  
 4—Soil + Oil-free Tuna Scrap  
 5—Soil + Oil-free Menhaden Scrap

building would probably be regarded as essential. The cost of this would be determined by local conditions. For a fish scrap plant it would not be necessary to erect a building as expensive as that required by a municipal garbage reduction plant such as that made the basis of the above estimate.

The operation of the plant would require the services of two men, who during the actual operation would devote all of their time thereto; if the steam requisite is supplied from the boilers already installed and operated, only a portion of the fireman's time need be charged to the degreasing plant. In the degreasing of garbage tankage the loss in gasoline averages 6 gallons per ton of product while the bulk of the gasoline is redistilled and used over and over again. The following estimate of the operating expenses of an eight-hour day may then be made:

One operator, 25 cents an hour	\$ 2.00
One laborer, 20 cents an hour	1.60
60 gallons of gasoline	7.20
3 tons of coal	4.50
1/3 of fireman's time	0.32
Repairs and miscellaneous expenses	1.00
<b>TOTAL PER DAY</b>	<b>\$16.62</b>
<b>TOTAL PER TON</b>	<b>1.66</b>

Interest on investment, \$25,000, at 6 per cent, is \$1,500, or per ton, on basis of 1,000 ton season's out-

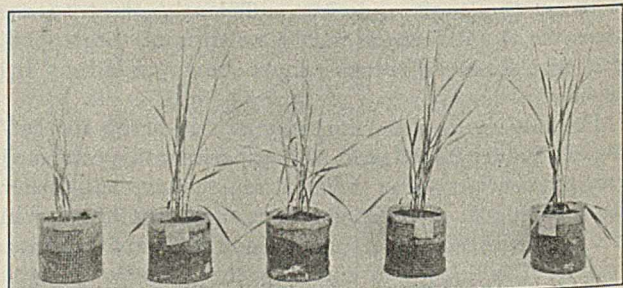


FIG. III—ORANGEBURG SANDY LOAM AND FISH SCRAP WITH AND WITHOUT OIL  
 1—Untreated Soil  
 2—Soil + Oil-free Sardine Scrap  
 3—Soil + Sardine Scrap Containing Oil  
 4—Soil + Oil-free Salmon Scrap  
 5—Soil + Salmon Scrap Containing Oil

put, \$1.50. It should be recalled in this connection that the outlay for equipment and building may be reduced materially below this figure. Hence the total cost of degreasing would be \$3.16 per ton.



Since the analyses of dried menhaden scrap made in this Bureau show the average content of oil to be approximately 6.99 per cent, it may be taken that each ton of scrap would yield 139.80 lbs. of oil, which, at 7.71 lbs. per gal., is equivalent to 18.13 gals. per ton. This at 23 cents per gallon<sup>1</sup> has a value of \$4.17 per ton. The cost of production being \$3.16, the profit per ton in oil recovered would be \$1.00, or for the season's production of 1000 tons, \$1,000.

If such a process were applied to scrap from salmon which, it is recalled, contains 12.69 per cent oil, the profit would be \$6.72 per ton, on the basis of the same operating expenses as above and of 30 cents per gallon for oil. Since the output of the individual plants on the Pacific Coast is not, on the average, 1,000 tons per season, central receiving stations could be erected in the various sections and the degreasing done there.

All the above estimates show that the oil recovered would pay for the process without any consideration being given to the enhanced fertilizer value of the product. When, however, this feature is considered, it is seen from the preceding pot experiments that on the average the fertilizing qualities of the fish scrap are increased by approximately 23 per cent.

#### CONCLUSIONS

The fish waste of the Pacific Coast is very high in fertilizer value. It averages higher than menhaden in its contents, as follows:

**MENHADEN:** Nitrogen, 8.43 per cent; phosphoric acid ( $P_2O_5$ ), 6.69 per cent; and oil, 6.99 per cent.

**SALMON, ETC.:** Nitrogen, 9.31 per cent; phosphoric acid ( $P_2O_5$ ), 6.72 per cent; and oil, 12.69 per cent.

The menhaden industry is much larger and older, but there is no doubt but that the salmon scrap industry will grow rapidly and soon equal the menhaden. This is especially true because of the increasing demands for nitrogenous fertilizers and the availability of salmon cannery waste.

The American Fertilizer Handbook for 1914, in reviewing the fish scrap fertilizer industry, gives the following conclusions: "Probably the most important feature to the fish manure business during the past year was the unusually large number of new companies formed to operate in this line. The industry, which was only a few years ago a comparatively unimportant one, is now one that is attracting the attention of financial men generally."

BUREAU OF SOILS, WASHINGTON, D. C.

#### NOTES ON THE COLORIMETRIC DETERMINATION OF PHOSPHORUS IN SOIL EXTRACTS

By C. E. MILLAR AND F. A. GANGLER

Received March 3, 1915

The colorimetric method for the determination of phosphorus suggested by Veitch<sup>2</sup> and perfected by

<sup>1</sup> This figure is the normal price quoted, but during the last two years the price has advanced rapidly because of poor fishing seasons. The catch in 1913 was only 60 to 70 per cent of the normal, and figures available thus far for this year show the catch to be still lower. At the present time crude menhaden oil is scarce, and the little that is obtainable brings from 37 to 39 cents a gallon. If these prices were applied to the above estimates, the profit would be increased greatly, but since they are not normal, it would be unfair to make general statements based upon them.

<sup>2</sup> J. A. C. S., 25 (1903), 169.

Schreiner and Brown<sup>1</sup> has been used to some extent for a number of years. Little or no data where this method has been applied to soil solutions have been published and the general feeling has prevailed that it was somewhat inaccurate in such work.

The writers were in need of a reliable method for determining small amounts of phosphorus in soil extracts and consequently an investigation of this method was undertaken. A series of tests emphasized the precautions brought out by Veitch: (1) Use filter paper as free of silica as possible such as Schleicher and Schüll's No. 589. (2) Use exact amounts of nitric acid and molybdate solution. The use of a poorer grade of paper caused a reading almost double that obtained when blank determinations were run with the better paper. By varying the amount of nitric acid it was found that quite a distinct color could be almost entirely dissipated. Varying amounts of molybdate solution also affect the color.

With the greatest care in the purification and use of all reagents it was found impossible to get blank determinations without a trace of color and in consequence a small factor of correction was used.

The samples of soil were taken with a 1 in. soil tube to a depth of 3 ft., every foot composing a separate sample. The samples were rubbed through a 1/4 in. sieve and the soil thoroughly mixed by rolling in an oil cloth. The sample was then quartered with a large spatula and two 100-gram samples weighed out. Each sample was obtained by taking portions from opposite quarters. Each 100-gram sample was rubbed with 500 cc. of water for 3 minutes in a mortar. After standing for 40 minutes the suspension was filtered in a Chamberland filter: 50 cc. of the filtrate were taken for analysis. This procedure gave two solutions from separate portions of a well mixed sample. The duplicates shown in Table I are determinations on these separate solutions and do not represent determinations on different portions of the same solution.

TABLE I—PARTS PER MILLION  $PO_4$  IN FILTRATES FROM SOILS

Plot No.	Depth Feet	$PO_4$ in duplicates	Plot No.	Depth Feet	$PO_4$ in duplicates	Plot No.	Depth Feet	$PO_4$ in duplicates
1	1	3.00 3.00	6	1	0.75 0.50	10	1	2.50 2.00
	2	3.00 3.00		2	1.00 1.00		2	2.50 2.50
	3	3.00 3.50		3	1.25 1.25		3	2.50 2.50
2	1	5.00 4.50	7	1	2.00 2.50	11	1	1.25 1.25
	2	3.50 4.00		2	2.50 2.00		2	1.25 1.25
	3	2.50 2.50		3	2.00 2.00		3	1.50 1.50
3	1	2.50 2.50	8	1	2.50 3.00	12	1	0.50 0.50
	2	2.50 2.50		2	2.00 2.50		2	0.50 0.50
	3	1.50 1.50		3	2.00 2.00		3	0.75 0.75
4	1	2.00 2.00	9	1	2.50 2.50	13	1	0.00 0.00
	2	2.00 2.00		2	2.50 2.00		2	0.25 0.25
	3	2.00 2.00		3	2.50 2.50		3	0.50 0.50
5	1	1.00 1.00	14	1	2.50 2.50	14	1	1.00 1.00
	2	0.75 0.75		2	2.50 2.00		2	1.25 1.25
	3	1.00 1.25		3	2.50 2.50		3	1.25 1.25

From Table I it would appear that if sufficient care is given to the purity of reagents and to the measuring out of all reagents, determinations of small amounts of phosphorus may be made in soil extracts with considerable accuracy.

AGRONOMY EXPERIMENT STATION  
KANSAS STATE AGRICULTURAL COLLEGE  
MANHATTAN

<sup>1</sup> J. A. C. S., 26 (1904), 1463.



## A NOTE ON THE FORMATION OF TRI-CALCIUM PHOSPHATE ON MIXING GROUND LIMESTONE WITH ACID PHOSPHATE

By R. N. BRACKETT AND BENJAMIN FREEMAN

Received January 4, 1915

About two years ago one of us, while visiting a fertilizer plant, was attracted by a large pile of ground limestone, which, upon inquiry, was found to be used as a filler in preparing lower grade acid phosphate from higher grade. It appeared somewhat strange that manufacturers should deliberately revert the water-soluble phosphoric acid, which they had been at so much pains and expense to produce. Besides, it seemed not improbable that there would be some insoluble phosphoric acid formed with a consequent danger of the manufacturer falling below his guarantee of available, if he took no account of this possibility. The chemist of the plant stated, however, that there was no such danger, as he had tried experiments and did not find any insoluble phosphoric acid formed.

In a recent discussion of the advisability of using ground limestone as a filler in fertilizers carried on in Atlanta, Ga., and published in "The American Fertilizer" during the past two years, the statement has been made that no insoluble phosphoric acid is produced on mixing ground limestone with acid phosphate.

In view of these statements, and because we had not been able to find any published experiments giving figures, it seemed worth while to make a carefully conducted set of experiments to determine whether any insoluble phosphoric acid is produced and, if so, whether the amount would be sufficient to endanger an available phosphoric acid guarantee. In the spring of 1913, therefore, we procured 100 lbs. each of acid phosphate and ground limestone, and after making a careful analysis of each, prepared mixtures as follows:

No.	1	2	3	4
Lbs. acid phosphate.....	14.0	15.5	17.0	10.0
Lbs. ground limestone.....	6.0	4.5	3.0	10.0

The materials were, after grinding separately, weighed as accurately as possible on a grocer's scale,

mixed thoroughly on paper and finally in wooden boxes; the contents of the boxes were then run through a small grinder, and sacked. Samples were drawn from the sacks with an Indiana fertilizer sampler, such as is used by our Fertilizer Inspectors in taking samples. The 4- or 5-pound sample thus drawn was quartered down to about 8 oz. and bottled for analysis.

On making the mixtures a considerable rise of temperature was noted, though it was not measured. Evolution of carbon dioxide took place immediately and continued for many days, as was shown by connecting a bottle of one of the mixtures with a bottle containing lime-water. This experiment was not carried to completion, owing to an unavoidable accident. The mixtures were analyzed at set intervals as shown below.

ACID PHOSPHATE	Per cent	GROUND LIMESTONE	Per cent
Total phosphoric acid.....	16.84	Lime.....	43.62
Water-soluble phosphoric acid.....	13.55	Phosphoric acid	Trace
Insoluble phosphoric acid.....	1.33		

### PERCENTAGE ANALYSES OF MIXTURES

Mixture	No. 1 W-S Ins.	No. 2 W-S Ins.	No. 3 W-S Ins.	No. 4 W-S Ins.
April 21st, immediately after mixing.....	6.15 1.07	8.30 1.15	10.50 1.24	2.40 0.83
May 10th.....	3.05 1.30	5.84 1.26	8.66 1.37	0.99 0.98
June 12th.....	3.31 1.39	6.39 1.66	8.15 1.59	1.10 1.11
Sept. 13th.....	3.38 1.46	3.31(a) 1.33	8.05 1.46	0.87 1.08

(a) This is probably an error as an analysis in November, 1913, gave about five per cent water-soluble.

All figures are the mean of closely agreeing duplicates.

These results seem to warrant the following conclusions:

I—Tri-calcium phosphate is produced on mixing acid phosphate and ground limestone.

II—The formation of the tri-calcium phosphate begins immediately on mixing, but increases slightly on standing, showing that the amount formed is a function of both time and temperature.

III—Considering the closeness with which manufacturers guarantee today, it appears necessary that the formation of insoluble in such mixtures be taken account of in making guarantees.

CLEMSON AGRICULTURAL COLLEGE  
CLEMSON COLLEGE, SOUTH CAROLINA

## LABORATORY AND PLANT

### APPARATUS FOR THE DETERMINATION OF SULFUR IN GAS<sup>1</sup>

By E. R. WEAVER AND J. D. EDWARDS

Received April 8, 1915

The sulfur apparatus which is shown in the accompanying illustration is the same in principle as the well-known Drehschmidt apparatus and its many modifications, the gas being burned and the oxides of sulfur collected by passing the products of combustion through an alkaline absorbing solution. The novel features of the apparatus illustrated are the burner and the combustion chamber.

The burner is similar to one described in a technological paper of this Bureau.<sup>2</sup> The method of igniting the gas and the arrangement of the secondary air in-

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

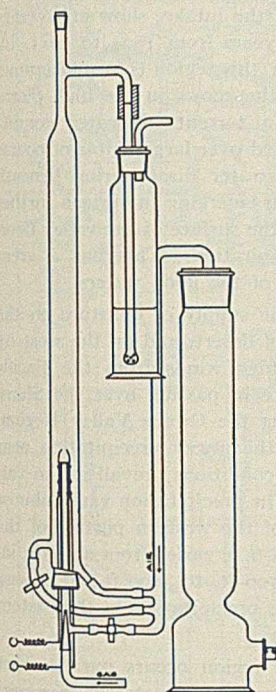
<sup>2</sup> "Determination of Sulfur in Illuminating Gas," McBride and Weaver, *Tech. Paper No. 20*, Bureau of Standards.

lets, however, are different. The platinum spiral which was heated to incandescence in order to ignite the gas has been replaced in the new type of burner with a pair of platinum terminals forming a spark gap. The inconvenience caused by the occasional burning out of the platinum wire is thus avoided. The platinum terminals are sealed to the porcelain burner tube by means of "sealing in" glass. Only a short length of platinum wire is necessary, nickel leads being soldered to the platinum terminals, just below the point where the latter are sealed to the porcelain tube. The stopper which closes the lower end of the combustion chamber also serves as a connector, the porcelain burner tube and the glass T piece being firmly fastened into it by means of Khotinsky or sealing wax. The small tip through which the gas enters just above the primary air inlet is also



held in with Khotinsky cement. The tip can be easily removed for cleaning, or tips of various sizes adapted to the gas to be burned can be inserted. The air necessary for complete combustion after being purified by passage through the large soda lime tower is supplied to the flame in two portions. The primary air is drawn in by the gas as it passes through the small tip; the secondary air enters through the two inlets at the side of the combustion chamber.

The combustion chamber, made of Jena glass tubing, is about 360 mm. long and about 25 mm. in internal diameter. The narrow tube at the top may be used for introducing water when it is desired to rinse out the apparatus; when in operation this tube is closed with a small cork. Satisfactory drainage is



provided by the sloping layer of paraffin or sealing wax covering the stopper at the bottom. When the burner is lighted the secondary inlet air keeps the base of the apparatus cool, but the rest of the combustion chamber up to the side tube is heated so that no condensation takes place on the walls. For that reason it is usually unnecessary to rinse out the combustion chamber. By means of a cork connector the first of a series of wash bottles is attached to the apparatus. Only one wash bottle is shown in the illustration, but three are usually required for satisfactory operation. In order that the suction may pull the gas steadily through

the wash bottles it is necessary that the end of the inlet tube of the first bottle be perforated with a number of small holes. With a single, large opening the operation of the burner is not steady.

Experience has shown that combustion of the sulfur to oxides is incomplete when the flame, because of too little primary air, is smoky or even strongly luminous without smoke, as well as when the supply of secondary air is not sufficient. This latter condition is shown by a flame with an indefinite or "ragged" outline. When the gas and air entering the burner are so regulated that the flame is non-luminous and clear-cut, combustion is complete and the results obtained have been more concordant than those obtained with any other apparatus in use in this laboratory.

The advantages of the apparatus are its small cost, simplicity of construction, and the fact that the difficulty of lighting and regulating the burner usually experienced in the use of apparatus of this type is entirely overcome. The platinum wires become heated by the gas flame and prevent the flame from going out when the pressure fluctuates. With a single adjustment it has been found possible to keep the flame

burning with gases varying in composition from pure hydrogen to pure acetylene and at pressures ranging from two to ten inches of water. Of course, combustion was not complete with such extreme variations. It is, however, easy to adjust the apparatus to burn completely any gas which can be burned in any Bunsen-type burner.

BUREAU OF STANDARDS  
WASHINGTON, D. C.

#### A MODIFIED PIPETTE

By SIDNEY BORN  
Received February 1, 1915

The accompanying sketch shows a form of pipette which has been found very useful in our laboratory. It is made by fusing a stopcock and a piece of bent glass tubing to a pipette. The advantages over the ordinary pipette are:

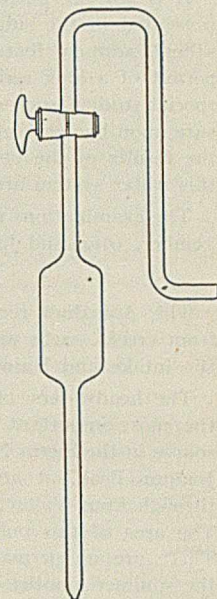
1. Safety—There is no danger of sucking up acid or dangerous liquids.

2. Ease of Manipulation—The stopcock ensures tighter closing and greater accuracy than use of a finger.

3. Accuracy—The line of demarcation is level with eye when using.

4. The pipette can be carried around full without losing any liquid.

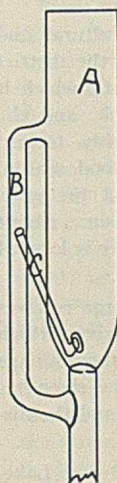
LABORATORY OF THE WM. J. LEMP BREWING Co.  
ST. LOUIS



#### AN APPARATUS FOR THE CONTINUOUS EXTRACTION OF A LIQUID BY ANOTHER, AND HEAVIER LIQUID

By ISIDOR GREENWALD  
Received March 23, 1915

The need of a convenient apparatus for the continuous extraction of a liquid with another, heavier liquid, has been felt for some time. The apparatus shown in the accompanying sketch is simple, compact and can readily be made by any glass-blower at little cost. For use, some of the extracting liquid is placed in the tube A. The liquid to be extracted is then added until the extracting liquid is forced up the tube C almost to its opening into B. The apparatus is then connected, in the usual manner, to a flask containing the extracting fluid and to a condenser. With the apparatus shown, chloroform extracted the caffeine from a 2.5 per cent solution within three hours. For substances extracted with difficulty, the apparatus may be made in a narrower, and longer, form. The apparatus may be modified by the use of ground-glass or mercury-sealed connections and also by the insertion of a stopcock in either A or C for the purpose of removing a sample of the extracted, or the extracting, fluid.



HARRIMAN RESEARCH LABORATORY  
ROOSEVELT HOSPITAL, NEW YORK



# ADDRESSES

## SANITARY FEATURES OF THE LOS ANGELES AQUEDUCT<sup>1</sup>

By E. O. SLATER<sup>2</sup>

A paper upon this subject is of special interest at this time because of the recent termination of two suits brought to enjoin the Los Angeles Bureau of Water Works and Supply from delivering water from the Aqueduct to consumers in Los Angeles, alleging that it is unsafe and unfit for human consumption.

It is not the purpose of this paper to review the testimony presented in the suits, but rather to endeavor to present the salient sanitary features of the system. While time did not permit of a long series of examinations, and although several special studies, such as effect of holding samples, effect of pressure upon bacteria, etc., were made and are not presented here, the results of the principal sanitary studies made to date of this water system are given in this paper.

The examinations were made in September, October, and November, 1914, and January, 1915.

### DRAINAGE BASIN

The Aqueduct receives water from the Owens River, and from creeks, wells and springs west of the Aqueduct between the intake and Haiwee Reservoir.

The headwaters of Owens River consist of several creeks, the most important of which is Deadman Creek, having its source in the Sierra Nevada Mountains on the east slope of San Joaquin Peak, at an elevation of about 11,000 ft. It flows through Long Valley, and in its course is fed by several creeks. The area of this portion of the drainage basin is 444 sq. mi. There are no permanent inhabitants in this region. During the summer months campers and cattlemen frequent the place, and several thousand head of cattle are pastured on the grassy meadow land during the warm months.

The river leaves Long Valley by way of the Owens River gorge. Stream gaugings at the mouth of this gorge show an average flow of 295 cu. ft. per second, from 1903 to 1908, inclusive. The river then flows through Round Valley, and in an easterly direction across the northern end of Owens Valley. Turning south near Laws, a railway station, it flows about three miles east of Bishop, and continues in a southerly direction about 65 mi., emptying into Owens Lake.

The only industries in all this region are agricultural and stock-raising and the most thickly settled part of the district lies about Bishop, a town of about 1,300 inhabitants, which is sewered, the sewage passing through a septic tank, and the effluent emptying into a slough which flows sluggishly toward Owens River, empties into the river during the flood season, but disappears before reaching the river the rest of the year. Bishop is the only sewered town in the drainage basin. About 14 mi. south of Bishop and 3 mi. west of Owens River is located the town of Big Pine, having about 300 inhabitants.

The Owens River between the intake and the gorge receives the drainage from an area of 737 sq. mi. west of the river, which area contains a majority of the inhabitants within the drainage basin. While the Inyo Mountain region east of the river has an area of 1922 sq. mi., there is very little drainage, and the district is sparsely populated because of lack of water.

The Aqueduct intake is about 40 mi. north of Owens Lake. A low diverting dam extending across the river controls the water entering the Aqueduct. The total area tributary to the Aqueduct south of the intake is 479 sq. mi. This region is very

sparsely populated. Independence, lying 2 mi. west of the Aqueduct with a population of about 280, is the only town, and there are a few large stock ranches.

South of the intake and west of the Aqueduct there are several creeks which had an average total discharge for the years 1906, 1907 and 1908 of 198 cu. ft. per second, of which about 50 per cent is discharged into the Aqueduct. In this area also, Black Rock Spring has a constant flow of 18 cu. ft. per second into the Aqueduct. The unlined Aqueduct receives considerable water from the underdrainage. Test wells have been sunk and it is estimated<sup>1</sup> that 140 cu. ft. per second may be developed from underground storage.

The records of the gauging station at Charlie's Butte on the Owens River, about 3 mi. north of the intake, show an average of 442 cu. ft. per second for the years from 1904 to 1911, inclusive. The high water period in this region is in midsummer and is caused by the melting of the snows in the high Sierra Nevada Mountains. The rushing torrent of water coming from the melting snows is discharged over large deltas of coarse material, a great portion of the water disappearing beneath the surface of these fans and again emerging in springs further down near the river, or coming to the surface of the valley floor, is lost by evaporation and transpiration. This has a great leveling effect upon the discharge of the flood waters.

Owens Valley is cut off from the supply of moisture on the east and south by a long stretch of desert, and on the west by high mountains. The moisture-laden winds from the Pacific Ocean lose much of their moisture in passing over the Sierra Nevada Mountains before reaching the Owens Valley Region. The result of these conditions is the heavy precipitation near the top of the range, while desert conditions prevail in the valley only a few miles to the east. The precipitation varies almost directly with altitude over most of the western portion of the drainage basin under consideration. It varies from about 5 in. in the valley at elevations from 3700 ft. to 4000 ft., increasing to about 40 in. at 12,000 ft. The precipitation in the eastern portion of this basin is slight.

While the precipitation in this region occurs over a short period, the snows in the mountains act as a storage reservoir, the water from the melting snow furnishing a run-off over a relatively long period of time. This enables the engineers in charge to predict from four to six months in advance the amount of water that will become available for storage in Haiwee Reservoir. This is an important feature in this system, for it allows time for the development of the wells and for the pumping of the well-water in the region near Independence.

Studies of the supply of surface water available for storage in Haiwee Reservoir show that during years of normal rainfall the reservoir can be maintained half full while supplying a constant draft of 420 cu. ft. per second. These same studies show that in the period of most severe drought during the 10 years on record, 1904 to 1914, namely the years of 1912 and 1913, the wells would be called upon to supply 32,500,000 gallons during 14 months, or an average supply of 120 cu. ft. per second.

The total area tributary to the Aqueduct is 2782 sq. mi. and the population is 4775, making an average population of 1.7 persons per sq. mi. Of this area 12.7 per cent is agricultural land and 4.3 per cent of the area is irrigated. Irrigation is probably nearer its ultimate acreage in this section than in any other mountainous section of the state, and it is safe to state that there will never be a marked increase of population within the drainage area.

<sup>1</sup> Presented before the Southern California Section of the American Chemical Society, Los Angeles, April 15, 1915.

<sup>2</sup> Manager Smith, Emery & Company's Los Angeles Laboratories.

<sup>1</sup> See U. S. G. S. Water Supply Paper 294.



The temperature of this basin is subject to great and sudden changes, due to the wide variations in altitude. The regions

of the months from November to March, inclusive, usually being below 50° F.

PHYSICAL FEATURES OF THE AQUEDUCT

The Aqueduct intake on the Owens River is at an elevation of 3812 ft. For 21 mi. below the intake the Aqueduct is fenced, open and unlined, with a capacity of 900 cu. ft. per second. Its bottom is about 8 ft. below the natural ground level, and it is in this section that the normal water level is above the bottom of the Aqueduct, so that water seeps into it.

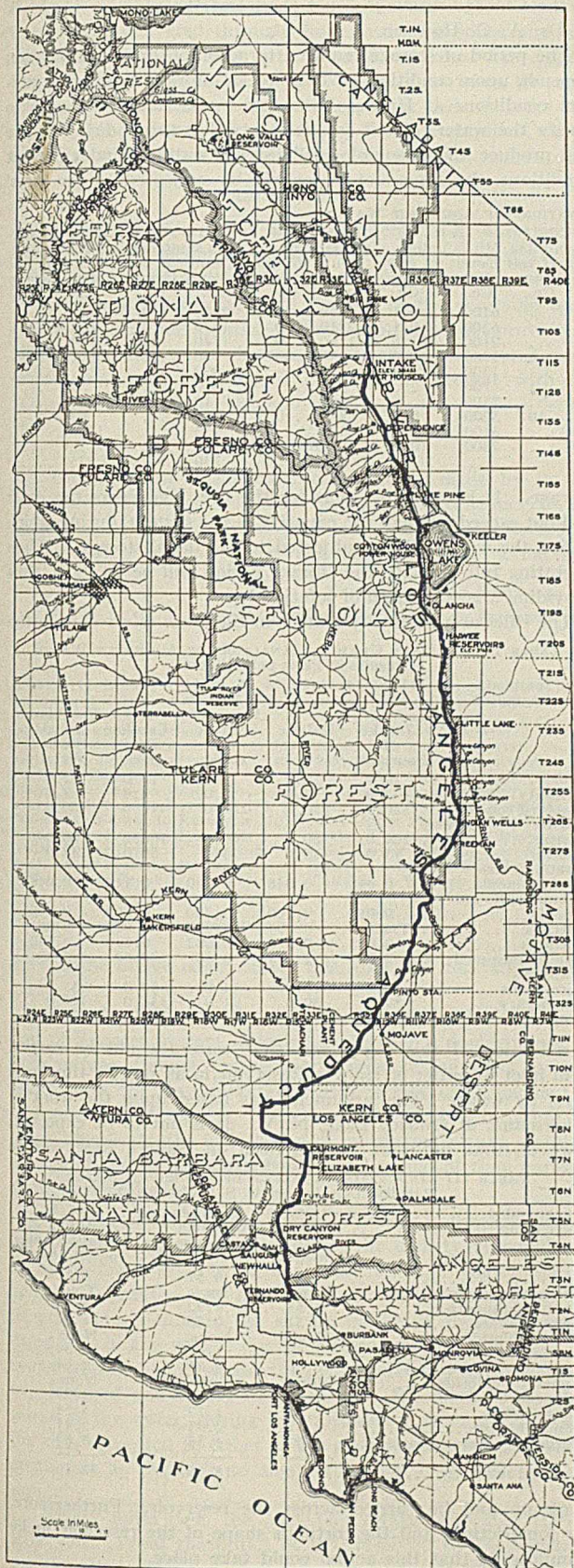
From the north end of the Alabama Hills to Haiwee Reservoir, 40 mi., the Aqueduct is fenced, open and concrete lined, with a capacity of 900 cu. ft. per second. A waste gate is located at the beginning of this section, and another one where Cottonwood Creek reaches the Aqueduct about 16 mi. north of Haiwee Reservoir. Through these gates undesirable water can be wasted.

The Aqueduct discharges water into the north end of Haiwee Reservoir. This reservoir, the most notable feature of the Aqueduct from a sanitary standpoint, is 7.5 mi. long, has a capacity of 20,843,000 gallons, has steep sides, is located in an almost rainless region, receives practically no water from its own natural basin, which is entirely uninhabited; when half full it is divided into three basins by very narrow constrictions, and when full it is divided into two basins. Its total area when full will be 2100 acres. It has a maximum depth of 81 ft. and an average depth of 30 ft. During the period of this investigation it was half full.

The effluent of Haiwee Reservoir is controlled by gates at varying elevations in a concrete tower. After passing through a short tunnel, the water is discharged into a temporary, open, concrete-lined canal, 2 mi. long, of 420 cu. ft. per second capacity. It is planned to replace this open canal with pipe for power development. From here the water flows through covered conduits, tunnels, syphons and flumes of 420 cu. ft. per second capacity, for 135 mi., and discharges into Fairmont Reservoir. At present the crest of Fairmont dam is at an elevation of 3024 ft., and the reservoir has a capacity of 1,890,000 gallons. It is planned to raise this dam to elevation 3035 ft., a total height of 115 ft., for power development. This acts as a safeguard, as a storage reservoir, and as a means for regulating the fluctuations of draft through the power plants to be located below in San Francisquito Canyon. The natural drainage basin of this reservoir is uninhabited.

From here the water is carried through Elizabeth tunnel, 26,870 ft. long, with a capacity of 1000 cu. ft. per second. The capacity is large in this section to accommodate the draft at the peak load of the power plants. At present the water discharges from this tunnel into San Francisquito Canyon and flows down it for 9 mi., but in a few weeks tunnels will be complete so that the water will flow directly through tunnels into Dry Canyon Reservoir, with a capacity of 342,000,000 gallons. This reservoir will serve to regulate the irregular flow that will be discharged through the power plants to be located in San Francisquito Canyon. It is 17 mi. between Fairmont and Dry Canyon Reservoirs. The natural basin of Dry Canyon Reservoir is uninhabited.

Tunnels and syphons, 12 mi. long, of 420 cu. ft. per second capacity, carry the water to the "Cascades" 1020 ft. long, located near San Fernando. These cascades serve to aerate the water. From here a fenced, open, concrete-lined canal 8775 ft. long carries the water to San Fernando Reservoir outlet tower. The San Fernando dam, one of the largest hydraulic earth fill dams in the world, will not be complete for another year. The water is carried by a steel syphon of 150 cu. ft. per second capacity, 12 mi. to Upper Franklin Canyon Reservoir. This reservoir has a capacity of 42 million gallons and its basin is uninhabited. Lower Franklin Reservoir, two miles below,



MAP OF THE LOS ANGELES AQUEDUCT AND ADJACENT TERRITORY

of agricultural land have hot summer weather, the temperature often exceeding 100° F., and cold winters, the mean tempera-



is not completed. At present the water flows from Upper Franklin Reservoir directly to the distributing mains at Third Street and Western Avenue, a distance of about 12 mi.

BACTERIOLOGICAL EXAMINATIONS

The samples were iced and shipped to the laboratory so that they were plated within 48 hours and usually within 24 hours from the time of sampling. They were taken and examined in duplicate.

The samples were plated in standard agar using 1/2, 2/10 and

principle. This knowledge has been made certain through the excellent work of Professors Russell, Jordan and Zeit at the time of the Chicago drainage canal case, and the more recent work of Dr. A. C. Houston.

The period of storage required to accomplish self-purification depends upon conditions. Two weeks' storage under the normal conditions at Haiwee Reservoir would doubtless serve to purify the water, and it is a certainty that thirty days' storage will produce an epidemiologically sterile water. Under present conditions, the Aqueduct water will be subjected to 470 days'

TABLE I—BACTERIOLOGICAL EXAMINATIONS OF AQUEDUCT WATER

DATE SAMPLED	9/3-14/14		9/15-18/14		9/23-26/14		9/27-29/14		10/12-16/14		11/15-18/14		11/19-21/14		1/22-23/15	
	1st sampling		2nd sampling		3rd sampling		4th sampling		5th sampling		6th sampling		7th sampling		8th sampling	
WHERE SAMPLED	Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>		Count <i>B. coli</i>	
	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.	Per Group	Cc.
Intake of Aqueduct.....	140	0.1	...	...	5200	0.1	...	...	6100	0.1	3430	1	2260	1	...	...
Conduit at Alabama waste gate....	160	...	...	...	4600	0.1	...	...	5300	0.1	2210	10	1530	1	...	...
Inlet, Haiwee Reservoir.....	105	...	170	...	2100	...	...	...	2100	1.0	1790	10	1740	10	40	...
Constriction in Haiwee Reservoir..	140	0.5	160	...	2000	...	1800	...	1000	10.0	840	10	900	...	...	...
Outlet, Haiwee Reservoir.....	60	...	65	...	1800	...	1500	...	1300	...	750	...	830	...	...	...
Inlet, Fairmont Reservoir.....	84	...	4000	0.1	1300	...	1700	...	1700	...	600	...	870	...	36	...
Outlet, Fairmont Reservoir.....	150	...	4500	...	1500	...	1900	...	2500	...	600	...	710	10	52	...
Inlet, Dry Canyon Reservoir.....	300	...	4000	...	8000	10.0	6500	10	3200	0.1	830	10	880	...	68	...
Outlet, Dry Canyon Reservoir.....	200	...	1000	0.5	7500	...	6200	...	3100	1.0	620	...	950	...	1460	10
Cascades.....	525	...	580	...	6700	...	7400	...	2800	10.0	...	...	...	...	...	...
San trap at San Fernando Dam...	375	...	2000	...	8200	...	7500	...	...	...	630	...	730	...	335	...

1/10 cc. dilutions, and lactose-bile fermentation tubes were inoculated with 1/10, 1 and 10 cc. of water sample. The tubes showing acid and gas formation were inoculated on to litmus-lactose agar or endo plates, and characteristic colonies fished and transplanted to peptone solution for indol production, nitrate solution for nitrate reduction, lactose milk for acid and clot, and gelatine for liquefaction. In Table I, the count is given as the average number of colonies per cc. on the six plates after incubation at 37° C. for 48 hours, and in the column "*B. coli* Group, cc" the smallest sample giving characteristic tests for *B. coli* is reported.

At first glance, the most striking feature of the bacteriological counts is the variation in total counts at a given station. This is caused by the fact that the end of the vegetative season comes suddenly in this region and that it and the fall "turnover" of the reservoir water took place during the period of examination.

The finding of *Bacillus coli* in samples taken at the inlet of Dry Canyon Reservoir is attributed to contamination in San Francisquito Canyon, where a road crosses the creek channel thirty-three times. The absence of *Bacillus coli* in all samples smaller than 10 cc. and in the great majority of 10 cc. samples taken below Franklin Reservoir, indicates that the two weeks' storage in Dry Canyon and Upper Franklin Reservoirs purified the water. As noted above, this is a temporary condition and there will be no chance for pollution to enter the water after leaving Haiwee Reservoir, except the accidental pollution by stragglers about the small reservoirs, which is guarded against by caretakers.

Below Dry Canyon Reservoir, the finding of *Bacillus coli* in occasional samples may be attributed to ducks, which were numerous on these reservoirs during the time of our work. In order to prove that the duck carried *Bacillus coli*, the fecal matter of duck killed on these reservoirs was examined and found to contain 50,000,000 typical *Bacillus coli* colonies per gram.

During the period of examination, the effluent from Haiwee Reservoir was 50 cu. ft. per second. It is estimated that the full capacity of 420 cu. ft. per second will not be required for 10 years. But it is the policy of the Water Department to always keep Haiwee Reservoir half full, thus providing at least 30 days' storage. Carefully prepared statistics for the ten years from 1904 to 1914 indicate that this storage can be provided when the constant effluent of Haiwee Reservoir is 420 cu. ft. per second, even through periods of drought, by the aid of pumped water.

The self-purification of stored water is a generally accepted

storage. It is estimated that for the next five years the draft will not exceed one-half the capacity of the system, during which period the water will be subjected to 120 days' storage. When operating full capacity the storage period will be 65 days, thus providing a good margin of safety.

The chief argument of plaintiffs in the cases referred to in the

TABLE II—SANITARY CHEMICAL ANALYSES OF AQUEDUCT WATER

Date sampled.....	Results in Parts per Million				
	11/17/14	11/20/14	11/16/14	11/15/14	11/12/14
Where sampled....	Intake of Aqueduct	Haiwee Res. cut between	Reservoir surface near tower	Dry Canyon Res. inlet	Franklin tunnel South Portal
Color.....	10.0	20.0	20.0	10.0	22.0
Turbidity.....	2.0	3.0	6.0	2.0	2.0
Dissolved solids.....	320.0	220.0	250.0	440.0	430.0
Volatile and organic matter.....	100.0	80.0	60.0	100.0	80.0
Chlorine.....	15.0	15.0	23.0	50.0	48.0
NITROGEN AS:					
Free ammonia.....	0.040	0.048	0.270	0.110	0.046
Albuminoid ammonia.....	0.054	0.100	0.260	0.102	0.200
Nitrites.....	Trace	0.006	0.007	0.002	0.001
Nitrates.....	0.083	0.076	0.083	0.670	0.340
Oxygen consumed....	2.80	2.52	3.50	2.80	2.40
HARDNESS:					
Permanent.....	12.0	15.0	14.0	50.0	35.0
Temporary.....	89.0	80.0	91.0	134.0	140.0
Total.....	101.0	95.0	105.0	184.0	175.0

introduction of this paper was that water would be carried from inlet to outlet of Haiwee Reservoir in as short a time as 3 days, by winds. This argument was based upon the work of Ackermann, at Owasco Lake, N. Y. It is not to be expected, however, that sufficient ice will form on Haiwee Reservoir to

TABLE III—INDUSTRIAL ANALYSIS OF AQUEDUCT WATER

Date sampled.....	Results in Grains per U. S. Gallon		
	9/26/14	9/26/14	8/24/14
Where sampled.....	Intake to Aqueduct	Aqueduct at Alabama waste gate	Aqueduct at Franklin Canyon power house
Silica.....	0.75	0.59	0.80
Iron and aluminum oxides....	Trace	Trace	Trace
Calcium carbonate.....	6.55	4.92	5.85
Calcium sulfate.....	0.51	0.46	1.02
Calcium chloride.....	None	None	None
Magnesium carbonate.....	1.73	1.67	2.59
Magnesium sulfate.....	0.36	0.36	1.64
Magnesium chloride.....	None	None	None
Sodium carbonate.....	2.60	1.98	1.24
Sodium sulfate.....	1.74	1.79	5.54
Sodium chloride.....	2.51	2.03	5.41
Volatile and organic matter....	5.03	4.56	8.07
Total solids.....	21.78	18.36	32.16

break up and be carried across the reservoir. Furthermore, the constrictions and the tortuous shape of the reservoir make it impossible that this action could take place.

CHEMICAL ANALYSIS

Since our time was limited and there seemed but little need



for chemical analysis at the trial, we did only enough work to give us an insight into the character and amounts of dissolved substances in the water. The sanitary chemical analyses, Table II, and the mineral analyses, Table III, indicate that the water being delivered through the Aqueduct is softer and contains less solids than the water from the present Los Angeles River supply. Also, it is to be expected that when the more soluble salts are leached from the reservoir beds and the concrete, and the water is not run through San Francisco Canyon, the water will contain less solids than at present.

#### BIOLOGICAL EXAMINATION

To conclude this paper without reference to this subject would leave it incomplete. Yet there has been no systematic work done to date which will warrant a public statement. It is to be expected that algae will flourish in the reservoir water during the summer months. The system does not provide for filtering the water, but chemical treatment of the stored water is contemplated. Aeration is provided at present with the "Cascades" near San Fernando.

#### CONCLUSION

A conclusion of this subject can best be made by stating the quality of water delivered through the Aqueduct to the consumer. A portion of the decision of Judge Lewis R. Works, rendered after hearing expert testimony for forty actual trial

mont, Dry Canyon and Franklin Reservoirs, three other basins having some value for storage purposes.

"A large portion of the testimony during the trial has been directed to the question of the efficacy of the entire system mentioned, and especially of Haiwee Reservoir, as a purifying agency, and many experiments have been conducted in the waters of the reservoir in order to determine the problem. It is not necessary now to state the nature of these experiments, nor to analyze the theories and arguments advanced by the various expert witnesses who have testified concerning them. It is sufficient to say that the great weight of the evidence demonstrates that Haiwee Reservoir is remarkably efficient as a great purifying unit in the Aqueduct system. This immense basin is over seven miles in length, with that distance between its inlet and outlet, and impounds, for a long period of time, certainly not less than thirty days, all waters which enter it. The reservoir is peculiarly adapted to the use for which it was principally designed. One of the leading expert witnesses in the case characterizes it as unique among the storage reservoirs of the world. Being in a region in which there is a rainfall of not to exceed five inches per annum, a region of porous, sandy soil, and entirely uninhabited, it is the recipient of no run-off from its own water-shed and it is therefore free from the contamination of such a run-off. The only influent of the reservoir is the Los Angeles Aqueduct, containing waters brought from the Owens River. The intake gates on the river may be closed

TABLE IV—TIME FACTOR IN SELF-PURIFICATION OF AQUEDUCT WATER  
Rates of Forward Travel of Water Estimated with Haiwee Reservoir  $\frac{1}{2}$  full and Other Reservoirs  $\frac{2}{3}$  Full

FROM	TO STATION AT	TIME IN TRANSIT OR STORAGE IN DAYS			
		With maxi- mum flow	272 m. g. d. draft	136 m. g. d. draft	With pres- ent flow
Intake of Aqueduct	Cottonwood Creek	0.907	1.242	1.565	2.930
Cottonwood Creek	Intake, Haiwee Reservoir	0.279	0.362	0.465	0.798
Intake, Haiwee Reservoir	Outlet, Haiwee Reservoir	38.300	38.300	76.600	402.500
Outlet, Haiwee Reservoir	Inlet, Fairmont Reservoir	1.549	1.549	1.888	3.098
Inlet, Fairmont Reservoir	Outlet, Fairmont Reservoir	4.750	4.750	9.500	47.900
Outlet, Fairmont Reservoir	Inlet, Dry Canyon Reservoir	0.113	0.113	0.138	0.226
Inlet, Dry Canyon Reservoir	Outlet, Dry Canyon Reservoir	1.050	1.050	2.100	10.600
Outlet, Dry Canyon Reservoir	Inlet, San Fernando Reservoir	0.139	0.139	0.169	0.278
Inlet, San Fernando Reservoir No. 1	Outlet, San Fernando Reservoir No. 1	11.992	11.992	23.975	0.055(a)
Outlet, San Fernando Reservoir No. 1	Inlet Upper Franklin Reservoir	0.106	0.106	0.106	0.775
Inlet, Upper Franklin Reservoir	Outlet, Upper Franklin Reservoir	0.718	0.718	0.718	2.154
Outlet, Upper Franklin Reservoir	Inlet, Lower Franklin Reservoir	0.008	0.008	0.008	
Inlet, Lower Franklin Reservoir	Outlet, Lower Franklin Reservoir	6.180	6.180	6.180	0.174(a)
Outlet, Lower Franklin Reservoir	Third St. & Western Ave., Los Angeles City	0.080	0.080	0.080	
	Total	66.171	66.589	123.492	471.488

(a) Reservoirs by-passed at present.

days in the above cases, states this ably and concisely, as follows:

"The scientific principles governing the selection and operation of a water system intended to furnish a domestic supply from surface streams requires a treatment of the water in order to rid it of the contamination which is inevitably incident to such a source of supply. This treatment consists in either the use of chemicals, the installation of infiltration plants, or in the storage of the water in reservoirs for a period of time requisite to its purification.

"If it be granted that the waters of Owens Valley are contaminated like all other surface waters, the density of population of its drainage area being the true index of contamination, and if it be granted that, for that reason, those waters would not be proper for domestic use at the intake of the Los Angeles Aqueduct, in the valley, does it follow that the water has not been purified when it reaches the point of delivery in Los Angeles, two hundred and eighty-six miles from the intake? In other words, is the water, during its transmission from the intake to the city, subjected to either of the methods of treatment above mentioned as requisite to the purification of a surface water supply?

"Ninety miles from the Aqueduct intake is located Haiwee Reservoir. From the outlet of that reservoir to Los Angeles is one hundred and ninety miles. During this progress over that distance, the water supply is halted, even if briefly, in Fair-

at will and there are frequent waste gates along the course of the Aqueduct, from the river to the reservoir, through which the waters of the great ditch may be entirely cast away. These instrumentalities conduce to a perfect control of the Haiwee influent and the waters may be diverted and wasted in periods of flood or at any other time of possible undue contamination from whatever cause.

"This peculiarly advantageous location of Haiwee is mentioned in passing, only, as the period of storage, which is allowed by its size and shape, is alone sufficient to guarantee to the people of Los Angeles a positive immunity from dangers residing in the waters before they leave Owens Valley, conceding that such dangers are there present, and without regard to the use of the waste gates mentioned, which furnish but an added factor of safety to a system safe enough without them."

#### THE REVIVAL OF THE USE OF NATURAL DYESTUFFS<sup>1</sup>

By EDWARD S. CHAPIN

Imagine, if you can, the following situation: The supplies of artificial dyestuffs have become exhausted. The European blockade of embargo, call it what you will, has continued in uninterrupted force. Capital has been too timid to manufacture artificial dyestuffs in this country. This situation we will

<sup>1</sup> Address before the 98th Meeting of the National Association of Cotton Manufacturers, Boston, April 28 and 29, 1915.



now consider. "Nothing but black and white," says one; "The country will have to wear white," cries another; a third asserts: "The mills of the country will have to shut down!" What is the truth? The truth is that natural dyestuffs can keep the mills of the Nation in operation, producing a diversification of shades and giving fast colors.

This paper does not propose to consider the question of the relative merits of natural dyestuffs *versus* artificial dyestuffs. The present is no time for controversy. It demands coöperation and construction. We must remember that before the days of the modern artificial dyes people wore colored garments. Ladies were gay and gallants tried to please long before Perkin discovered mauve. A careful reading of any of the works of the masters of detailed description of the past century—of Dickens, Thackeray, Victor Hugo, or Goethe—will reveal interesting evidence of color and colored fabrics. Even more so the standard text-books on dyeing, of fifty or seventy-five years ago, consider the whole range of the spectrum. It is truly remarkable the multi-colored and fast effects that the dyers of the old school achieved with limited means and facilities. It is quiet within the memory of many of this audience, when the earlier aniline colors were distrusted by the general public because of their comparative fugitiveness, and it took much industrious advertising and scientific development of new and better products to overcome this prejudice.

The dyers and chemists of today are in a position to secure with natural dyestuffs better results than the dyers of former days. The forms of natural dyestuffs were not so perfect formerly as today. Then the dyer was forced to use the dyestuffs in the form of chips or ground bark or ground leaves; today he has ready at hand the essential coloring matter of the natural dyestuffs in the form of extracts, pastes, or powders, and in many instances the coloring matters have been worked up by chemical treatment so that they dye more readily and give brighter and faster results. The march of chemical and mechanical science contributes to the solution of the task. Chemical science in recent years has found the exact chemical composition and nature of the natural dyestuffs, so that they can now be dyed most intelligently and in accordance with the highest development of the theory and the practice of dyeing. New and improved chemicals and dyeing assistants are at the disposal of the dyer. New forms of dyeing apparatus and improved mechanical devices help further. Improved dyeings are to be expected in response to persistent and intelligent work, and during the past months such results have been secured in many instances.

#### AVAILABLE NATURAL DYESTUFFS

For the dyeing of cotton the following natural dyestuffs are available: logwood, fustic, bark or quercitron, flavine, hypernic and the various redwoods, catechu or cutch, gambier, sumac, madder, Persian berries, and indigo. Of these dyestuffs all except madder, Persian berries, and indigo are available in large quantities.

Logwood is the product of a large tree known botanically as *Hematoxylon campechianum*; which grows abundantly in the West Indies and Mexico. The supply of logwood is not petering out as some have erroneously imagined; the logwood forests have not all been cut off. There are well-nigh limitless virgin forests of logwood in Haiti, Jamaica and Mexico. Reforestation and cultivation are the simplest of operations. The logwood tree is a veritable weed—it spreads itself; twelve years alone elapses between the seed and the tree ready for cutting for commercial purposes. Cultivation consists in keeping the forests thinned out, so that the luxuriant tropical growth will not form an impenetrable jungle. It may fairly be said that never before has there been available more logwood than today.

Fustic, also known as old fustic, Cuba wood and yellow wood,

comes from a tree known botanically as *Morus tinctoria* or *Maclura tinctoria*. It is a native of Brazil, Mexico, and several of the West Indian Islands. Quercitron bark is the inner bark of a species of oak, the *Quercus nigra* or *Quercus tinctoria*, a native of America. It grows abundantly in Pennsylvania, Georgia, and the Carolinas. Flavine is the name given to a preparation of quercitron bark. It contains the principal coloring matter of quercitron bark, quercetin, in nearly chemically pure state. Hypernic is the name given to the color extracted from the various soluble redwoods. These are principally Brazil wood, peach wood, sapan wood, and lima wood. Brazil wood grows in the forests of Brazil. Peach wood is a native of Mexico. Sapan wood grows in Siam, Japan, and the East Indies. Lima wood is imported from Peru. Catechu or cutch and gambier closely resemble each other in properties. They are obtained from various species of acacia, areca, and uncaria, growing in India. Sumac consists of the leaves, leaf-stalks and small twigs of several species of *Rhus*. This shrub is remarkably common and widely spread, growing in Sicily, Tuscany, France, Spain, Algeria, Canada, and the United States, particularly in Virginia.

The various regions from which these natural dyewoods come are with unimportant exceptions outside the inhibiting influence of the war. Accordingly, they are all available. Even prior to the war these dyestuffs were in large general use—much more extensively than is generally realized—so that the present additional demands from the textile mills find an industry well fitted to take on extra burdens and to perform needed services.

#### BLACK DYEING OF COTTON

Black is the color most widely demanded by the trade, and will accordingly first engage our attention. For black dyeing logwood has been and still is the most generally all-round useful black dyestuff. It can be used not only for the coloring of cotton but also of wool and silk and a great variety of fibers. There are three methods of applying logwood on cotton: (1) the stuffing and saddening; (2) the bluestone soda ash; (3) the mordanting methods.

#### THE STUFFING AND SADDENING METHOD

In this method of dyeing, the cotton, as piece goods, yarn, or raw stock, is first impregnated with the logwood by passing it through or boiling it in a concentrated logwood extract solution; it is then dried or whizzed to fix the logwood or remove an excess not taken up by the fiber; finally it is passed through a bath of chemicals, usually chrome, or chrome and bluestone, or copperas, to develop the black. Two illustrations of this process will be given: one on piece goods, and the other on raw stock.

LOGWOOD BLACK ON PIECE GOODS—This process makes use of two boxes and has been in constant successful use for the past four years in the dyehouse of a large producer of black dyed cotton piece goods.

The apparatus consists of a stock tank for the logwood liquor and a logwood dye-bath, three sets of drying cans, a stock tank for the chrome liquor and a chrome bath, a steam box, a wash mangle, and a washer. The logwood box and the chrome box are provided with guide rolls, and above the center of each box are three squeeze rolls. The guide rolls and the squeeze rolls are so related that the cloth in its passage through both the logwood and the chrome baths is twice immersed and twice squeezed.

The dry bleached pieces are run into the dye-bath and over the first four rolls, squeezed and given a second run in the dye-bath over the second four rolls, followed by another squeeze. From the dye-bath the pieces are dried over three sets of drying cans. The passage through the chrome bath follows imme-



diately and here, as in the dyeing, there are two immersions and two squeezes. After the chroming, the goods are steamed, and then washed. The washing is very thorough, first by passage through a wash mangle, and then through a washing machine. After washing, the goods are again dried and then finished.

STOCK LIQUOR	CHROME LIQUOR
125 gallons water	125 gallons water
110 lbs. logwood extract, 51° Tw.	49 lbs. bichromate soda
5 gallons acetic acid No. 8	3 lbs. soda ash, 58°
Temperature of dye-bath—near boil	Time of immersion—about 2 seconds
Time of immersion—10 seconds	Time of steaming—about 10 seconds

The speed of the machine, 45 to 50 yards a minute, corresponds to a production of about 3,000 yards an hour; but a speed of 75 yards to the minute (4,500 yards an hour) is possible.

The goods are used as linings for suitings, overcoats, and the like, where a black is needed that will not stain white when wet hot-pressed. The logwood process is preferred because of the low cost of production, and the excellent fastness of the result.

**LOGWOOD BLACK ON RAW STOCK**—The following method is being employed in a Klauder-Weldon dyeing machine, coloring 1,000 pounds of cotton to a batch.

Run for one hour at a boil in a 10 per cent solution of logwood extract, prepared by dissolving 10 pounds logwood extract 51° Tw. to every 12 gallons of water. This solution will stand 4° Tw. at 70°. Take out of machine and whizz. Repack in machine, and strike with 4.5 per cent bluestone and 1.5 per cent soda chrome. Run in striking bath 1 1/4 hours; wash well. Soap in a 0.5 per cent solution of soap; wash and dry. The logwood bath is saved and brought up to 4° Tw. for further dyeings. This method gives a remarkably full and rich black on stock of excellent fastness to fulling and of moderate fastness to light.

**THE BLUESTONE SODA ASH METHOD**

The bluestone soda ash method of dyeing cotton, or the ash black as it is commonly called, is a favorite method because of its simplicity.

The following recipe is a slight modification of a bluestone soda ash logwood black formula used in a large mill for the coloring of raw cotton, and illustrates well the general principles and practice that are obtained in the successful dyeing of cotton with logwood in the single bath:

DYE-BATHS FOR 100 LBS. RAW COTTON	Starting bath Lbs.	Second bath Lbs.	3rd or standing bath Lbs.
Logwood extract, 51°.....	60	40	20
Soda ash, 58°.....	6	4	3
Bluestone.....	3	2	1.5

Boil 1 1/2 hours. Throw out the stock and allow to drain. Oxidize for two hours, or until the full shade is developed, turning occasionally.

After the standing bath is obtained, enter the first lot for a second dip in the standing bath. After this, one immersion is usually sufficient. If extra heavy shades of black are required, give two immersions or increase the amount of dyestuff and chemicals in the standing bath. If a jetter shade of black is desired, use an ounce of cutch extract for every pound of logwood extract. Some dyers find it advantageous to use also an ounce of sumac extract for every pound of logwood extract.

The bluestone soda ash logwood black can be utilized for the dyeing of other forms of cotton, as cotton yarn, cotton warps and the like; and for the dyeing of a wide variety of cotton fabrics. The following series of formulae are taken from practice:

**DYEING COTTON YARN**—For dyeing cotton yarn, black dye is usually preferred. Black dye is a logwood extract, which contains a proportion of tannin-bearing material, such as chestnut extract. It gives a very good deep black at an exceedingly low cost.

DYE-BATHS FOR 100 LBS. COTTON YARN	Starting bath Lbs.	Second bath Lbs.	Third or standing bath Lbs.
Black dye.....	50	25	20
Soda ash.....	20	8	3
Blue vitriol.....	10	4	1.5

Boil 1 1/2 to 2 hours, lift and oxidize 2 or 3 hours. By after-treating with 1 per cent chrome at 150° to 160° for 20 minutes, the fastness to washing is made excellent.

**DYEING COTTON WARPS**—For 650 pounds warp, prepare a bath containing:

130 lbs. logwood extract, 51°	18 lbs. soda ash	12 lbs. blue vitriol
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Give four runs, boiling. Sadden in another tub with 6 lbs. copperas, at 120° F.; finish. This gives a very good black.

The following recipe is an example of a successful application of the use of salt in the bluestone soda ash logwood black. A Klauder-Weldon machine was used in dyeing.

For 800 pounds raw cotton prepare a starting bath containing:

370 lbs. logwood extract, 51°	18 lbs. soda ash
18 lbs. blue vitriol	10 lbs. common salt

Boil the cotton for 2 hours. Oxidize for 2 hours. Afterwards wash in:

8 lbs. soap	15 lbs. sal soda
5 lbs. common salt	1 qt. ammonia

Dissolve the chemicals for the washing in about three-quarters of a barrel of water, and feed onto the cotton at 120°. Continue washing one-half hour.

For a standing bath, gradually reduce the amount of dyestuff and chemicals above given during four or five baths to one-half the quantities.

The bluestone soda ash logwood black can be used for all purposes where fastness to fulling is not required. It is faster to light than the stuffing and saddening black.

**THE MORDANT METHODS**

By mordant methods is meant those methods in which the mordant is fixed on the cotton previous to the logwood treatment. Two of these methods will engage attention: (1) the iron; (2) the chrome.

**1. THE IRON MORDANT BLACK**—The iron mordant logwood black has always been employed when a black of special fastness to fulling and light is required. The following recipe is for coloring warps in a four-box machine:

**LOGWOOD BLACK ON WARPS**—Boil up 25 per cent extract of sumac in the boxes, run in the yarn, and leave over 1 day (36 hours, or more). Treat to two runs in clear lime-water, followed by two runs in pyrolignite of iron, 3° Tw.

In practice the volume of liquor in the iron liquor machine is so small that the readings of the hydrometer are not of much value. It is best to add between 20 per cent and 25 per cent iron liquor, one-half before each run, and to squeeze the warps lightly. Much of the liquid is removed from the bath, and it is generally necessary to add some water on every set. Wait twenty to thirty minutes before washing. Then treat to 1 run in clear lime-water and wash again.

15 per cent conc. extract logwood;	3 per cent conc. extract fustic;
1 per cent copper sulfate	

Add one-half the logwood and one-half the fustic, bring the temperature of the bath to 140° F., and make one run. Add the remainder of the logwood and fustic, raise the temperature to 170° F., and make one run. Raise the temperature to a boil and make six runs. Add the copper sulfate in solution, half on the fifth and half on the sixth run, there being eight runs in all. Then wash with 1 run.

One per cent potassium bichromate

Add one-half the bichromate to make one run at 180° F. Add the remainder and make one run at the same tempera-



ture. Wash with 2 runs. Finish with 3 per cent lard oil and 3 per cent soft soap (one run).

The above process can be shortened considerably with equally satisfactory results, by the use of the machinery constructed for the dyeing of sulfur colors. These machines give longer immersions than the old Scotch tubs, and have heavier nips.

#### FOUR-BOX MACHINE

First run	{	First box: 50 per cent sumac extract, 180° F.; nip
		Second box: 30 per cent nitrate of iron; cold; nip
		Third box: Lime solution; cold; nip
		Fourth box: Water
Second run	{	Three boxes of logwood
		30-40 per cent to each box, boiling
		Fourth box: Wash

Practically the same processes may be used for pieces.

2. THE CHROME MORDANT BLACK—The chrome mordant black came into being in response to the request to dye logwood blacks on raw stock in a vacuum dyeing machine. In this machine the methods above described, except the iron mordant method, do not give any results at all.

The use of a chrome mordant to develop and to fix logwood on wool is a well-known dyeing process. It yields blacks of excellent fastness to fulling, light, and various other agencies, and of exceptional beauty. The idea to adapt this method of dyeing wool to obtain equally fast and handsome results on cotton has long been alluring. Various methods of mordanting the cotton with chrome that have been tried in the past have not met with wide or permanent success.

The trouble has always been either that the chrome would not go on the cotton fiber or was deposited so loosely that in washing it nearly all came off.

These difficulties have recently been overcome by the use with the chrome of a compound (invented by a well known chemist) which causes the chrome to exhaust onto the cotton and to be deposited so firmly that even severe washing will not strip it off.

The preliminary studies for the practical use of this new method of mordanting cotton were made in the model laboratory of the American Dyewood Company. This laboratory is fully equipped with small size dyeing machines of latest invention. Through the courtesy of Mr. W. A. Mitchell the work has passed beyond the laboratory stage. Mr. Mitchell generously offered the use of the dyehouse of the Massachusetts Cotton Mills for trials on a practical scale; and the results obtained in the laboratory of the American Dyewood Company have thus had the benefit and the test of the splendid personnel and equipment of Mr. Mitchell's plant.

The following recipe was employed in the coloring of 150 pounds of raw cotton in a vacuum dyeing machine:

**BLACK ON RAW COTTON**—After loading the machine, fill with water and bring to a boil. Boil ten minutes to ensure thorough wetting out of the cotton. Add 6 lbs. of soda chrome dissolved in three pails of water, and after the chrome liquor has well circulated, add slowly 3 lbs. of chrome assistant dissolved in 2 pails of cold water. Boil one hour; wash. Fill the machine with water and bring to a boil. Prepare a half barrel of logwood extract liquor 15° Tw. containing 10 per cent fustic, and six pails of clear lime-water. Boil the logwood liquor well. Add slowly to the machine, and boil one hour. Wash. Strike cold with 1 lb. of bluestone and 8 oz. of chrome. Wash and finish as usual. Soaping improves the beauty of the shade, but is not essential.

The more concentrated the chrome liquor the more quickly the cotton takes up the chrome and the less the time required for boiling. From two-thirds to five-sixths of the chrome is exhausted on the fiber. The logwood liquor is not exhausted, but should be run off and kept for use in subsequent baths. The heavier the black required, the more concentrated should be the logwood liquor.

This process gives a black of excellent fastness to fulling and to light. The stock cards readily and the feel is especially satisfactory.

The process has been tried practically only on raw cotton. It has given good results in the laboratory on yarn and pieces. As the coloring of raw cotton in a vacuum dyeing machine is the hardest test of a process, there is good reason to believe that the new chrome mordant method can be adapted in practice to the coloring of the other forms of cotton and in the various other dyeing apparatus.

3. FASHION SHADES ON COTTON—Next in importance to black come the fashion shades. Many artificial colors are so brilliant that the great fear of many people has been that without these the consuming public could not be satisfied. A few illustrations will show that besides blacks the natural dyewoods can be made to yield a wide variety of fashion shades.

In dyeing the fashion shades, the stuffing and saddening method and the mordant method are applicable.

**CATECHU OR CUTCH AND GAMBIER BROWNS**—These valuable dyestuffs yield browns of specially pleasing tone and satisfactory fastness. The following recipe represents the method of dyeing a medium shade of cutch brown on pieces in a jigger:

For 100 lbs. of goods use 50 lbs. of good extract cutch. Enter goods nearly at a boil. Add the color in two ends. Then add 5 lbs. of bluestone. Bring to a boil, and boil one hour; shut off steam and allow to run from one-half to three-quarters of an hour. Draw off liquid and run in 2 lbs. of chrome. Run twenty minutes at 140° F. Rinse and dry. For a standing bath the amount may be reduced one-third. Gambier may be used in place of cutch and acts similarly.

For the toning of browns, fustic, bark and flavine are available as yellows, and hypernic as a red. Logwood, sumac, and copperas can be used for darkening.

Two illustrations follow: a light, bright brown dyed in a four-box machine, and a dark brown dyed in a jigger.

**LIGHT SHADE OF BRIGHT BROWN**—Prepare gambier, bark, and chrome solutions at 10° Tw. The gambier and the bark are divided between the first two boxes. Use fifteen pails of gambier and nine pails bark. The third box contains cold water, and the fourth box the chrome. Use eight quarts of chrome liquor. After leaving the chrome bath the goods are well washed in a water mangle. Repeat the process. Dry and size.

**DARK BROWN**—Prepare a solution in the jigger containing for 100 lbs. of goods: 10 lbs. hypernic crystals; 5 lbs. logwood extract, 51° Tw.; 15 lbs. extract of fustic, 51° Tw.; and 15 lbs. extract of bark, 51° Tw. Add the color in two ends. Boil one-half hour; shut off steam. Add 1 lb. of bluestone. Run fifteen minutes. Add 2 lbs. chrome. Run fifteen minutes. Wash.

The use of logwood for blacks has so overshadowed the other natural dyestuffs that the thought of violets, oranges, reds, bright yellows and blues does not come easily to mind when natural dyestuffs are mentioned. For this particular purpose, the new mordant process is especially adapted. On the table, in addition to sample dyeings of the other processes described, are a range of bright fashion shades colored by the new mordant process from natural dyestuffs.

In discussing this process earlier in the paper, mention was made only of the ability of the new assistant to exhaust chrome on the fiber. This chemical is also able to fix other mordants—aluminum sulfate, tin crystals, copperas, and blue vitriol, on cotton, and so firmly that washing will not strip the mordants. These mordants then react with the natural dyestuffs to produce a diversification of shades. Thus fustic on a tin or aluminum mordant produces brighter yellows than on a chrome mordant. Logwood on a tin mordant gives violet to bordeaux shades of excellent brightness.



## CURRENT INDUSTRIAL NEWS

By M. L. HAMLIN

THE CHEMICAL TRADE OF THE UNITED STATES  
IN 1914

The following list of the imports and exports of chemicals and related products to and from the United States in 1913 and 1914, taken from the *Z. angew. Chem.*, 28 (1915), III, 125, shows clearly the effect of last year's economic depression and the war. Of 118 items of imports, 70 show a decrease in value from last year. The total imports of "chemicals, drugs, dyes and medicines", according to official federal statistics, fell from \$101,300,000 in 1913 to \$87,700,000 in 1914, a decrease of 13.4 per cent. Of this amount \$49,400,000 represented duty-free imports in 1914 as against \$62,200,000 in 1913; dutiable im-

ports amounted to \$38,300,000 in 1914 and \$39,100,000 in 1913.

The list of exports is based on export manifests and is not as accurate as the list of imports. Under the official class "chemicals, drugs, dyes and medicines," the values for the exports of 1914 and 1913 are given as, respectively, \$29,000,000 and \$26,800,000, 1914 thus showing an increase of 8.2 per cent. This increase, taken together with the fact that of 73 items, 54 show a falling off, indicates that there is a concentration of effort towards exporting certain classes of goods; the exports of gasoline show an increase, for example, of over \$2,400,000, gas and fuel oil more than \$8,000,000, cartridges, \$3,500,000, etc.

	1913		1914	
	1000 lbs. units	\$1000 units	1000 lbs. units	\$1000 units
<b>CHEMICALS:</b>				
Potassium carbonate.....	21,437	653	15,891	287
Potassium hydroxide, not in sticks <sup>1</sup>	6,326	246	.....	.....
Potassium hydroxide with not over 15 per cent NaOH <sup>2</sup> .....	2,264	89	7,197	287
Potassium cyanide.....	1,023	144	1,246	80
Potassium chloride.....	427,524	7,120	337,081	5,741
Potassium sulfate.....	79,076	1,633	72,528	1,569
Potassium nitrate, raw.....	9,877	263	2,230	75
All other potash salts, dutiable.....	6,115	555	5,214	482
Sodium cyanide.....	.....	.....	2,423	367
Sodium nitrate (1000 tons).....	626	21,631	544	15,229
All other soda salts, dutiable.....	11,176	325	.....	629
The same, duty-free.....	.....	.....	.....	26
Ammonium chloride.....	9,019	466	7,842	395
Ammonium sulfate.....	116,562	3,957	148,242	4,476
Arsenic compounds.....	6,688	286	4,079	165
Chloride of lime.....	61,605	510	34,540	333
Potassium citrate.....	3,301	500	4,359	725
Iodine.....	240	526	463	951
Magnesite, not purified.....	335,868	1,669	241,166	1,298
Carbolic acid.....	7,502	558	6,902	394
Oxalic acid.....	7,423	365	8,165	423
Other acids, dutiable.....	.....	533	.....	1,147
Other acids, duty-free.....	.....	383	.....	242
Sulfur, raw (1000 tons).....	14.6	278	22.8	410
Sulfur ore with over 25% S (1000 tons).....	849	3,611	977	4,706
Tartar.....	29,066	2,780	27,436	3,028
<b>DRUGS AND MEDICINES:</b>				
China bark.....	2,809	307	3,945	538
Quinine sulfate and all other China bark products (1000 oz.).....	2,971	562	2,968	703
Opium, at least 9 per cent morphine.....	553	2,391	416	1,976
Medicinal preparations.....	.....	1,430	.....	753
Fusel oil or amyl alcohol.....	5,983	1,087	3,531	525
Hops.....	7,313	2,946	7,483	2,584
Licorice root (1000 tons).....	49.7	1,775	51.6	1,872
Vanilla beans.....	1,034	2,530	835	2,184
Mineral water (1000 doz. qts.).....	1,188	993	951	874
<b>DYES AND TANNING MATERIALS:</b>				
Alizarine and alizarine dyes.....	5,918	1,493	4,249	1,217
Coal-tar dyes.....	.....	7,111	.....	6,845
Paints, pigments and lacquers.....	.....	2,160	.....	2,243
Indigo.....	8,345	1,138	7,927	1,189
Aniline salts.....	4,479	322	2,245	181
<b>LOGWOOD AND OTHER DYE WOODS:</b>				
Logwood.....	38	469	41	522
Quebracho wood.....	80	985	72	919
Other dye woods.....	6	86	8	123
Mangrove bark.....	11	250	6	150
<b>OTHER TANNING MATERIALS:</b>				
Sumach.....	1000 lb. units	38	41	522
All other tanning materials.....	9,863	218	13,533	337
Dye and tanning extracts:				
From quebracho.....	85,718	2,221	114,326	3,100
All others.....	8,513	314	8,380	270
Lead pencils.....	.....	599	.....	567
<b>GUMS AND RESINS:</b>				
Camphor, raw, natural.....	4,190	1,118	3,488	950
Camphor, refined and synth.....	644	211	1,054	369
Chicle.....	13,401	5,120	5,897	2,178
Copal, Kauri and Dammar.....	31,709	3,193	28,647	2,963
Gambir ( <i>Terra japonica</i> ).....	16,330	658	13,706	494
Shellac.....	20,463	3,058	19,637	3,027
Other resins, duty-free.....	.....	1,615	.....	1,172
Other resins, dutiable.....	.....	269	.....	828
<b>RUBBER AND RUBBER SUBSTITUTES:</b>				
Balata.....	1,509	792	2,015	880
Guajule.....	4,870	2,130	2,276	790
Guttajuletong.....	36,421	1,766	18,664	857
Gutta percha.....	873	200	1,923	337
Caoutchouc.....	115,881	76,821	143,065	70,473
Caoutchouc waste.....	36,738	3,193	19,119	1,357
Substitutes.....	.....	97	.....	63

<sup>1</sup> To October 3, 1913.<sup>2</sup> From October 4, 1913.

	1913		1914	
	1000 lb. units	\$1000 units	1000 lb. units	\$1000 units
<b>FERTILIZERS:</b>				
Guano.....	19	538	26	763
Kainite.....	466	2,207	330	1,551
Salts.....	223	2,150	168	1,843
Bone meal and ash materials.....	35	837	36	891
All other fertilizing materials.....	.....	4,996	.....	5,055
<b>OILS, WAXES, ETC.:</b>				
<b>Ethereal oils:</b>				
Oil of lemon.....	371	721	486	897
Other ethereal oils, duty-free.....	.....	2,804	.....	26
Other ethereal oils, dutiable.....	.....	1,196	.....	2,063
<b>Plant oils:</b>				
Cocoa butter.....	4,413	1,223	1,244	349
Coconut oil.....	72,196	6,258	58,012	5,147
Cottonseed oil.....	11,407	724	16,017	869
Linseed oil.....	162	87	580	263
Chinese nut oil.....	5,678	2,370	4,018	1,503
Peanut oil.....	1,502	1,038	982	675
Olive oil, for technical use.....	564	369	748	475
Olive oil, for domestic use.....	5,179	6,777	6,718	8,421
Rapeseed oil.....	1,149	712	1,490	732
Palm oil.....	54,072	3,631	49,092	3,155
Palm nut oil.....	27,746	2,445	21,089	1,869
Soya bean oil.....	14,221	693	12,555	657
<b>Animal oils:</b>				
Codliver oil.....	751	305	1,893	684
All others.....	1,582	530	1,459	464
<b>Mineral oils:</b>				
Raw mineral oil.....	713,100	10,945	910,351	10,023
Benzine, gasoline, etc.....	15,483	1,472	12,751	1,121
All others.....	2,777	580	1,345	357
<b>Mineral wax:</b>				
Vegetable wax.....	7,255	555	6,812	442
Sulfur oil (olive residues).....	5,294	1,146	5,160	1,099
All other similar oils and fats.....	10,450	717	13,045	853
<b>MISCELLANEOUS:</b>				
Asbestos.....	87	1,929	64	1,408
Asbestos products.....	.....	390	.....	360
Graphite.....	26	2,110	20	1,398
Coke.....	94	443	121	556
<b>Mica:</b>				
Mica.....	1000 lb. units	2,887	981	846
Platinum, unworked.....	1000 lb. units	51.4	1,979	32.1
Platinum, in blocks, sheets, etc.....	1000 lb. units	66.6	2,960	40.2
Platinum, crucibles, dishes, etc.....	1000 lb. units	.....	105	.....
<b>Coal tar preparations, neither dyes nor medicinal, dutiable:</b>				
Coal tar preparations, neither dyes nor medicinal, duty-free.....	1000 gal. units	.....	782	.....
Creosote oil.....	1000 lb. units	69,022	4,081	48,839
Glue.....	1000 lb. units	9,530	907	20,652
Glue, raw materials.....	1000 lb. units	.....	1,852	.....
Perfumes and toilet articles.....	1000 lb. units	.....	2,044	.....
Horse hair, artificial.....	1000 lb. units	.....	107	.....
<b>Silk, artificial:</b>				
Thread, etc.....	1000 lb. units	2,305	2,877	2,923
Other forms.....	1000 lb. units	.....	655	.....
Soap, Marseilles.....	1000 lb. units	4,532	348	4,289
Soap, all other.....	1000 lb. units	.....	402	.....
Photographic paper.....	1000 lb. units	.....	1,275	.....
Photographic films and plates.....	1000 lb. units	.....	1,056	.....
Explosives and fireworks.....	1000 lb. units	.....	723	.....
Matches.....	1000 lb. units	.....	758	.....
Gelatine.....	1000 lb. units	.....	2,015	.....
Glycerine, raw.....	1000 lb. units	38,270	4,695	24,787
<b>Electric lamps:</b>				
Arc lamps.....	1000 piece units	2.4	43	0.3
Carbon filament lamps.....	1000 piece units	1,011	64	562
Metal filament lamps.....	1000 piece units	5,688	481	7,243



EXPORTS	1913		1914	
	1000 lb. units	\$1000 units	1000 lb. units	\$1000 units
Calcium carbide.....	32,362	946	32,750	989
Calcium acetate.....	74,056	2,158	47,897	833
Copper sulfate.....	4,169	212	7,387	328
Sodium compounds.....	.....	.....	.....	735
Acids:				
Sulfuric.....	9,689	104	13,176	140
All others.....	.....	381	.....	620
Tons.....	89	1,600	98	1,807
Sulfur, raw.....	.....	.....	.....	.....
	1000 gal. units		1000 gal. units	
Methyl alcohol.....	1,951	827	1,161	479
Dyes.....	.....	357	.....	538
Tan bark extract.....	.....	508	.....	1,084
	1000 lb. units		1000 lb. units	
Ginseng.....	182	1,480	155	1,265
Roots, herbs, barks, etc.....	.....	476	.....	410
Medicines, patent and proprietary.....	.....	6,966	.....	6,521
Baking powder.....	2,956	866	2,858	779
Washing powder, etc.....	11,224	506	12,683	533
Petroleum jelly, vaseline, etc.....	.....	635	.....	640
SOAP AND TOILET ARTICLES:				
Toilet soaps.....	.....	2,185	.....	1,801
Other soaps.....	55,528	2,672	59,514	2,863
Perfumes and toilet preparations.....	.....	1,575	.....	1,514
Soap materials (fat, etc.).....	.....	5,117	.....	4,421
EXPLOSIVES:				
Cartridges.....	.....	3,015	.....	6,567
Dynamite.....	13,310	1,498	11,303	1,214
Gunpowder.....	1,284	360	867	290
Other explosives.....	.....	652	.....	1,967
OILS: Vegetable oils, fixed and pressed:				
Cottonseed oil.....	264,779	17,991	216,309	14,684
Corn oil.....	17,789	1,219	16,204	1,127
	1000 gal. units		1000 gal. units	
Linseed oil.....	1,591	784	266	154
Other fixed oils.....	.....	418	.....	393
Animal oils (total).....	2,507	1,250	871	542
Including: Fish oil.....	1,187	319	155	47
Lard oil.....	88	102	102	81
Mineral oils:				
Raw oil.....	194,570	8,448	124,736	4,959
Illuminating oil.....	1,119,441	72,042	1,010,449	64,113
Lubricating oil.....	207,639	29,609	191,648	26,316
Gasoline.....	117,728	17,419	162,669	19,898
Other light distillates.....	70,329	10,674	47,024	5,391
Gas oil and fuel oil.....	359,009	9,991	634,297	18,019
All others.....	67,850	1,134	69,210	1,205
Paraffin and paraffin wax.....	236,046	8,177	188,823	6,435
	1000 lb. units		1000 lb. units	
Ethereal oils:				
Peppermint oil.....	112	367	119	309
Other ethereal oils.....	.....	254	.....	229
NAVAL STORES:				
Rosin.....	2,605	13,563	1,749	8,068
Tar, turpentine and pitch.....	179	526	419	541
	1000 gal. units		1000 gal. units	
Turpentine oil.....	20,024	8,161	11,118	5,189
FERTILIZERS:				
Phosphate rock:				
High-grade hard rock.....	473	4,735	282	2,818
Land pebble.....	891	5,255	681	3,948
Other grades.....	2	6	1.1	5.5
Other fertilizers.....	73	1,667	64	1,311
MISCELLANEOUS:				
Graphite.....	5,384	392	3,921	277
Coke.....	882	3,310	592	2,234
	1000 lb. units		1000 lb. units	
Mercury.....	86	44	108	71
Celluloid.....	.....	1,317	.....	1,109
Caoutchouc:				
Waste.....	6,560	768	4,187	409
Reclaimed.....	4,988	837	6,250	872
	1000 ton units		1000 ton units	
Wood flour.....	17.7	738	11	484
	1000 lb. units		1000 lb. units	
Hops.....	25,701	7,484	11,056	2,926
Glue.....	2,362	260	2,248	243
Candles.....	2,683	253	3,153	308
	1000 piece units		1000 piece units	
Electric lamps:				
Arc.....	7.7	134	2.1	43
Carbon filament.....	1,844	255	608	88
Metallic filament.....	1,091	302	1,348	278
	Running feet		Running feet	
Photographic films for cinematograph (unexposed).....	114,124	3,056	88,401	2,581
Other sensitized products.....	.....	2,107	.....	1,498
Vulcanized fabrics, etc.....	.....	777	.....	652
	1000 bbl. units		1000 bbl. units	
Cement.....	2,964	4,271	2,140	3,089

EXPORTS	1913		1914	
	1000 lb. units	\$1000 units	1000 lb. units	\$1000 units
PAINTS AND VARNISHES:				
White lead.....	15,062	905	17,646	1,017
Zinc oxide.....	28,933	1,136	31,183	1,409
Lampblack.....	.....	470	.....	389
Other pigments.....	.....	724	.....	684
	1000 gal. units		1000 gal. units	
Ready mixed paints.....	907	1,167	772	974
Lacquers and varnishes.....	1,130	1,107	863	834
Similar products.....	.....	1,819	.....	1,596
Printers' ink.....	.....	435	.....	421
Other inks.....	.....	197	.....	152
Blacking.....	.....	698	.....	546
Pencils.....	.....	611	.....	500

### THE GERMAN LEAD INDUSTRY

A number of German works, members of the German Sales Bureau for Rolled and Pressed Lead Manufacturers, have, according to *Engineering* 99 (1915), 247, formed a combine under the name of the United Lead and Tin Works, Limited, Cologne, and have also entered into an agreement with the Rhenish-Nassau Mining Company, Stolberg. A central rolling-mill will be erected in direct connection with the works. The new firm, after the erection of the central works, will remain a member of the above-mentioned sales bureau, an agreement having been arrived at to this effect. The new company, however, will not only manufacture goods for the sales bureau, but also specialties, which the different works hitherto have manufactured for their own account. The Gelsenkirchen Lead Works, which is at present idle, will be extended and maintained as a kind of center for the coal district. The capital of the new company amounts to 3,150,000 marks.

### A NEW TYPE OF OIL CARRIER, THE CYLINDRICAL TANK STEAMER "RICARDO A. MESTRES"

A new type of oil-carrying steamer has recently been built in England; in it the oil, instead of being carried in ordinary holds with straight bulkheads, is contained in large vertical cylindrical tanks, so that there is a freedom from webs and stiffeners on the internal surface, the consequence being that the process of cleansing is greatly expedited and more effective. The tanks are of sufficient capacity to take the full dead-weight load of heavy oil, and ordinary cargo or light oil can be shipped in the spaces between the outer walls of the cylindrical tank and the sides of the ship, this space being divided up into a number of compartments by water-tight bulkheads.

A vessel of this type, the "Ricardo A. Mestres," is illustrated in a recent issue of *Engineering*; she was constructed for the Transcontinental Petroleum Company, and is the third of her type to be put into service.

This vessel has a length between perpendiculars of 365 ft., a breadth extreme of 50 ft. 9 in., and moulded of 50 ft. 6½ in., while the depth moulded is 29 ft. 3 in. She is built with a double bottom extending throughout the full length of the ship, with the usual fore peak, in which oil fuel may be carried in supplement to the oil fuel in the athwartship bunker immediately in front of the boiler compartment, which, with the engine-room, is placed in the after part of the ship. There are five tanks for the carrying of heavy oil. The forward tank has a capacity of 32,850 cu. ft., the other four of 38,025 cu. ft. each; the hold-tanks, at the side of and between the cylindrical tanks, on the port as well as the starboard side, are of a capacity each of 10,642 cu. ft. In addition, oil may be carried in the five double-bottom tanks, as marked on the longitudinal section; and these, including the accommodation of the expansion trunks formed in connection with the decks, make the total capacity of the cargo spaces up to 285,793 cu. ft. Excluding the expansion trunks, the total capacity is 263,968 cu. ft. In addition, there is bunker capacity of 26,183 cu. ft.



### TRANSVAAL GOLD-MINING

The fact does not appear to be generally recognized, according to *Engineering*, 99 (1915), 380, that since September last year the production of gold in the Transvaal has on the whole shown a greater output than in the corresponding months of the previous year. The output in October was valued at \$15,100,000, as compared with \$14,800,000 in October, 1913; in November at \$14,800,000, as compared with \$13,900,000; in December at \$14,350,000, as compared with \$13,900,000; in January at \$14,900,000, as compared with \$13,400,000; and in February at \$11,500,000, as compared with \$12,900,000. Transvaal gold-mining is, however, threatened with a special war tax by the South African Union.

### THE CANADIAN CHEMICAL MARKET

According to *Chemische Industrie*, 38 (1915), 74, prohibition of the exportation of chemicals from England combined with the stoppage of German exports has made Canada dependent almost entirely on American chemical products. Among those chemicals which are especially sought for in Canada are carbolic, salicylic, oxalic, citric and tartaric acids, camphor, cocaine, morphine, codeine, glycerine, hydroquinone, menthol, vegetable oils, potassium permanganate, sodium benzoate and salicylate, and santonine. The prices of these articles have reached from 200 to 900 per cent of their normal values.

### MONOPOLY FOR NITROGEN PRODUCTS IN GERMANY

The German Government has introduced a measure of great importance to the chemical industry—*viz.*, a proposal for the establishment of a trade monopoly for various nitrogen products, to remain in force until March 31, 1922 [*Engineering*, 99 (1915), 455]. After that date the Act can be prolonged by fresh legislation. The measure is described as having been due to the present emergency, and comprises: (a) Inorganic minerals containing nitrogen; (b) nitrogen products manufactured synthetically, as well as natural products; (c) manures, containing nitrogen, coming under (a) and (b). The monopoly will affect the different kinds of saltpeter, nitride of sodium, ammonium products, guanidine, nitric acid, etc. It will affect both the Norwegian and the Swedish industries within that branch, which have a market of some importance in Germany.

### TIN MINING IN SIAM

A feature of the tin mining industry which centers around the Straits is the increased production obtained from Siamese Malaya and Siam itself. [*Mining Journal*, 4157 (1915)] Nowhere has the tin dredging industry had so much success, and the scale of operations at the present time is the most extensive anywhere. For the last financial year, 1913-1914, eight dredges were at work, which produced black tin yielding 1,800 tons of metal from 4,700,000 yards of gravel treated. This number has been added to since, and there are now thirteen dredges at work and more under construction. Apart from the dredging industry the output of metal would probably show a declining tendency. The output for the last four years in metal is as follows:

1910-1911.....	4,900 tons	1911-1912.....	5,900 tons
1912-1913.....	6,600 tons	1913-1914.....	6,800 tons

D. G. ANDERSON

### CHINA CLAY IN ENGLAND

The present state of the China clay trade in Cornwall is, according to the *Paper Makers' Journal*, No. 3 (1915), exceedingly quiet. Comparatively little business is being done in any grade. Many of the China clay works are shut down entirely, and others are working short time.

The demand for China clay from America has fallen off considerably, and the scarcity of shipping, combined with high freights and insurance, is proving very detrimental to the home trade. The industry on the whole is badly hit, and most of the works at present working are engaged in development work. Stocks are accumulating and in many cases the dries are closed.—A.

### ENAMELLED WIRE

During the past few months enamelled wire has obtained a very great popularity for very many purposes, and considerable success has been achieved in its manufacture by way of eliminating the early defects which manifested themselves. Even now, however, there are complaints that for certain purposes difficulties arise owing to the apparent inability to coat the wires absolutely evenly with the enamel in the enamel bath. The particular complaint which has just come under notice [*Mechanical World*, 1475 (1915)] has reference to the use of this wire for telephone purposes, especially in tropical countries, but it is not altogether certain that the complaints may not be due to isolated instances rather than to there being a generally unsatisfactory result. That such wires are giving satisfaction is indicated by their use in the Post Office Telephone Department, where very stringent tests are imposed. The practice of the G. P. O. is to insist that such wires shall be able to withstand an electrical pressure of 1000 volts after immersion in caustic soda, sulfuric acid, nitric acid, and hydrochloric acid, for 48 hours, and potash for 35 minutes. It is also a fact that more than one manufacturer of telephone apparatus in which enamelled wire is used is quite satisfied with the product he is obtaining; but manufacturers of this wire will probably welcome having their attention drawn to the fact that complaints are even now made. It is suggested that simple enamel insulation is not suitable for very fine-gauged wires, and it is more or less to these that such complaints as are made relate.—A.

### LIQUID FUEL FOR INTERNAL COMBUSTION ENGINES

According to *The Engineer*, No. 3095 (1915), 408, one of the problems which will shortly have to be faced in a thorough manner by the chemists of Great Britain, is that of providing an alternative fuel for the class of engines that are now dependent for their operation on petrol and benzol. In 1914 the world's output of crude oil amounted to 57 million tons and the highest possible yield of petrol from the whole quantity is placed by Professor Lewes at 1,700,000,000 gallons, of which amount the United States, alone, last year used 1,200,000,000 gallons and Great Britain over 200,000,000.

The two fuels from which petrol is likely to receive the chief opposition in the future are, of course, benzol and alcohol. The yield of the former is, however, almost infinitesimal, and there is not much likelihood of any material increase in the production. Taken at 1.8 gallons per ton of coal, the total amount, from the whole of the coal carbonized in Great Britain last year would be only 9,000,000 gallons. That the Germans had been alive to the valuable properties of benzol is shown by the fact that nearly all the benzol produced in the coke ovens in England has been exported to Germany, chiefly for use in the dye industry.

The Germans also commenced to replace all the old beehive ovens by recovery ovens, free of cost, and took payment in benzol. Recognizing the necessity for economy in this class of fuel at the present time, the Germans are now said to be employing for military transport purposes a mixture containing 80 per cent alcohol and 20 per cent benzol, to which is added 200 grains of naphthalene. The last-named ingredient is first dissolved in the benzol, which, in turn, is mixed with the alcohol and, according to Professor Lewes, the resulting mixture gives five-sixths of the power of petrol. Unfortunately, much of the benzol now



on the market, and especially that produced by gasworks, has an injurious effect upon the engine, owing largely to the presence in it of sulfuric acid.

One of the leading motor car manufacturing firms has taken the pains to investigate the effects of poor quality benzol upon lubricating oil and has found that when sulfuric acid is present in the benzol a semi-solid deposit is formed in the crank case, due to the leakage of benzol past the pistons. This deposit consists of carbon and sulfuric acid and the acid rusts the valves and stems. The best remedies for this state of things are more thorough washing of the spirit or, failing this, the mixing of the benzol with petrol in the proportion of 65 per cent benzol and 35 per cent petrol, the alkaline ingredients in the latter neutralizing the acid content of the benzol.

Everything, however, points to alcohol as the fuel of the future. The thermal value of alcohol is only about one-half that of petrol or benzol, but whereas it is not advisable to use a higher compression pressure with the last-mentioned fuels than about 80 lbs. per sq. in., with alcohol the compression may be raised to a pressure of 200 lbs. without fear of preignition, and the quantity of air required to complete combustion is little more than one-half. Last year the Royal Automobile Club appointed a committee to investigate and report on alcohol as a fuel. The report has not yet been published, but the most important problem which this body will have to investigate is that of finding a suitable denaturant which will satisfy the excise authorities. If the efforts of this committee result in the abatement of the duty and some modification of existing restrictions on the manufacture of alcohol, capital will no doubt be readily found to provide factories for the production of the fuel in such quantities as will, at any rate, serve to prevent the further rise in price of petrol on which so much of the nation's welfare depends.—A.

#### BRITISH BOARD OF TRADE

During the month of May the British Board of Trade have received enquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Aluminum ware	Bimetallic strips for use as compensating devices in recording thermometers, in brass and 36 per cent nickel steel or similar combinations
Artificial horse hair	Black-lead pencils (cheap)
Belts and belting	Metal ink bottles for covering with leather
Celluloid boxes	Nickel ink bottles for attaché cases
Slip lid zinc tins	White glass bottles, to take screw caps
Camel hair brushes	Brass-headed chair nails
Bronze powder	Carnauba wax (fatty gray quality in lumps)
Celluloid buttons	Celluloid device for holding papers straight, for use with typewriting machines
Case-hardening compositions	Cast iron cylinders for carbolic acid
Cellulose extract	Celluloid in solid rods and tubes
Acetate of lead	Butyric acid, 90 per cent
Aniline oil	Epsom salts (B. P. and commercial)
Antimony oxide	Sodium nitrate (refined)
Chloride of magnesite	Xylene (o, m, and p)
Cresol	Enamelled iron clock dials
Phthalimide	Vulcanized hair combs
Red phosphorus	Pressed bone dominoes
Salicylate of soda	Glue, dry, for boot and shoe trade
Salicylic acid	Filtering pulp as used in breweries
Zinc oxide	Opal shades for electric lights
Collapsible tubes	Leather and imitation leather
Lactometers	Machinery for making leather cloth
Bismuth subnitrate	Machinery for molding celluloid into rings and hooks
Caffein-sodium benzoate	Machinery for printing pottery transfers
Guaiaacal	Skeinng machines for splitting rods
Phenyl salicylate	Machine for wire stitching
Sodium bromide	Malacca canes (about 15 feet long) for use as drain rods in conduit work
Fustic extract	Metal foil—Brass foil and Dutch metal foil
Logwood extract	Metal tubes, seamless, in very fine gauges for making hypodermic needles
Carbon for arc lamps	Paper—cigarette paper, and paper for pottery transfers
Porcelain insulators	Steel sheets coated with brass, copper and nickel
Brown ware	Spent animal charcoal
Lanoline	Thermometers (clinical and dairy)
Galalith substitute	Typewriting supplies (ribbons, etc.)
Gelatine	Waste liquors from wood paste
Lithopone	Vegetable ivory in tubes
Locks for tin trunks	Vulcanite beads
Mirrors	Tungsten powder
Olive oil soap	
Barytes	
Crude antimony ore	
Sacks	
Preserved egg preparation	
Tanning materials	
Springs (spiral steel)	
Steel thimbles	

Firms who may be in a position to supply any of the above articles are asked to communicate with the Director of the

Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.—A.

#### IRON PRODUCTION OF THE U. S.—MAY, 1915

The total pig-iron output of the United States in May was 2,263,470 tons, or 73,015 tons a day, against 2,116,494 tons in April, or 70,550 tons a day. With 205 furnaces in blast June 1st, or ten more than on May 1st, the active capacity was 74,343 tons, against 71,385 tons one month previous. Pig-iron production is now at the rate of 27,400,000 tons a year. On April 1st it was at 26,000,000 tons, and on January 1st at 18,000,000 tons a year.

Comparison of last month's iron output with previous months of the past three years (figures here representing gross tons) is as follows, according to the *Iron Age*:

	1915	1914	1913
May.....	2,263,470	2,092,686	2,822,217
April.....	2,116,494	2,269,995	2,752,761
March.....	2,063,834	2,347,867	2,763,563
February.....	1,674,771	1,888,670	2,586,337
January.....	1,601,421	1,885,054	2,795,331
	1914	1913	1912
December.....	1,515,752	1,983,607	2,782,737
November.....	1,518,316	2,283,603	2,630,854
October.....	1,778,186	2,546,261	2,689,933
September.....	1,882,577	2,505,927	2,463,839
August.....	1,995,261	2,545,763	2,512,431
July.....	1,957,645	2,560,646	2,410,889
June.....	1,917,783	2,628,565	2,440,745

#### OUTPUT OF PORTLAND CEMENT IN U. S.—1915

The output of Portland cement last year, according to the *New York Evening Post*, totaled 88,230,170 barrels, valued at \$81,789,368. This was a decrease in quantity of 3,866,961 barrels, and a decrease in value of \$10,768,249, compared with 1913. Pennsylvania and Indiana held first and second places, respectively, as producing States.

#### U. S. TRADE IN APRIL

The following table from the monthly report of the Bureau of Foreign and Domestic Commerce, Department of Commerce, shows a gain in trade in all classes of merchandise.

	1915	1914	1913
<b>EXPORTS, APRIL</b>			
Crude material.....	\$ 44,355,870	\$ 37,627,006	\$ 47,556,871
Foodstuffs, crude.....	59,414,365	6,328,730	13,209,610
Foodstuffs, partly prepared.....	46,618,860	19,590,417	26,178,111
Partly manufactured.....	38,451,343	31,844,607	37,044,590
Manufactures, complete.....	90,503,475	62,557,755	70,664,000
Miscellaneous.....	9,693,543	1,021,188	1,580,524
Total domestic.....	\$289,037,456	\$158,969,703	\$196,233,706
Foreign exp.....	5,708,661	3,582,867	3,579,732
<b>TOTAL EXPORTS.....</b>	<b>\$294,746,117</b>	<b>\$162,552,570</b>	<b>\$199,813,438</b>
<b>IMPORTS, APRIL</b>			
Crude material.....	61,714,060	\$ 65,868,163	\$ 52,987,666
Foodstuffs, crude.....	22,685,047	20,414,438	15,991,013
Foodstuffs, partly prepared.....	33,806,036	25,064,922	18,243,578
Partly manufactured.....	19,227,750	27,164,602	29,278,333
Manufactures, complete.....	21,775,507	34,082,964	28,937,438
Miscellaneous.....	1,367,706	1,167,025	756,436
<b>TOTAL IMPORTS.....</b>	<b>\$160,576,106</b>	<b>\$173,762,114</b>	<b>\$146,194,461</b>

#### TAR DEHYDRATION AND TOLUOL RECOVERY

The question of the dehydration of tar has lately attracted considerable attention in England, since prepared tar is being generally adopted for road construction and the light oils driven off in the process of dehydration contain all the toluol and phenol originally in the tar, products now in urgent demand for the manufacture of explosives. One ton of average crude gas-works tar yields, when dehydrated, 160 gallons of prepared tar, 30 gallons of light oils, and 10 gallons of ammoniacal liquor. An average sample of 200 cc. of the such light oil, washed with caustic soda, gave 18 per cent of tar acids; on fractionating the washed oil, the following results were obtained:

Temp.	Per cent product	Temp.	Per cent product
Up to 100° C.	35 Benzol	120° to 125° C.	28 Solvent naphtha
100° to 120° C.	10.5 Toluol	Residue	40.5 Creosote

The oil also contained 6 per cent of very good pyridine. The quantities of fuel required per ton of tar distilled are with plants actually at work, 67 lbs. of breeze or 450 cu. ft. of gas of 500 B. T. U. [*J. Gas Lighting*, 130 (1915), 330].



# SCIENTIFIC SOCIETIES

## THE SEATTLE MEETING

The 51st Annual Meeting of the American Chemical Society will be held at the University of Washington, Seattle, August 31st to September 2nd. The Hotel Frye, corner 3rd Avenue and Vesler Way, has been chosen as headquarters. Cowen Park and Ravenna cars, which pass headquarters on 3rd Avenue, lead, without transfer, to the University grounds, reaching the 40th Street entrance to the Campus in 35 minutes.

REGISTRATION will take place in the lobby of Hotel Frye on August 30th and in Bagley Hall, University of Washington, on August 31st and September 1st. All members and guests should register on arrival and are requested to secure banquet tickets on registration. Special excursions to points of interest may be arranged for at the registration desks, and guides will be provided.

### PROGRAM OF MEETING

- AUGUST 30, 7.30 P.M.—**Complimentary dinner to the Council**, at the Hotel Frye, by the Science Faculty of the University of Washington; followed by business meeting.
- AUGUST 31, 10.00 A.M.—**Opening meeting** at Meany Hall.  
**Addresses of Welcome**—HON. ERNEST LISTER, Governor of State, and PRESIDENT HENRY SUZZALO, of the University of Washington.  
**Response**—DR. H. K. BENSON.  
**Address**, "Chemical Industry,"—DR. LEO. H. BAEKELAND.  
 1.30 P.M.—**Division Meetings**, Bagley and Science Halls.  
 3.00 P.M.—**Complimentary Reception and Tea**, for ladies, University Campus.  
 8.00 P.M.—**Complimentary Smoker** by Seattle Commercial Club.  
 8.00 P.M.—**Complimentary Organ Recital**, for ladies.
- SEPTEMBER 1, 10.00 A.M. and 1.30 P.M.—**Division Meetings**.  
 10.00 A.M.—**Complimentary automobile ride**, for ladies.  
 4.30 P.M.—**Complimentary automobile trip** from University Campus to Hotels *via* boulevard system.  
 8.00 P.M.—**President's Address**—PRESIDENT CHARLES HOLMES HERTY; followed by business meeting.
- SEPTEMBER 2—**Excursion on Puget Sound** for inspection of harbor facilities and the fishing industry.  
 8.00 P.M.—**Subscription Banquet** (Price, \$3.00).  
 11.55 P.M.—Special train leaves Seattle for Mt. Ranier Park (See THIS JOURNAL, 7 (1915), 545).

### LOCAL COMMITTEES (SEATTLE)

The following local committees are in charge of the arrangements for the meeting:

- EXECUTIVE**—H. G. Byers, *Chairman*; E. J. Bartells, *Vice-Chairman*; H. L. Trumbull, *Secretary*; J. E. Bell, *Treasurer*; H. K. Benson, *Councilor*.  
**FINANCE**—H. K. Benson, *Chairman*; M. J. Falkenburg, C. A. Newhall, Rex Smith, C. E. Bogardus, J. H. Linton, H. Maschmedt, E. J. Bartells.  
**EXCURSIONS**—E. J. Bartells, *Chairman*; C. E. Bogardus, E. A. Dieterle, George Grindord.  
**PRESS**—Lee A. White, *Chairman*; E. E. Hurja, I. F. Laucks, E. O. Heinrich, Frank Sternberg.  
**RECEPTION AND REGISTRATION**—J. H. Linton, *Chairman*; M. J. Falkenburg, H. L. Trumbull, S. C. Langdon.  
**BANQUET**—R. W. Clough, *Chairman*; H. K. Benson, A. L. Knisely.  
**SMOKER**—M. J. Falkenburg, *Chairman*; J. H. Linton, Rex Smith, A. Jacobson.  
**LADIES' ENTERTAINMENT**—Mrs. C. A. Newhall, *Chairman*; Mrs. H. Maschmedt, Mrs. C. E. Bogardus, Miss Glenola Behling, Miss Ruby Clift, Mrs. Ray Clough, Mrs. H. G. Byers.

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Washington Annex	Single, \$1.50 to \$2.50	Double, \$2.00 to \$4.00

THE ARCTIC CLUB, located across Prefontaine Square from headquarters, will keep open house to delegates with dining-room and ladies' dining-room open all day. A limited number of rooms are available, and delegates may secure the same by writing M. J. Falkenburg, Pioneer Square, Seattle.

## THE DETERMINATION OF MOISTURE IN SHELLAC

Both orange and bleached shellac give off volatile matter at temperatures approaching 100° C. Bleached shellac alters chemically at these temperatures losing its solubility in alcohol.

For these reasons the usual methods of determining water by heating in the air bath at 100° to 110° C. are not applicable in the analysis of shellac.

**SAMPLING**—Bleached shellac is sold in three forms, as hanks or bars containing approximately 25 per cent water, as ground bleached in pulverized form with about the same water content, and as bone-dry or kiln-dried shellac. The latter is prepared by drying the ground bleached shellac in the air or in vacuum driers at moderate temperatures: it may contain, depending upon the completeness of the drying and weather conditions, up to 10 per cent or more of water.

In sampling bone-dry bleached shellac a fairly large portion (about a pound) should be taken from different parts of the barrel and finely ground by running quickly through a coffee mill. No attempt must be made to sieve it. It should be rapidly mixed and transferred to a Mason jar provided with a screw cap and rubber ring seal; the jar should not be more than two-thirds full, leaving room for a thorough mixing by shaking the contents; it must be kept in a cool place and tested as promptly as possible. If too warm the shellac may become partly caked, in which case the lumps must be broken up by shaking the bottle.

In sampling bars or hanks it is recommended that a whole hank be taken. It should be crushed and ground as rapidly as possible. Ground bleached may be treated as above, bearing in mind that the large amount of moisture present makes rapid handling imperative.

**MOISTURE DETERMINATION**—*Method 1*: From 5 to 10 grams of the sample should be weighed in flat-bottomed dishes about four inches in diameter or in watch glasses ground to fit and provided with a clamp. The shellac is then placed in a desiccator freshly filled with concentrated sulfuric acid. The contents of the dish should be spread out in a thin layer to expose as large a surface as possible. The desiccator is exhausted by a vacuum pump as completely as possible. With a good vacuum (3 mm. pressure or better) constant weight will be obtained in between 24 and 48 hours. Absolutely dry bleached shellac is quite hygroscopic and the final weight should be taken as rapidly as possible.

*Method 2*: The same results may be obtained by drying the shellac in a well ventilated air bath from 3 to 6 hours at 100°–110° F. (38°–43° C.). One or two electric light bulbs provide a convenient source of heat. The temperature should not be allowed to rise above 43° C., otherwise sintering may occur and retard drying. With poorly ventilated ovens the drying may take much longer. Completeness of drying should be ascertained by continuing the treatment to constant weight. It is recommended that analysts check the accuracy of results obtained in the oven by comparison with a test made in a vacuum desiccator before relying exclusively on the oven.

**NOTE**—When the determination of alcohol-insoluble matter in bleached shellac is required, the sample must be dried if in the form of bars or ground bleached, as the water present dilutes the alcohol to a point where solution may not be complete. Prolonged heating at the temperatures of 38°–43° C. stated above may render the shellac partly insoluble and it is recommended that in preparing shellac for this determination a separate portion be dried by exposure to the air in a thin layer without the application of heat.

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RESULTS OF SOME CO-OPERATIVE WORK ON DETERMINATION OF SULFUR IN PYRITES; SOME OBSERVATIONS ON DETAILS OF MANIPULATION, SOURCES OF ERROR, AND ON BARIUM SULFATE AS PRECIPITATED UNDER DIFFERENT CONDITIONS<sup>1</sup>

By H. C. MOORE

After several experiences, when we had submitted portions of the same ground laboratory sample to several laboratories for sulfur analysis, we found that a good general agreement of the results reported was quite unusual. Since it generally appeared, upon investigation, that all laboratories had followed practically the same details of analysis, the cause of these disagreements was not apparent. We then decided to make a study of this matter and the best plan seemed to be that of co-operative work on carefully prepared samples. Accordingly, two large samples were ground to pass 80 mesh and were separately mixed. Sealed portions of these samples were sent to several laboratories with the request that they determine sulfur by their usual

committee on sulfur determination in pyrites, blends, etc., to the 6th International Congress of Applied Chemistry.<sup>1</sup> The methods followed were those of Lunge and of Silberberger. The maximum difference by each method was nearly 1 per cent.

Many investigators, and especially Allen and Johnston,<sup>2</sup> have pointed out several causes, or sources of error, accountable for differences in results obtained by the Lunge method. Allen and Johnston determined quantitatively the effect of these errors and found the greatest to be due to the presence of ammonium salts in the solution in which barium sulfate is precipitated. We also made a quantitative study of this error and our results, Table IV, confirm closely the results of Allen and Johnston, and show that by the modified Lunge method this error affects the results by from 0.3 to about 1.0 per cent sulfur.

We also made a study of the methods of effecting oxidation and solution of the sample (Results, Table II), and found two sources of error following the Lunge method: (1) loss of sulfur presumably by volatilization and (2) loss due to incomplete oxidation. In Sample 15,095 free sulfur separated when treated with the nitro-hydrochloric acid: in such a case another error

TABLE I—SULFUR RESULTS REPORTED BY THE SEVERAL LABORATORIES ON THE TWO SAMPLES OF PYRITES

Lab. No.	Analyst	Per cent S—Dry basis		METHOD OF ANALYSIS
		15095	15096	
1	B	38.88	46.91	Modified Lunge method. (a) Two precipitations of iron by NH <sub>4</sub> OH. Iron residue not tested for sulfur.
	A	38.63	46.79	
2		38.60	46.63	Same as No. 1.
3		38.74	47.06	Av. of several modifications of Lunge.
4		38.93	46.60	Practically same as No. 1, except iron residue was dissolved and sulfur precipitated by BaCl <sub>2</sub> .
5	W	38.73	47.00	Modified Lunge. Made 2nd evaporation with HNO <sub>3</sub> -HCl mixture. One precipitation of iron by NH <sub>4</sub> OH. Iron residue not tested for sulfur.
	B	39.24	47.06	
	L	39.21	47.34	
6		39.50	47.63	Lunge. BaSO <sub>4</sub> dried at 130° C.
7	A	39.41	47.38	Allen and Bishop method. (b)
	B	39.54	47.40	
	C	39.43	47.32	
8		40.00	47.88	Lunge. One precipitation of iron by NH <sub>4</sub> OH. Sulfur precipitated in iron residue. BaCl <sub>2</sub> solution added all at once.
9		39.23	47.62	Modified Lunge. One precipitation of iron by NH <sub>4</sub> OH. Iron residue not tested for sulfur.
10		39.48	47.63	Method not reported.
11		39.55	47.62	Modified Lunge. Allen and Bishop method of solution. One precipitation of iron by NH <sub>4</sub> OH. Iron residue dissolved in HCl and sulfur precipitated.
12	S	39.53	47.76	Modified Lunge. One precipitation of iron by NH <sub>4</sub> OH. Iron residue dissolved in HCl and sulfur precipitated.
	H	39.21	47.76	
13		39.56	47.45	Modified Lunge. Two precipitations of iron by NH <sub>4</sub> OH. Iron residue dissolved in HCl and sulfur precipitated. Beaker containing precipitated BaSO <sub>4</sub> left on steam bath over night before filtering.
		39.54	47.59	
14		39.37	47.28	Allen and Bishop Method.
		39.47	47.28	
		39.21	47.38	
		39.70	47.38	
15		39.19	47.19	Electrochemical method of A. M. Smoot. (c) Method of Smoot, except cold precipitation of BaSO <sub>4</sub> according to Allen and Bishop.
		39.59	47.19	
		39.59	47.44	
16		39.19	47.88	Modified Lunge. Two evaporations with HNO <sub>3</sub> -HCl mixture.
		39.15	47.87	
				Allen and Bishop method.

SUMMARY OF ABOVE RESULTS (excepting those of Laboratory 10 and 14)

	MODIFICATIONS OF LUNGE METHOD		ALLEN AND BISHOP METHOD	
	Sample No. 15095	Sample No. 15096	Sample No. 15095	Sample No. 15096
Max. per cent sulfur.....	40.00	47.88	39.59	47.87
Min. per cent sulfur.....	38.60	46.60	39.15	47.31
Aver. per cent sulfur.....	39.18	47.28	39.47	47.49

(a) By modified Lunge method is meant some one of the numerous modifications. By most of these modifications BaSO<sub>4</sub> is precipitated by the slow addition of BaCl<sub>2</sub> solution.

(b) "An Exact Method for Determination of Sulfur in Pyrites Ore." 8th International Congress of Applied Chemistry, 1, 33.

(c) Engineering and Mining Journal, 94, No. 9.

method and when reporting their results to describe briefly their details of analysis. Results have been received from seven-teen laboratories and appear in Tables I, II and III; these results present about the usual disagreement.

The following laboratories and analysts participated in the work:

- McCandless Laboratory..... Atlanta, Ga.
- N. P. Pratt Laboratory..... Atlanta, Ga.
- Stillwell & Gladding..... New York, N. Y.
- Pennsylvania Salt Manufacturing Company..... Philadelphia, Pa.
- A. M. Smoot, Ledoux & Company..... New York, N. Y.
- W. S. Allen, General Chemical Company..... New York, N. Y.
- F. B. Carpenter, Virginia-Carolina Chem. Company... Richmond, Va.
- W. D. Richardson, Swift Fertilizer Company..... Chicago, Ill.
- C. W. Hackman, Swift Fertilizer Company..... Atlanta, Ga.
- W. C. Dumas, A. M. Lloyd Laboratory..... Atlanta, Ga.
- C. A. Butt, International Agricultural Corporation... Atlanta, Ga.
- F. K. Wanner, Tennessee Chemical Company..... Nashville, Tenn.
- W. D. Drummond, Planters Fertilizer & Chem. Co... New Orleans, La.
- Paul Rudnick, Armour Fertilizer Works..... Chicago, Ill.
- H. G. Hackman, Armour Fertilizer Works..... Chrome, N. J.
- R. Neu, Armour Fertilizer Works..... Jacksonville, Fla.
- R. D. Caldwell and H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.

Results of similar co-operative work were reported by the

<sup>1</sup> Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915. Recommended for publication by the Committee on Research and Methods of Analysis, Division of Fertilizer Chemists.

would be introduced unless this free sulfur were oxidized and brought into solution.

The most general method for determining sulfur in pyrites has been either that of Lunge or some modification of this method. Allen and Johnston<sup>3</sup> have shown that accurate results are impossible by any modification of the Lunge method, or when barium sulfate is precipitated in solutions containing ammonium salts, unless as the result of a nice balancing of the plus and minus errors, or by applying certain empirical corrections. The fact, however, that some laboratories, by certain modifications of this method, get results which agree with those of the later and more exact methods, either that of Allen and Bishop<sup>4</sup> or of Smoot,<sup>5</sup> shows that they have employed details of analysis which have produced conditions favorable to a nice balancing of the plus and minus errors.

Laboratory 6 seems to have effected a compensation of errors

<sup>1</sup> Also published in *Zeit. fur angew Chemie*, 1905, p. 449.

<sup>2</sup> *J. Am. Chem. Soc.*, 32 (1910), 588.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> 8th International Congress of Applied Chemistry, 1, 33.

<sup>5</sup> *Engineering and Mining Journal*, 94, No. 9.



by drying the barium sulfate at 130° instead of igniting. Our investigation shows that under certain conditions (see Table IV) very good results are obtained by this practice.

Attention is called to the results of Analyst 14, Mr. A. M. Smoot, to whom credit must be given for some very interesting observations relative to the co-precipitation of calcium sulfate with barium sulfate. He found that his results on Sample 15096 by the modified Lunge method<sup>1</sup> and his electrochemical method were normal, but that results on Sample 15095 by the same methods were unusual in that higher results were obtained

an aliquot for analysis. The result of this procedure did not agree quite so well for some reason as those by the regular method. The method of Smoot also appears to be an excellent one except that suitable electrical apparatus is not available in all laboratories.

From the foregoing and from the results in Tables I to IV, we might conclude that the disagreement in results in Tables I, II and III is due partly to the different methods of analysis and partly to the personal factor or different ways of handling the same method.

TABLE II—RESULTS BY ANALYST A OF OUR LABORATORY

METHOD	Per cent sulfur on dry basis	
	No. 15095	No. 15096
(1)—Modified Lunge. 0.5-g. samples treated with 10 cc. nitro-hydrochloric acid (a) (also KClO <sub>3</sub> on Sample 15095) and after 15 minutes placed on steam plate and evaporated. Evaporated again with 10 cc. HCl and took up residue with 1 cc. HCl and 100 cc. water. One precipitation of iron by NH <sub>4</sub> OH and filtrate, 350–400 cc., boiled to expel excess NH <sub>3</sub> before precipitating. Iron residue dissolved in dil. HCl and sulfur precipitated.	39.19	47.13
(2)—Same as (1) except sample and acid mixture stood one hour in cold before heating on steam plate.	39.21	47.16
(3)—Same as (2) except sample and acid mixture stood about 12 hours in cold before heating on steam plate.	39.34	47.26
(4)—Same as (1) except that sample and acid mixture stood from one-half to one hour cold and then after evaporation, made six successive evaporations with 5 cc. nitro-hydrochloric acid.	39.24	47.31
(5)—Same as (3) making one extra evaporation with 5 cc. nitro-hydrochloric acid.	39.48	47.34
(6)—Same as (3) except that sample and acid mixture stood in cold 10–15 minutes before putting on plate.	39.21	47.08
(7)—Same as (1) except using Allen and Bishop method of solution.	39.21	47.28
(8)—Allen and Bishop method.	39.37	47.53

(a) 3 parts by volume of conc. HNO<sub>3</sub> and 1 part conc. HCl.

by the modified Lunge method than by the electrochemical method. He then found that this sample contained a considerable amount of carbonate of lime and found on further investigation that quite an appreciable error had resulted from the co-precipitation of calcium sulfate with barium sulfate. He then combined the barium sulfate precipitates from two determinations (averaging 39.21 per cent), made by the electrochemical method and determined the per cent of CaO. His results follow:

Weight of the combined precipitates of BaSO <sub>4</sub>	2.8544 grams
Weight of CaSO <sub>4</sub>	0.0478 gram = 1.13% S
Weight of actual BaSO <sub>4</sub>	2.8066 grams = 38.55% S
<b>TOTAL</b>	<b>= 39.68% S</b>

The error therefore due to co-precipitation of calcium sulfate amounted to 0.47 per cent sulfur. He then made two determinations by the same method except that precipitation of barium sulfate was made by the method of Allen and Bishop. The results of these two determinations checked perfectly at 39.70 per cent sulfur. The two precipitates were combined and tested as before with the following results:

Weight of combined precipitates of BaSO <sub>4</sub>	2.8896 grams
Weight of CaSO <sub>4</sub>	0.0136 gram = 0.32% S
Weight of actual BaSO <sub>4</sub>	2.8760 grams = 39.50% S
<b>TOTAL</b>	<b>= 39.82% S</b>

The error in this case amounted to only 0.12 per cent sulfur, indicating that the co-precipitation of calcium sulfate is much less on cold precipitation by the method of Allen and Bishop than by hot precipitation.

Allen and Bishop showed that, by their method, 1 per cent calcium had no appreciable effect on the results. It is likely, however, that Sample 15095 contains calcium<sup>2</sup> in excess of this amount. At any rate, Mr. Smoot seems to have made a very interesting observation.

It will be noted from an examination of the results in Tables I, II and III that those obtained by the Allen and Bishop method are much more concordant than those obtained by the modifications of the Lunge method. The objections to the Allen and Bishop method are the large amount of barium sulfate to filter and wash; also the enormous beakers in which precipitation is made. This objection, however, we have successfully removed by using a smaller sample and correspondingly smaller beakers, as indicated under Methods 3 and 4, Table III. We also made a number of determinations by using a larger sample and after reducing with aluminum in a flask, made to volume and took

<sup>1</sup> Eng. Min. J., 94, No. 9.

<sup>2</sup> One complete analysis covering one month's shipment of this same kind of ore shows 2.48 per cent calcium.

Some chemists have claimed that some pyrites samples, even when kept in tightly stoppered bottles, undergo oxidation, thus reducing the per cent of sulfur in the sample. While this is doubtless true in some cases, yet it will hardly help to explain the disagreement of results in Tables I, II and III, since some

TABLE III—RESULTS BY ANALYST B, OUR LABORATORY

The results in this table were obtained over a period of a little over two months and several of the sealed portions of each sample were used in this work. Under Method 1, Sample 15096, for example, the first two results listed were obtained 6/4/14 and the last three results in the same list on 8/10/14. The other five results in this list were obtained between these dates. This would indicate that these samples did not change or oxidize on standing.

METHOD	Per cent sulfur on dry basis		
	No. 15095	No. 15096	No. 15096
(1)—Allen and Bishop (a)	39.50	47.41	47.49
	39.44	47.41	47.45
	39.56	47.44	47.36
	39.54	47.40	47.48
	39.52	47.49	47.43
Av.,	39.51	Av.,	47.43
(2)—Allen and Bishop, except that solution was filtered from insoluble residue before reducing with aluminum		47.43	47.47
		47.47	47.46
		47.45	47.48
		Av.,	47.46
(3)—Allen and Bishop, except used 0.5495 gram samples. Treated with 6–8 cc. Br-CCl <sub>4</sub> mixture and then 10 cc. HNO <sub>3</sub> and evaporated. Added 10 cc. HCl and again evaporated. Treated residue with 1 cc. conc. HCl and 50–100 cc. hot water. Added 0.1 g. Al powder to reduce iron, filtered and washed. Added 2.4 cc. conc. HCl and diluted to about 640 cc. and precipitated with 50 cc. 5 per cent BaCl <sub>2</sub> sol. cold and without stirring.	39.56		
	39.56		
	39.54		
	Av.,	39.55	
(4)—Allen and Bishop, exactly like (3), except that BaSO <sub>4</sub> was dried for 8 hrs. at 130° C. and weighed before ignition.	Dried Ignited(b)	Dried Ignited	
	40.55	39.69	48.41
	40.51	39.64	48.61
	40.40	39.57	48.59
	40.40	39.57	47.56
	Average,	40.49	39.63
		48.54	47.55
(5)—Allen and Bishop, exactly as described by author (1.3738 g.) except that BaSO <sub>4</sub> was dried for 18 hrs. at 130° C. and weighed before ignition.	Dried Ignited	Dried Ignited	
	40.37	39.56	48.41
	40.19	39.45	48.42
	40.29	39.52	48.42
	40.23	39.52	47.48
	Av.,	40.27	39.51
		48.42	47.46
(6)—Modified Lunge: 0.5495 g. sample, Allen and Bishop method of solution with final treatment like Method 1, Table II. BaSO <sub>4</sub> dried for 18 hrs. and weighed before ignition.	Dried Ignited	Dried Ignited	
	39.39	39.07	47.83
	39.50	39.08	47.83
	39.63	39.24	47.85
	39.43	39.09	47.73
	39.43	39.09	47.30
	Average,	39.49	39.12
		47.81	47.325

(a) Loc. cit.

(b) Ignited; heated to constant weight over high temperature burner.

of the results obtained by the Allen and Bishop method, more than a year ago, agree almost perfectly.

The fact that such disagreements in results are not unusual is a matter of considerable importance to the fertilizer industry since it is the largest single user and manufacturer of sulfuric acid.<sup>1</sup> This clearly proves the need of some standard method

<sup>1</sup> A. M. Fairlie, in "American Fertilizer Handbook," 1914, p. 35.



for determining the sulfur in pyrites. Such a method need not be used, unless desired, but it would at least provide a basis for standardizing other methods and be the method of final reference in case of disputes.

A few observations with reference to barium sulfate may be of interest. The barium sulfate precipitates from a hot and a cold solution differ in appearance and some results would indicate that their compositions also differ. When barium sulfate is precipitated in a hot solution and especially in solutions containing ammonium salts it is very fine while barium sulfate

TABLE IV—RESULTS BY ANALYST B, OUR LABORATORY, ON  $H_2SO_4$  SOLUTION The sulfuric acid solution was standardized by titration against C. P.  $Na_2CO_3$  using the same aliquot as used in (2) to (8) below. Calculating the  $Na_2CO_3$  value into terms of sulfur equals 45.18 per cent S, agreeing almost perfectly with the results by the methods (1) and (2) below. Precipitates of  $BaSO_4$  stood over night before filtering; they were then dried for 18 hrs. at  $130^\circ C.$ , weighed, ignited and weighed again.

	PERCENTAGE SULFUR	
	Dried	Ignited
(1)—Aliquot of $H_2SO_4$ solution (corresponding to about 4.5 g. $BaSO_4$ diluted to 1600 cc., added 10 cc. conc. HCl, and precipitated cold without stirring, by adding 125 cc. 5 per cent $BaCl_2$ solution, as described by Allen and Bishop.) <sup>(a)</sup>	45.99	45.16
	45.96	45.15
	45.98	45.15
Av.,	45.98	45.15
(2)—Aliquot of $H_2SO_4$ solution (corresponding to about 1.8 g. $BaSO_4$ ) diluted to 640 cc., added 4 cc. conc. HCl and precipitated as in (1) with 50 cc. 5 per cent $BaCl_2$ solution.	46.04	45.17
	46.11	45.16
	46.11	45.19
	46.10	45.19
Av.,	46.09	45.18
(3)—Same aliquot as (2) diluted to 350–400 cc. with water, heated to boiling and precipitated by adding 25 cc. hot 10 per cent $BaCl_2$ solution drop by drop, stirring continuously.	45.29	45.09
	45.34	45.13
	45.34	45.12
Av.,	45.32	45.11
(4)—Same aliquot as (2), diluted to 350–400 cc. water, added methyl orange, and made neutral with $NH_4OH$ , then added 3 drops conc. HCl and precipitated as in (3).	45.48	44.90
	45.48	44.94
Av.,	45.48	44.92
(5)—Same as (4) except 1 g. $NH_4Cl$ was added before precipitation of $BaSO_4$ .	45.26	44.81
	45.16	44.87
Av.,	45.21	44.84
(6)—Same as (5) except that 2 g. $NH_4Cl$ were added.	45.26	44.88
	45.23	44.85
Av.,	45.245	44.865
(7)—Same as (5) except that 4 g. $NH_4Cl$ were added.	45.17	44.74
	45.02	44.63
	45.07	44.62
	45.12	44.66
Av.,	45.095	44.66
(8)—Same as (5) except that 6 g. $NH_4Cl$ were added.	45.11	44.65
	44.96	44.52
	44.96	44.53
	44.92	44.47
Av.,	44.99	44.54

(a) "An Exact Method for Determination of Sulfur in Pyrites Ore," 8th International Congress of Applied Chemistry, 1, 33.

precipitated in a cold solution, by the method of Allen and Bishop, is coarse and of crystalline form. Some results (Table IV) indicate that barium sulfate, whether precipitated in a hot or cold solution, holds water in combination. If this is true it would explain the statement of Allen and Johnston<sup>1</sup> that barium sulfate holds water up to  $500^\circ$ . We found (Tables III and IV) that when barium sulfate precipitates were dried at  $130^\circ$  and weighed, the results agree quite as well as when the precipitates were fully ignited and again weighed. The average loss on ignition for precipitates formed in cold solution was 2.02 per cent (average of four results) and the corresponding average loss (average of four results, Table III) for the two samples of pyrites was 2.01 per cent. The average loss on ignition for precipitates formed in a hot solution, no ammonium salts present, was 0.48 per cent (average of two results). We also found that where the precipitate had been made in hot solution and in the presence of ammonium chloride that the loss on ignition amounts to very close to 1 per cent. If it is permissible to assume that this loss in weight is due to water of crystallization, which is only an assumption, then the formula for barium sulfate precipitated in a cold solution, by the method of Allen and Bishop, would be  $15BaSO_4 \cdot 4H_2O$  and for barium sulfate precipitated in a hot solution, no ammonium salts present, would be  $16BaSO_4 \cdot H_2O$ .

<sup>1</sup> J. Am. Chem. Soc., 32 (1910), 559.

From the results of this work, the following conclusions may be drawn:

I—The disagreement of results reported by the different laboratories on these samples of pyrites, and determined by some modification of the Lunge method, is about in line with past experiences.

II—The results by the Allen and Bishop method show a much better agreement.

III—The sources of error in the Lunge method brought out in this work are (1) loss of sulfur presumably by volatilization, (2) loss of sulfur in the insoluble residue due to incomplete oxidation, (3) loss due to presence of ammonium salts, (4) co-precipitation of calcium sulfate which is greater in hot precipitation than in cold.

IV—Barium sulfate precipitated under different conditions appears, from some results obtained, to have varying compositions both physically and chemically.

The writer wishes to express here his thanks to all those who have participated in this work and especially to Mr. A. M. Smoot for the account of his interesting observations.

ARMOUR FERTILIZER WORKS, ATLANTA, GA.

### AMERICAN INSTITUTE OF CHEMICAL ENGINEERS SEVENTH SEMI-ANNUAL MEETING LOS ANGELES AND SAN FRANCISCO, AUGUST 18 AND 25-28, 1915

The Seventh Semi-annual Meeting of the American Institute of Chemical Engineers will be held in Los Angeles and San Francisco, California, on August 18 and 25–28, respectively. The tentative itinerary published in THIS JOURNAL, 7, 448, has been accepted with a few minor changes. The complete program may be obtained by writing to Secretary J. C. Olsen, Cooper Union, New York City.

#### PROGRAM OF PAPERS

A New Electrolytic Process of Sewage Disposal. J. C. OLSEN AND WM. H. ULRICH.

The Improvement of High Boiling Petroleum Oils, and the Manufacture of Gasoline as a By-Product Therefrom, by the Action of Aluminum Chloride. A. M. MCAFEE.

Wine Making. ARTHUR L. LACHRAN.

Costs as Applied to Professional Businesses. R. A. GOULD.

Resources and Possibilities of Chemical Industry in the Southwest. EDGAR BARUCH.

Manufacture of Cream of Tartar. OTTO BEST.

Present State of the Thiogen Industry. S. W. YOUNG.

The Purification of Sewage by Aeration in the Presence of Activated Sludge. E. BARTOW.

Electrical Precipitation Method. W. A. SCHMIDT.

#### PROGRAM OF EXCURSIONS

In addition to points of local and geographic interest the following plants will be visited:

LOS ANGELES—Oil-burning Power Plant; Salt Plant; Kelp Industry; Beet Sugar Factory; Orange, Walnut and Fruit Orchards; Whittier and Fullerton Oil Fields (Wells, Casing-head Gas Plants, etc.); Oxnard Beet Sugar Factory; American Olive Co. Plant; Bishop & Co. Plant (candy making, fruit preserving, etc.).

SAN FRANCISCO—Oil Gas Works (Mr. Edward C. Jones will explain the process); Vineyard and Wineries at Winehaven.

#### COST OF TRIP

Transportation for entire round trip (22 days), Pullman lower berth, Grand Canyon side trip, sight-seeing trips at Colorado Springs, Pike's Peak, Santa Barbara and Del Monte, all meals on trains (estimated at \$1.00 each), berth and meals on steamer, San Francisco to Astoria and Duluth to Buffalo—\$249.00.

The following items are not included in the above figure: Yosemite Valley trip (meals, lodging and transportation)—\$52.35; Yellowstone Park trip (meals, lodging and transportation)—\$53.50; Hotel accommodation and other expenses in San Diego, San Francisco, Seattle, Butte, Anaconda, St. Paul and Duluth (17 days).



## NOTES AND CORRESPONDENCE

### CONDITIONS OF THE RUSSIAN TREASURY DEPARTMENT COMPETITION ON THE INDUSTRIAL USES OF ALCOHOL

#### REAGENTS FOR DENATURING ALCOHOL

In order to encourage the wide-spread utilization of alcohol (wine spirits), for technical purposes, an international competition is announced consisting of three prizes, *viz.*, 30,000, 15,000 and 5,000 rubles (\$15,000, \$7,500 and \$2,500) for the discovery of new denaturants or for the improvement of present denaturing processes, which, while assuring the free circulation of denatured alcohol, will make impossible its use for drinking purposes. The new denaturing agents must satisfy the following conditions:

1—The denaturing agents must convert the alcohol into a liquid which is absolutely unsuitable for drinking purposes by imparting an unpleasant taste to the alcohol or by having a violent physiological action on the organism (nausea, vomiting, diarrhea).

2—The denaturing agents must not give rise to a suffocating odor which would make the utilization of the alcohol for the needs of every-day life difficult or injurious.

3—The denaturing agents must not leave a residue after combustion nor contain substances which would be injurious to the apparatus in which the alcohol is burned.

4—Separation of the denaturing agents of the alcohol by simple means, such as removal by water, salting out, filtration through carbon, simple distillation, etc., should be impractical.

5—The primary materials used in the preparation of the denaturing agents should be among such as can be obtained in Russia in sufficient amounts.

The period fixed for the presentation of the statements of competitors expires January 1, 1916.

The statements should be presented, written in Russian or French, to the General Bureau of Indirect Contributions and the Alcoholic Commission (Glavnoé Oupravlenié Neocladnich Sborow i Casennoj Prodagy Pitej à Pétrograd) in packages bearing an assumed name; in a separate envelope, bearing the same assumed name, the name and address of the competitor should be indicated.

In the statement of discoveries the composition of the proposed denaturing agent, the quantity necessary per "vedro" (12.3 liters) of alcohol and its value should be stated.

Samples of the denaturing agents should be added to the statement mentioned above and the quantities of these should not be less than one kilo.

The offerings made will be examined by a Competition Commission made up of persons designated by the Minister of Finance. Included in this Commission will be representatives of the Ministries and General Bureaus interested as well as representatives of science and industry.

In case of an invention or improvement of especial value, the Commission will have the right to assign several or all prizes of the competition to one individual.

The examination of the statements presented and the assignment of prizes will take place July 1, 1916, at the latest.

The decisions of the Competition Commission will be confirmed by the Minister of Finance.

The Government reserves the right to utilize the methods of denaturing which receive the above-mentioned prizes without indemnifying the inventors in any other way.

#### NEW INDUSTRIAL APPLICATIONS OF ALCOHOL

An international competition is announced to encourage the extensive development of the application of alcohol or its derivatives for heating, lighting and for the production of motor

power as well as to stimulate the utilization of alcohol in the various industrial branches of chemical technology. For this purpose the following prizes are offered:

1—Three prizes of 60,000, 30,000, and 10,000 rubles (\$30,000, \$15,000 and \$5,000) for the invention of a new process for the utilization of alcohol in the preparation of a product which would be absolutely different in nature than the alcohol used in its production. As examples of such products may be mentioned vinegar, ether, and chloroform, etc.

2—Three prizes of 50,000, 20,000 and 5,000 rubles (\$25,000, \$10,000 and \$2,500) for the invention of a new process for the utilization of alcohol in the preparation of a product in which the alcohol or its derivatives (*e. g.*, sulfuric, ether, etc.) constitutes one of the component parts of the products or the solvent but under such conditions that the alcohol can not be recovered economically from the product in question. As examples of such products may be mentioned pharmaceutical and perfumery preparations.

3—Three prizes of 30,000, 15,000 and 5,000 rubles (\$15,000, \$7,500 and \$2,500) for the invention of a new process for the utilization of alcohol in an industry in which the alcohol or its derivatives (*e. g.*, sulfuric, ether, etc.) would serve as the intermediary and provisional solvent or as the extractive agent or precipitant. As examples of such applications may be mentioned the production of smokeless powder, the manufacture of artificial silk, etc.

4—Four prizes of 75,000, 50,000, 30,000 and 20,000 rubles (\$37,500, \$25,000, \$15,000 and \$10,000) for the invention or improvement of apparatus for the utilization of alcohol for feeding internal combustion motors.

5—Four prizes of 75,000, 50,000, 30,000 and 20,000 rubles (\$37,500, \$25,000, \$15,000 and \$10,000) for the invention or improvement of apparatus having as their object the utilization of alcohol or its derivatives for heating.

6—Four prizes of 50,000, 30,000, 15,000 and 5,000 rubles (\$25,000, \$15,000, \$7,500 and \$2,500) for the invention or improvement of apparatus in which alcohol is used for lighting.

The period fixed for the presentation of statements of competitors expires January 1, 1916.

The statements should be presented written in Russian or French to the General Bureau of Indirect Contributions and the Alcoholic Commission (Glavnoé Oupravlenié Neocladnich Sborow i Casennoj Prodagy Pitej) in packages with an assumed name; in a separate envelope bearing the same assumed name, the name and address of the competitor should be given.

The statement mentioned above should contain detailed descriptions of the conditions for the application of the alcohol with figures on the economics of the application calculated on the basis of an alcohol cost of 2 copecks per unit of alcohol (123 cc. absolute alcohol at a temperature of 15.5° C.).

The statements referring to the prizes indicated in Sections 1 to 3 should include samples of the products and the amount of these should be at least one kilogram.

The statements referring to the prizes indicated in Section 4 should be accompanied by a complete motor and detailed drawings of the parts of the motor which represent the nature of the invention, at the same time indicating the necessary dimensions.

The statements referring to Sections 5 and 6 should be presented with specimens of apparatus for using the alcohol (burner distributors, aeolipiles, lanterns, lamps, etc.) and with detailed drawings showing the dimensions of the apparatus.

As regards the classes indicated in Sections 4, 5, and 6, the object of the prizes to be assigned will be (conjointly or separately) not only the inventions or improvements relative to the construction itself of the apparatus using the alcohol, but also



the mixtures of alcohol with other substances and the methods of utilization of these mixtures to increase the calorific power of the alcohol.

The samples of substances to be added to the alcohol, if not found on the Russian market, should be sent in sufficient amounts to make detailed trials; in any event, not less than five kilograms.

In estimating the improvements relating to internal combustion motors the preference in the assignment of the prizes will be given to such separate improved parts as can be readily adapted to internal combustion motors and which belong to existing types and make possible the advantageous utilization of alcohol or its mixtures in place of other kinds of fuel.

The statements presented will be examined by a Competition Commission made up of persons designated by the Minister of Finance. Taking part in this Commission will be representatives of the Ministries and General Bureaus concerned as well as representatives of science and industry.

The prizes will be assigned only to those inventions or improvements of which it may be assumed that they would imply an appreciable consumption of alcohol.

In the case of inventions or improvements of especial value the Commission will have the right to assign several or all prizes in that class to one person.

The examination of the statements made and the assignment of prizes will take place July 1, 1916, at the latest.

The decisions of the Competition Commission will be confirmed by the Minister of Finance.

The inventor reserves the right to exploit his invention and to protect it by taking out a certificate of protection.

#### NOTE ON FERMENTATION OF FOODS CONTAINING BENZOIC ACID<sup>1</sup>

Occasionally it is observed that foods to which sodium benzoate has been added undergo fermentation. While working with apple juice during the last few seasons, sodium benzoate was added while the juice was running from the press. The juice was then transferred to casks holding 2500 gallons where it was clarified to a degree of perfect brilliancy and then drawn off into new freshly paraffined kegs. Sometimes a few of these kegs would soon show signs of a very vigorous fermentation while all of the others would remain in perfect condition for several months. Thus it appeared that there are yeasts that will grow in the presence of benzoic acid, and that such cells had found their way into the kegs that were showing evidences of fermentation. To determine this, some fresh apple juice was sterilized and the action of benzoic acid on several yeasts noted. With a pure wine yeast and Fleischmann's baker's yeast, 0.1 per cent of benzoic acid would inhibit the growth of the yeast as well as completely check the fermentation where

<sup>1</sup> Author's abstract of paper presented before the St. Louis Section of the American Chemical Society, March 8, 1915.

the yeast has been permitted to become very vigorous before adding the benzoic acid (a more or less common belief prevails that benzoic acid will not prevent fermentation after the yeast has been permitted to become active). With the yeast taken from the kegs, however, 0.1 per cent of benzoic acid had no inhibiting effect whatever; 0.2 per cent had a weak retarding action, while 0.3 per cent had a complete inhibiting effect.

3601 SALENA STREET, ST. LOUIS  
March 24, 1915

GEO. LANG, JR.

#### PAPER PULP AS AN AID IN FILTRATION

To prepare the pulp, make a mixture of one part strong  $\text{HNO}_3$  with four parts water in a wide mouth bottle. Add ordinary filter paper. Shake vigorously till the mixture is reduced to a fine smooth pulp. Throw the mass on a Buchner funnel, wash free of acid, then mix the pulp with water to form a thin liquid that will pour easily for use.

This pulp has been found most indispensable for the filtration of the ammonium citrate solution from the digestion of phosphates for the determination of available  $\text{P}_2\text{O}_5$  which is done as follows: Fit a filter paper (9 cm. S. & S. 595) into a 2-in. filter cone. Fill full with paper pulp, and after part of the water has run through, press the mass against the sides of the cone extending above the edge of the filter paper. In filtering, the cone may be filled full, as the paper pulp prevents leaking at the top of the filter paper. The complete filtration and washing to a volume of 400 cc. or more is usually complete in five minutes or less, instead of the half an hour or more which is frequently required without the paper pulp.

If ashless paper pulp is used it may replace asbestos for use with Gooch crucibles. After ignition nothing remains but the precipitate.

UNIVERSITY OF CALIFORNIA, BERKELEY  
February 8, 1915

P. L. HIBBARD

#### KNOWLEDGE AND RESEARCH—CORRECTION

*Editor of the Journal of Industrial and Engineering Chemistry:*

My address on "Knowledge and Research," delivered before the University of Pittsburgh, at the dedication of the new building of the Mellon Institute, and reported in your issue for April [7 (1915), 328] contains an erroneous statement, which I desire to correct; namely, I said, in passing, and by way of illustration, that Mr. Edison had received, in perfecting his inventions, certain aid from Dr. Ira Remsen. This was not true; and I wish to withdraw the statement. To go further, and explain how I was misled to make it, would be giving too much importance to a slip of memory which did not in the least affect my argument, and which is only worth notice because any error, however small, ought to be corrected at once.

29 WEST 39TH STREET, NEW YORK  
April 29, 1915

R. W. RAYMOND

## PERSONAL NOTES

Sir Arthur Herbert Church, formerly professor of chemistry at the Royal Academy of Arts, London, and known for his contributions to chemistry and mineralogy, has died at the age of eighty-one years.

Robert Stewart, professor of chemistry in the Utah Agricultural College, has been appointed associate professor of soil fertility and assistant chief in soil fertility in the Agricultural Experiment Station at the University of Illinois.

Jacob Lund, chemist, Christiania, Norway, has received the "Polyteknisk Förening's" gold medal for his work on fats, an abstract of which may be found in *C. A.*, 8 (1915), 1516.

In an infringement suit brought by the General Bakelite Co.

against George J. Nikolas, of Chicago, for infringing the Bakeland patents Nos. 954,666, April 12, 1910, 1,018,385, Feb. 20, 1912, and 1,037,719, Sept. 3, 1912, decision was rendered in the United States District Court, Eastern District of New York, on June 12th, by Judge Thomas Chatfield, holding all three patents valid and infringed. The decree covers about 60 pages and carefully reviews the details of the testimony of both plaintiff and defendant, and discusses at length the prior art as disclosed in this case. The trial was held in open court under the new rules of patent practice, and lasted for 23 days, beginning on December 9, 1913. The testimony filled 1396 typewritten pages. The defendant submitted 47 prior patents and many literature references which were alleged to contain prior disclosures. All



of these citations were carefully considered by Judge Chatfield and rejected.

The June 15th meeting of the Southern California Section of the A. C. S. took the form of a joint dinner with the technical societies of Los Angeles—Civil Engineers, Electrical Engineers, Mechanical Engineers, Mining Engineers, Architects, and Engineers and Architects. The meeting was addressed by Wm. Mulholland and by Dr. James A. B. Scherer, president of Throop College of Technology, on the subject, "Service of the Technical Man to the Community."

Mr. Will H. Coghill wishes to announce that after seven years in the practice of ore testing at Chicago he has removed his laboratory to 3705 Hueco Street, El Paso, Texas, where he will continue in the same line of work.

Dr. Francis Clifford Phillips and Mrs. Phillips were the guests of honor at a testimonial dinner given on June 3rd at the German Club, Pittsburgh, Pa., by one hundred former students and friends who desired to show their love and esteem upon the occasion of Dr. Phillips' retirement from active service as professor of chemistry in the University of Pittsburgh. Dr. Phillips, who is well known professionally because of his contributions to the chemistry of gases and his active participation in the interests of the American Chemical Society, has occupied the Chair of Chemistry at Pittsburgh since 1875 and is retiring under the terms of the Carnegie Foundation. Among the speakers at the dinner were Drs. Walther Riddle, Albert E. Frost, R. B. Carnahan and J. H. James, and Professor Alexander Silverman. As an expression of their high regard for his devotion to the University of Pittsburgh, the former students of Dr. Phillips presented him with a check for \$1000.00.

The annual spring excursion of the Northeastern Section of the American Chemical Society, on June the 11th, consisted of a visit to the chocolate and cocoa factory of the Walter M. Lowney Company in Mansfield, Massachusetts, followed by a dinner at the Mansfield Tavern, at which Mr. Lowney addressed the Section on the "Story of Chocolate and Cocoa." About seventy-five members and guests were present.

The Hoskins Manufacturing Company announces the appointment of Mr. W. C. Tharp as District Manager in charge of its Pittsburgh office, to succeed Mr. I. J. Shults, resigned. Mr. Tharp has formerly been associated with the Republic Iron and Steel Company, the Scientific Materials Company and the Metallurgical Testing Laboratory of Pittsburgh.

A monument to the late Professor J. H. van't Hoff was unveiled at Rotterdam on April 17th. It consists of a bronze statue,

double life-size, in sitting position, and has been placed in front of the school at which Professor van't Hoff was educated.

Dr. Edward Kohman, who has been an instructor in Chemistry at Yale, has just been appointed Chief Dairy Chemist at the University of Illinois.

Albert Plaut, president of Lehn and Fink and one of the most prominent figures in this country's drug trade for many years, died in his fifty-eighth year, in New York, on June 17th.

The Spring Meeting of the American Society of Mechanical Engineers was held in Buffalo, New York, June 22nd-25th, with headquarters at Hotel Statler. An appropriate program of papers was given and excursions were conducted to Niagara Falls, via the Gorge Route trip, where the power plants both on the American and Canadian sides were inspected; visits were also made to the Shredded Wheat Company's factory, the Falls Chocolate Company, and various manufacturing plants in and around Buffalo.

Prof. Charles Baskerville addressed the Interstate Cotton Seed Crushers Association at their annual convention in Birmingham, May 18th, on his new process for refining vegetable oils.

John D. Lewis, manufacturer of dyestuffs at Providence, R. I., died at his home in that city on Thursday, May 20th, in his seventieth year. Mr. Lewis studied at Brown University with the class of 1868 and later entered upon the manufacture of dyestuffs with his father. In addition to his activities as a manufacturer Mr. Lewis was also the representative of several foreign dye and chemical companies.

Two anonymous gifts of \$150,000 and \$100,000 have been made to the Massachusetts Institute of Technology for dormitories. Funds with which to construct the mining building, some \$225,000, have been offered to the Institute by Charles Hayden, '90, of Boston, and T. Coleman du Pont, '83, and S. Pierre du Pont, '90, of Wilmington, Del., past and present presidents of the du Pont de Nemours Powder Co. T. Coleman du Pont, it will be remembered, with his gift of \$500,000, made the purchase of the Technology site in Cambridge possible. Charles A. Stone, '88, and Edwin S. Webster, '88, of Boston, will provide a residence for the president.

Herbert M. Wilson, engineer in charge of the Pittsburgh Experiment Station of the United States Bureau of Mines, has resigned from the government service to become the director of the Coal Mine Insurance Association. This organization is a newly formed combination of ten American and British insurance companies associated for the joint underwriting of coal-mine accident insurance.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### BUREAU OF THE CENSUS

**Cottonseed Crushed and Linters Obtained.** Preliminary Report, post-card form dated March 18, 1915. This card gives a statement of the number of establishments crushing cottonseed from the crops of 1912, 1913, and 1914 with a statement of the quantity of seed crushed and the quantity of linters obtained. The summary is as follows:

YEAR	No. of cottonseed-oil mills	Cottonseed crushed Tons	Linters obtained Running bales
1912.....	857	4,579,508	602,324
1913.....	870	4,767,802	631,153
1914.....	880	5,493,899(a)	772,270(a)]

(a) Includes 681,315 tons of seed estimated to be crushed and 95,360 bales of linters to be obtained after the date of the March canvass.

### BUREAU OF FISHERIES

**The Menhaden Industry of the Atlantic Coast.** ROB L. GREER. Document No. 811, Appendix III to the report of the U. S. Commissioner of Fisheries for 1914. 27 pp. Paper, 10 cents. This report gives a history and a statistical summary showing the extent of the menhaden fisheries up to the end of 1912. The methods of fishing and the apparatus employed are described and the fishing grounds and season summarized. The processes used for cooking, pressing and drying of the material as well as the properties of the oil and scrap are described in detail. Prices are given for the various parts of equipment required in each process and summaries of costs included.



## BUREAU OF STANDARDS

Methods of Measuring the Inductances of Low-Resistance Standards. FRANK WENNER, ERNEST WEIBEL AND F. B. SILSBEE. Scientific Paper 246. 21 pp.

A Study of the Atterberg Plasticity Method. CHARLES S. KINNISON. Technologic Paper 46. 18 pp. The practical significance of the Atterberg factor and the rating of clays based on shrinkage or water of plasticity are discussed. The Atterberg factor when used alone is of little significance but when coordinated with the water of plasticity, as recommended in this paper, it appears to be possible to differentiate between the non-sticky or safe working clays and the sticky varieties which are difficult to work.

## GEOLOGICAL SURVEY

The Production of Lead in the United States in 1914. C. E. SIEBENTHAL. Preliminary Report. 1 large sheet, dated April 2, 1915. This advanced statement is prepared in order to give at the earliest practicable date reliable figures of the lead production in the United States in 1914. The data given are prepared on confidential reports from each lead smelting and refining company in operation in the United States during that year. The import and export data are taken from records of the Bureau of Foreign and Domestic Commerce. The report shows that the production of primary refined lead (that is, lead smelted from ore) in the United States in 1914 was 542,122 short tons, or an increase of 17 per cent over the preceding year. The primary lead refined and available for consumption in the United States was approximately 450,000 tons, an increase of 7 per cent over 1913. The production of the United States in 1913 is reported as 32.4 per cent of the world production for that period. The report includes price curves for a 3-year period, giving the average weekly price of lead in New York and London. There is also included a list of all the lead smelters and refineries in the United States, Canada, and Mexico. The exports of domestic lead are reported as 20,000 tons during the period March to June, 1914 and 38,500 tons during July to December, 1914. During 1914 the imports of lead in all forms amounted to approximately 57,000,000 lbs., more than 46,000,000 lbs. coming from Mexico. These imports are less than 50 per cent of the amount for the preceding year which in turn was less than any year preceding since 1906 or earlier.

Advance Statement of the Production of Copper in the United States in 1914. B. S. BUTLER. Unnumbered leaflet, dated April 5, 1915. 4 pp. The production of primary and secondary copper by the regular refining plants in the United States during 1914 is given (in pounds) as follows:

	PRIMARY		SECONDARY
	Domestic	Foreign	
Electrolytic.....	991,573,073	323,358,205	27,702,928
Lake.....	158,009,748	.....	.....
Casting.....	21,506,325	.....	4,224,052
Pig.....	39,334,043	.....	.....
Total.....	1,210,423,189(a)	323,358,205(a)	31,926,980
	1,533,781,394		
TOTAL OUTPUT.....			1,565,708,374

(a) The distribution of refined copper of domestic and foreign origin is only approximate, as an accurate separation at this stage of manufacture is not possible.

If the output of plants treating purely secondary material is added to the production of the regular refining companies, the contribution of domestic plants of the United States to the world's supply of copper for 1914 is found to be 1,790,000,000 lbs. In addition to the output of metallic copper the regular refining companies produced bluestone with a copper content of 8,602,861 lbs.

The apparent domestic consumption of refined new copper during 1914 was 711,600,000 lbs. If to this quantity of new refined copper is added the 256,000,000 lbs. of secondary copper and copper in alloys produced during the year, it is found that a total of about 968,000,000 lbs. of old copper was available for domestic consumption.

The Production of Sand-Lime Brick in 1914. JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States 1914. Part II. 7 pp. Production of sand-lime brick in 1914 is summarized as follows:

Number of active firms reporting.....	68		
Quantity (thousands).....	Common brick	[Front brick	
Value.....	178,352	11,307	
Average price per M.....	\$1,118,402	\$119,923	
TOTAL VALUE.....	\$6.27	\$10.61	\$1,238,325

This summary indicates that the value of the output decreased 14.5 per cent as compared with the 1913 output.

A Gold-Platinum-Palladium Lode in Southern Nevada. ADOLPH KNOPF. Bulletin 620-A. 18 pp. (Separate from Contributions to Economic Geology 1915.) The ore of the Boss gold mine in the Yellow Pine mining district, Clark County, Nevada, has recently been shown to be rich in platinum and palladium. The occurrence of platinum and palladium in this Nevada gold ore is of some interest, inasmuch as a review of the known distribution of platinum in veins shows that the Boss vein is one of the few primary deposits in which metals of the platinum group are present in more than traces, and, with one possible exception—the New Rambler deposit in Wyoming—it is the only primary deposit of economic importance in which these metals are the constituents of predominant value.

The report includes a description of the location, the history, the geology and the general mineralogic features of this district. Analyses of the ore are reported and there is given a general discussion of the known lode occurrences of platinum throughout the world and a comparison of the Boss deposit with those previously known.

The Coalville Coal Field, Utah. CARROLL H. WEGEMANN. Bulletin 581-E. Separate from Contributions to Economic Geology, 1913. Part II. Pp. 161-187. The purpose of this study was to work out in detail the rock structure, correlating so far as possible the coal beds exposed at the several localities, outlining the probable productive area, and making estimates as to the depth of the beds within it. The general character of the coal is considered and the beds are discussed by townships.

Mineral Deposits of the Santa Rita and Patagonia Mountains, Arizona. F. C. SCHRADER, with contributions by J. M. Hill. Bulletin 582. 373 pp. and 25 plates. The purpose of this paper is to furnish a general idea of the character, occurrence, distribution, and development of the mineral resources of a desert area comprising about 1,400 sq. mi. in Pima and Santa Cruz counties, Arizona, 26 mi. southeast of Tucson. The physiography, geology, and water supply of the area are briefly discussed and the mining districts, camps, and properties are considered in detail. The deposits include gold, silver, copper, lead, zinc, tungsten, molybdenum, and building materials. Topographic and geologic maps of the area discussed and of parts of it, maps, plans, and sections of some of the mines and their workings, and half-tone plates showing geologic features, make up the illustrations.

Geology and Coal Resources of North Park, Colorado. A. I. BEEKLY. Bulletin 596. 121 pp. 12 plates. This bulletin describes the geography, stratigraphy, structure, and economic geology of North Park, a great natural depression in the Rocky Mountains of northern Colorado, sharply defined as a topographic unit by its prominent, almost continuous rim of mountain crests 2,000 to 5,000 ft. above the bottom of the basin. On account of its remoteness from frequented routes of travel, very little has been known of the geology of this basin until recent years. As coal is the most valuable known mineral resource of North Park, this report calls special attention to the coal deposits, discussing their occurrence and development and the production and estimated tonnage of the mines. The illustrations consist of a geologic map and sections of North Park, sections of coal beds, and photographic views of geologic features.



Contributions to Economic Geology, 1913. Part I. Metals and Nonmetals Except Fuels. F. L. RANSOME AND H. S. GALE. Bulletin 580. 462 pp. This bulletin is made up of 16 brief reports on investigations of mineral deposits made in 1913. In each case items of economic interest are reported, but little material of purely scientific significance is given. The more important of the reports have already been reviewed in This JOURNAL.

#### BUREAU OF MINES

**Metallurgical Treatment of the Low-Grade and Complex Ores of Utah.** D. A. LYON, R. H. BRADFORD, S. S. ARENTZ, O. C. RALSTON AND C. L. LARSON. A preliminary report issued jointly by the Bureau of Mines and the Department of Metallurgical Research of the University of Utah, Engineering Station. Technical Paper 90. 40 pp. Paper, 5 cents. The principal topics discussed in this report are the following: Methods of mining and mining conditions in Utah (gold, silver, lead, copper and zinc); situation and extent of the low-grade ores; metallurgical treatment of the ores; processes having a possible application for Utah ores; availability of certain raw materials for use as reagents; discussion of the allied problems, especially fuel supply and electric energy costs.

**Mining and Milling of Lead and Zinc Ores in the Wisconsin District, Wisconsin.** CLARENCE A. WRIGHT. Technical Paper 95. 39 pp. Paper, 10 cents. This report gives a description of the zinc and lead mining districts, the ore deposits and their field relations, together with an elaborate discussion of the mining and ore-dressing practice, and the labor, cost, accident, and other factors of operating interest.

**Permissible Explosion-Proof Electric Motors for Mines; Conditions and Requirements for Test and Approval.** H. H. CLARK. Technical Paper 101. 14 pp. Paper, 5 cents. The Bureau of Mines has applied the term "explosion proof" to motors constructed so as to prevent the ignition of gas surrounding the motor by any sparks, flashes, or explosions of gas or of gas and coal dust that may occur within the motor casing. This paper mentions the details of construction that the bureau considers essential for satisfactory service and describes tests of an explosion-proof mining-machine motor and accessories approved by the bureau.

The conditions under which motors may be labeled as approved by the Bureau are described and the "caution" and "approval" plates which are permitted are illustrated. One satisfactory make of motor has already been examined. The test proved that the protection of the motor, starting rheostat, and cable reel was adequate at the time of testing. It is, therefore, considered that with reasonable care the equipment can be maintained permanently in an explosion-proof condition. The equipment has therefore been approved by the Bureau as permissible for use in gaseous mines.

**The Condensation of Gasoline from Natural Gas.** GEORGE A. BURRELL, FRANK M. SEIBERT AND G. G. OBERFELL. Bulletin 88. 106 pp. Paper, 15 cents. "This report treats of a method for preventing some of the waste of the natural gas incidental to oil mining. This method, the condensation of gasoline from natural gas, offers to the oil operator and others a profitable means of utilizing some of the oil-well gas now being wasted. The most desired constituent of crude oil is obtained, the production of oil is not hindered, and the gas, after extraction of gasoline, can be returned to the leased area to drive pumps or into pipe lines for uses to which natural gas is ordinarily put, usually with its fuel value lessened only in slight degree."

In discussing these subjects the growth of this industry is described, and a general discussion given of the constituents of natural gas, their properties and the factors which affect the yield of gasoline from natural gas. Methods of determining the probable yield and flow of gas with the pilot tube and methods

of gas analysis are described. The conditions under which the life of wells is sufficient to justify the installation of recovery plants is discussed and data are given as to methods of compression and costs both for installation and operation of the plants. Scientific data are given as to the properties of various gases and their constituents.

**A Primer on Explosives for Metal Miners and Quarrymen.** CHARLES E. MUNROE AND CLARENCE HALL. Bulletin 80. 125 pp. Paper, 25 cents. This report is an elementary discussion of combustion and explosion; blasting and mine explosives; fuse, detonators, and electric detonators; and the proper methods for the use of explosives in quarrying, excavation work, metal mining, and tunneling; including a discussion of the storage, handling, and thawing of explosives and a list of permissible explosives. The report covers metal mining and quarrying giving information which corresponds to that published in Bulletin 17 of this Bureau as applying to the coal mining industry.

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**European Markets for Fish.** Miscellaneous Series 25. 36 pp. Paper, 5 cents.

**Some Aspects of Iron and Steel Industry in Europe.** Special Consular Reports 71. 48 pp. Paper, 5 cents. (Review to be given next month.)

#### COMMERCE REPORTS—MAY, 1915

Ireland produces annually 47,000 tons of salt and imports 33,000 tons, the imports being chiefly from Spain and Italy. The chief salt works is at Antrim where there is a vein 80 feet thick, the salt being obtained partly as rock salt, and partly from brines. (P. 528.)

Export of natural indigo from England is now permitted. (P. 561.)

Pocahontas coal is about to be used on Brazilian railways. (P. 565.)

At Kingston, Canada, talc is quarried from open pits, and is crushed and reduced to 200 mesh, for use in paper making and foundry purposes. (P. 569.)

The American Peat Society whose object is the furtherance of the use of peat in this country, will meet in Detroit, September 20-22, 1915. (P. 571.)

In Moscow, there is a marked increase in the demand for chemicals including carbolic acid and chloride of lime for disinfectants, potassium ferrocyanide, cottonseed oil, citric acid and nitrate of soda. (P. 572.)

Argentina is having some difficulty in finding a market for linseed, quebracho logs, bones, fertilizers, sugar and wine. (Pp. 580-8.)

Of the large amount of soda ash and soda crystals made in Germany in 1913, only a small portion was exported, *viz.*, \$36,000 worth to Austria-Hungary and Switzerland. (P. 588.)

A new tin foundry is to be erected at Santiago, Chili, to smelt Bolivian ores. (P. 594.)

Under the title "British Solution of the Dyestuff Problem," commercial agent Thos. H. Norton discusses in detail the organization of "British Dyes (Ltd.)," the new company organized to develop the dyestuff industry in Great Britain. The government has subscribed nearly half the capital and also \$500,000 for a research laboratory. Most of the stock has been subscribed. Shareholders will have priority in receiving available supplies. The largest existing plant, that of Read, Halliday, and Sons has been acquired. A proposal to pledge stockholders to use only dyes from the new company for five years after the war, was abandoned. The government has permitted all manufacturers to use all patents the property of persons in belligerent countries, suitable royalties to be paid after the war. All alcohol to be used in the dye industry is untaxed. Efforts are being made to cooperate with the Swiss factories. There is some criticism because there is no chemist on the Board of Directors. No



means has yet been provided for protecting the industry from German competition after the war. (Pp. 596-602.) (See also THIS JOURNAL, 7 (1915), 538.)

Owing to a greatly increased demand in England for high-speed steels, the price has advanced greatly, as well as that of ferrotungsten and ferrochrome, while ferrovanadium has remained stationary. (P. 609.)

An export tax on boric acid and borates has been levied in Chili. The nitrate industry is slowly improving. (Pp. 618-9.)

A report on the oil, seed, and cake trade of Hull, England, includes statistics of the manufacture and prices in 1913, 1914 and 1915, of linseed, cottonseed, castor beans, rape seed and soya beans, and the corresponding oils and cake. (Pp. 629-31.)

In order to stimulate the production of coke oven by-products required for explosives, fuel, and fertilizer the German government is seeking to extend the use of coke as fuel on railways and in manufacturing. (P. 637.)

Export of coal from Great Britain except to colonies and allies, has been forbidden. (P. 641.)

Owing to the increased price of copper, the mining industry of British Columbia is improving. (P. 658.)

Efforts are being made to conduct the washing of wool in Argentine instead of abroad, and obtain the wool-grease as a by-product. (P. 717.)

The market in China for American and other ginseng still continues, in spite of the conclusion of many doctors that it has no therapeutic value. (P. 728.)

The Second Pan-American Scientific Congress will be held in Washington, D. C., from December 27, 1915 to January 8, 1916. The United States Government has appropriated \$50,000 toward the Congress. (P. 739.)

Among the principal resources of Alaska are gold, copper, silver, coal, fish oils, gypsum, marble, and tin. (P. 740.)

Almost no sugar beet seed is raised in the United States. The principal producer is Germany, which exports 30,000 tons annually. The "mother beet seed," *i. e.*, the seed used to plant beets for the production of seed, is mostly raised in Holland. (P. 750.)

Paraguay produces 70 per cent of the world's output of "petitgrain oil," the essential oil extracted from the leaves of the wild orange, from \$20,000 to \$50,000 worth being annually exported to the United States for use as a drug. (P. 755.)

The price of aniline dyes in Japan is ten times the normal price. (P. 769.)

In a review of the "Dyestuff Situation in the United States," Commercial Agent Thomas H. Norton states that the existing supplies are so low that the stock of foreign dyes will be practically exhausted by July 15, 1915. The two cargoes of dyes, whose shipment was permitted by the British Government, have not been sent from Germany although there is an ample stock there. While the recovery of coke oven by-products in America is being greatly increased, the demand for benzol and toluol for explosives is restricting the amounts available for dyes. The American output of aniline is now sufficient to meet the needs of the dyestuff industry. Most of the contracts are for three years, at a price to be determined by the market price. All the American dyestuff plants have enlarged their plants, and most of the important intermediates are now being made here. There is a marked increase in the demand for natural dyestuffs, especially "quercitron" extracted from the black oak, the only natural dyestuff indigenous to the United States. No provision has yet been made for the manufacture of alizarin or synthetic indigo in the United States. It is believed that a self-contained American coal tar industry is possible under existing tariff conditions, provided there is protection against "dumping." (Pp. 770-9.)

The world's output of copper in 1914 was 10 per cent less than in 1913. (P. 797.)

Japan is importing some phosphate rock from the Marshall Islands, now under Japan, in place of part of the American supply. (P. 811.)

#### STATISTICS OF EXPORTS TO THE UNITED STATES (Pp.)

FRANKFORT DISTRICT.	BAVARIA—Sup. 6b	SAXONY—Sup. 6c
GERMANY—708	Aluminum powder	Beer
Chemicals	Beer	Chinaaware
Dyestuffs	Brass	Earthenware
Paper	Bronze	Drugs, etc.
Steel and iron	Electric light carbons	Essential oils
Platinum	Celluloid	Wood pulp
Hides	Earthenware	Bone meal
Zinc dust	Chinaaware	Caustic potash
Spelter	Glassware	Colors and inks
Copper	Gold and silver leaf	Fertilizer
Barytes	Hops	Hides
Colors	Lava stone	Oil of roses
Bronze	Paints	Oxalic acid
	Paper	Peptomangan
	Burgundy pitch	Montan wax
	Lithographic stones	Wool grease
AUSTRIA - HUNGARY—	Tin foil	Enameled ware
Supplement 1a	Glue	Tungsten powder
Beer	Matches	
Brass	Pumice stone	
Chinaaware	Gelatine	
Uranium	Manganese oxide	BRITISH HONDURAS—
Earthenware	Rags	Supplement 21a
Glassware	Steel balls	Chicle
Glue		Rubber
Hops		
Kaolin	HAWAII—790	
Mineral water	Sugar	
Rennet	Molasses	
Mineral salts	Hides	ONTARIO—Sup. 23d
Zinc oxide		Corundum
Barium chloride	BRISTOL ENGLAND—	Aluminum
Potassium perman-	Supplement 19i	Asbestos
ganate	Animal charcoal	Beeswax
Enamel paints	Ammonium chloride	Bones
Fusible enamel	Bleaching powder	Brass
Hides	Fuller's earth	Carbon
Sod oils	Hides	Acetone
Steel tubing	Glue	Acetic acid
Aluminum	Iron ore	Arsenic
Antimony		Hydrochloric acid
Paraffin	GREECE—Sup. 7a	Nitric acid
	Olive oil	Sulfuric acid
	Soap	Tartaric acid
HAMBURG — Supple-	LIVERPOOL—Sup. 19h	Wood alcohol
ment 6a	Aluminum	Ammonium sulfate
Cement	Dried blood	Aniline dyes
Ceresin	Bones	Calcium
Stearin	Carbolic acid	Casein
Paraffin	Ammonium sulfate	Ceasote oil
Acids	Sal ammoniac	Cobalt oxide
Coal tar preparations	Bleaching powder	Fusel oil
Earthenware	Calcium chloride	Glycerine
Chinaaware	Glycerine	Chicle
Glassware	Gum tragasol	Gambier
Metals	Soda ash	Kauri
Essential oils	Sodium cyanide	Calcium acetate
Fusel oil	Sodium silicate	Menthol
Mineral oil	Sodium sulfide	Potassium hydrate
Palm oil	Coal and coke	Potassium cyanide
Palm kernel oil	Copper	Coal, etc.
Paints	Earthenware, etc.	Cyanamid
Paper	Fertilizer	Fibers
Tar	Fibers	Gold and silver
Varnish	Glassware	Wool grease
Wood pulp	Glue	Hides
Albumen	Hides	Rubber
Sugar	Crude rubber	Iron ore
Antimony	Ferromanganese	Iron and steel
Cantharides	Tin plate	Manganese ore
Carmonile	Oil cake	Mercury
Coriander	Cocanut oil	Mica
Dyewoods	Palm oil	Feldspar
Ergot	Palm kernel oil	Nickel ore and matte
Lycopodium	Soya bean oil	Cottonseed-oil
Clay	Oleostearin	Oleo oil
Coal, etc.	Paints, etc.	Ketone oil
Fertilizer	Paper stock	Paper stock
Fibers	Salt	Platinum
Tin	Artificial silk	Graphite
Glue stock	Tin	Diamonds
Wool grease	Wax	Silicon
Gums	Potassium carbonate	Artificial silk
Gutta percha	Potassium chlorate	Marble
Hides	Potassium hydrate	Pyrites
Rubber	Antimony	Talc
Ivory nuts	Tanning extracts	Tan bark
Jute and sisal		Tin
Mica	CANADA—767	Wax
Rennet	Pulp wood	Zinc scrap

#### DEMANDS FOR AMERICAN GOODS (Pp.)

PALERMO, ITALY—570	ENGLAND—622	IRELAND—710
Coal	Glass:	Animal fats
Fuel oil	Plate	Glue
CYPRUS—571	Sheet	COLUMBIA—744
Glass	Flint	Iron
Chinaaware	Bottle	Steel
TURKEY—804	CANARY ISLANDS—669	CHINA—758
Cement	Fertilizer	Paints

NOTE—The above items are for May 1 to 21 inclusive; the rest of the May reports will be covered next month.



The manufacture of "asbestos slates" for roofing, has been started in Japan. (P. 813.)

The French Government has created a special bureau in the Department of Commerce to foster the production and supply of chemical and pharmaceutical products. Supplement 5*b*. (P. 15.)

Special Supplements published during the month follow. In general they contain discussions of the manufacturing and trade conditions and in most cases, import and export statistics.

Austria-Hungary—1 <i>a</i> .	British Honduras—	Panama—35 <i>a</i> .
France—5 <i>b</i> .	21 <i>a</i> .	Brazil—40 <i>a</i> .
Germany—Hamburg	Canada—Ontario—	British Guiana—44 <i>a</i> .
6 <i>a</i> ; Bavaria—6 <i>b</i> ;	23 <i>d</i> .	
Saxony—6 <i>c</i> .	Canada—23 <i>e</i> .	
Greece—Patras—7 <i>a</i> .	Cuba—25 <i>a</i> .	China—Hongkong—
United Kingdom—		52 <i>a</i> .
Liverpool—19 <i>h</i> ;	Mexico—San Luis	Australia—60 <i>b</i> .
Bristol—19 <i>i</i> .	Potosi—32 <i>a</i> .	

#### DEPARTMENT OF AGRICULTURE

Soils of Massachusetts and Connecticut with Especial References to Apples and Peaches. HENRY J. WILDER. Department Bulletin 140. Contributions from the Bureau of Soils. 73 pp. Paper, 25 cents. This report is largely of agricultural interest as the character of the soil is discussed only in its relation to fruit production.

Tests of Wood Preservatives. HOWARD F. WEISS AND C. H. TEESDALE. Department Bulletin 145. Contributions from the Forest Service. 20 pp. Paper, 10 cents. The following summary of the investigation indicates the scope of the report.

"The practical value of a preservative depends very largely upon the conditions under which it is used, and investigations to determine its value must necessarily be broad. The following points were considered in the tests:

"1—The important chemical and physical properties of the preservative.

"2—The effect of the preservative on the strength of the wood treated with it.

"3—The ability of the preservative to penetrate and diffuse through wood.

"4—The permanency of the preservative after its injection into wood. This involves a study of its volatility and leachability.

"5—The combustibility of wood treated with the preservatives.

"6—The toxic efficiency of the preservative in preventing the growth of wood-destroying fungi.

"7—The corrosive action of the preservative on steel.

"8—The effect of the preservative on paint applied to the wood subsequent to treatment.

No systematic tests were made on the effect of the preservative as an electrolytic or in contaminating drinking water, nor were any tests made which relate to a special or limited use."

Soil Erosion in the South. R. O. E. DAVIS. Department Bulletin 180. Contribution from the Bureau of Soils. 23 pp. Paper, 10 cents. Only the mechanical effects and the mechanical means of prevention are discussed. The chemical influences on the soil due to erosion are not described.

Morphology of the Barley Grain with Reference to Its Enzyme-Secreting Areas. ALBERT MANN AND H. V. HARLAN. Department Bulletin 183. Contribution from the Bureau of Plant Industry. 32 pp. Paper, 15 cents. The discussion given in this paper is of particular interest as indicating the desirable and undesirable properties of barley in connection with malting. There is included a discussion as to the source of diastatic ferments and as to the location of diastase secretion. This Bulletin is of interest to agronomists, brewery chemists, maltsters, and others.

Loss in Tonnage of Sugar Beets by Drying. HARRY B. SHAW. Department Bulletin 199. Contribution from the Bureau of Plant Industry. 12 pp. Paper, 5 cents. The conditions which affect the moisture content in sugar beets as well as the sugar losses which occur during storage of beets are discussed. A number of suggestions are given as to the relation of the shrinkage to the price of the beets and methods for adjusting prices on the basis of sugar making value.

Field Studies of the Crown-Gall of Sugar Beets. C. O. TOWNSEND. Department Bulletin 203. Contributions from the Bureau of Plant Industry. 8 pp. Paper, 5 cents. This paper is summarized as follows:

1—There are at least two distinct types of sugar-beet galls.

2—The crown-gall of sugar beets is caused by a bacterium or a number of closely related bacteria.

3—Sugar-beet galls appear to have an injurious effect upon the quality of the roots.

4—The galls themselves are low in purity and therefore detrimental in the milling processes.

5—Sugar-beet galls sometimes cause the beet roots to decay, but, so far as general field observations can determine, they do not appear otherwise to affect the tonnage.

6—This disease may be held in check by a proper system of crop rotation with grain-producing plants.

Weeds Used in Medicine. ALICE HENKEL. Farmers' Bulletin 188. Contribution from the Bureau of Plant Industry. 45 pp. "Some of the plants coming within this class are in many States at present subject to antiweed laws, and farmers are required to take measures toward their extermination. It seems, therefore, desirable to make these pests sources of profit where possible. In many cases, when weeds have been dug, the work of handling and curing them is not excessive and can readily be done by women and children.

"The prices paid for crude drugs from these sources are not great and would rarely tempt anyone to pursue this line of work as a business. Yet, if in ridding the farm of weeds and thus raising the value of the land the farmer can at the same time make these pests the source of a small income instead of a dead loss, something is gained. In order to help the farmer to obtain the best possible prices for such products, instructions for collecting and preparing crude drugs derived from weeds are here briefly given."

This subject is of more than usual interest under the present conditions when the drug market is so largely affected by the failure of certain European supplies.

Leguminous Crops for Green Manuring. C. V. PIPER. Farmers' Bulletin 278. Contribution from the Bureau of Plant Industry. 27 pp. Largely of agricultural interest.

Cottonseed-Meal for Feeding Beef Cattle. W. F. WARD. Farmers' Bulletin 655. Contribution from the Bureau of Animal Industry. 8 pp. The conditions under which cottonseed-meal is a valuable and economic feedingstuff are discussed, but the bulletin gives little of direct chemical interest except indicating the proper conditions for the utilization of this product of the cottonseed industry.

Manufacture and Use of Unfermented Grape Juice. GEORGE C. HUSMANN. Farmers' Bulletin 644. Contribution from the Bureau of Plant Industry. 16 pp. This bulletin gives instructions for making grape juice for home use as well as the directions for commercial operation.

Effect of Fertilizers on the Physical Properties of Hawaiian Soils. WILLIAM MCGEORGE. Bulletin 38 of the Hawaii Agricultural Experiment Station. 31 pp. Paper, 5 cents.

Notes on Hydrocyanic-Acid Content of Sorghum. J. J. WILLAMAN AND R. M. WEST. Journal of Agricultural Research, 4 (1915), 170-85; also available as a separate. A contribution from the Agricultural Experiment Station of the University of Minnesota.

Effect of Soil Moisture on Changes in Surface Tension of Soil Solution Brought About by Addition of Soluble Salts. P. E. KARRAKER. Journal of Agricultural Research, 4 (1915), 186-92. A Preliminary Report.

Manual of Procedure for Guidance of State Health, Food, and Drug Officials. Compiled by J. S. ABBOTT. 12 pp. Obtainable only through the Bureau of Chemistry.

Rules and Regulations Governing Importation of Cotton Lint into the United States. Adopted by the Federal Horticultural Board. Dated May 14, 1915. 10 pp. Paper, 5 cents.



## BOOK REVIEWS

**Chemistry of Familiar Things.** By SAMUEL SCHMUCKER SADDLER, S.B., xiii + 320 pp. Illustrations: 23 plates and 6 figures. Philadelphia and London: J. B. Lippincott Company, 1915. Price, \$1.75.

A number of books have been written for the instruction of the reader possessing little or no chemical knowledge. Some of these "demochemical" works have neither simplicity of style nor clearness of expression; in others the authors failed to exercise ingenuity in the selection of subject material, in the elimination of irrelevant matter, or in the presentation of the essentials, while still others are not free from incautious and extravagant statements, likely to create false impressions. To serve happily their intended purpose, such treatises should be entertaining in exposition; the chapters thereof should be consecutive and clear, and the points emphasized therein should be the important ones. These criteria of excellence are very exacting indeed, which accounts for both the number of popular works on chemistry which have been prepared in the endeavor to meet the requirements of the "intelligent" lay-reader and the poor reception accorded so many of these. The great difficulty has been to give a presentment of facts garbed in an interestingly attractive style, since it is quite simple, owing to the availability of the literature of chemistry, for one experienced in teaching the science and possessing mature judgment, to select suitable material; and the writings of few authors, and among these the three books of the late Dr. Robert Kennedy Duncan merit first mention, are touched with a certain largeness and attraction of form and are yet without perissology.

The twenty-two chapters of Sadtler's book deal with many diverse subjects (historical development of chemistry; the periodic system; light; heat; combustion and insulation; air, oxidation and ventilation; water; alkalies and salts; metals; gold and silver; the earth's evolution; soil and its conservation; food elements and food classes; individual foods; animal feeding; fermentation; chemistry of the body; soaps, solvents, and paints; paper and textiles; leather and rubber; silicious substances and glass; and definitions) and contain a fund of carefully selected information; but they are merely wholesome without being either artistic or adapted to arouse the reader's interest. In other words, the book will serve a useful purpose if it is read, for while the author is not literose, his composition is one of the most comprehensive popular expositions of every-day practical chemistry which has been brought to the reviewer's attention, and accuracy prevails throughout.

RAYMOND F. BACON

**Methods in Metallurgical Analysis.** By CHARLES H. WHITE. D. Van Nostrand Co. Price, \$2.50 net.

Professor White has written a book that is very good of its kind, but of a kind of which we already have more than enough. Why will not some of our colleges teach analytical chemistry instead of schemes of analysis? To be sure it would involve more work for the instructors, but they are not in the least afraid of work or at all unwilling to undertake it if it will improve results. The majority of the analysts turned out yearly know only definite schemes, but are utterly lost if asked to check the accuracy of a method or to devise a new one. Routine analyses in most works are made not by chemists but by boys trained for the particular purpose and working under the direction of a chemist. To obtain suitable chemists for this purpose is very difficult, largely owing to the methods of instruction in vogue.

The book starts with a clear and very condensed statement of the definitions and descriptions of the principal operations. This is followed by detailed directions for the analysis of the common metallurgical materials and products. The methods

are clearly described and the illustrations are adequate. The plan of the work involves a great deal of repetition, but there is no more of this than is unavoidable under the circumstances. The methods described have the sanction of practice, nearly all being in common use, though in some cases well-known sources of error are not pointed out. For instance, the great danger of the contamination of precipitates of the hydroxides of iron and alumina with silica derived from the ammonia, or the certainty of high results in the volumetric determination of zinc when the ores contain cadmium. Where several alternative methods are given, no criticism of them is made, and their relative accuracy and suitability for different purposes is not pointed out.

Prof. White rightly insists on the necessity of testing weights and volumetric apparatus—a matter that is frequently neglected. He also repeatedly points out the necessity of standardizing volumetric solutions under identically the same conditions in all respects as are present when the unknown solution is titrated.

The book, like all of its kind, will be useful in many cases as it brings together a great deal of information now scattered through many journals and books.

GEO. C. STONE

**Leavening Agents.** By RICHARD N. HART, B.S. Published by the Chemical Publishing Company, Easton, Pa. 90 pp. 13 illustrations. Price, \$1.00.

This book, in which yeast and baking powders are briefly discussed from the manufacturer's point of view, will be found helpful to any one seeking information as to the method of yeast manufacture. The work could to advantage be enlarged on the biochemical side so that the chemist having a yeast problem to investigate might be able to obtain suggestions as to how to proceed.

A little over a page is given to "Tests for Yeast," the Metzler test being proposed. This test is misleading, particularly if a flour is used having low fermenting value, or one encouraging abnormal fermentation.

A concise description of baking powders is given and the author does not hesitate to express his views on the subject. "In a baking powder it is not a question of whether alum is harmful, or phosphate and cream of tartar wholesome, but of whether their residues in bread are deleterious." . . . "there is no record as yet of injurious results from using any baking powder well made by any of the standard formulae." If a writer had expressed such an opinion a few years ago, it would have invited much controversy and some would have condemned him to the "scrap heap." Happily, however, the time has come when manufacturing problems relating to foods can be looked at from a rational view-point. Some of the subject matter in the book could have been more judiciously selected, as on page 60 the test referred to is in reality a test of recipe rather than a test of flours.

In the chapter on milk powder only meager mention is made of skim milk powder and no analyses are given. Many bakers use skim milk powder, supplying the fat in forms cheaper than the butter fat in the more expensive whole milk powders.

In the discussion of "Salt-Rising Fermentation" it is quite apparent why the culture methods have come into use with the manufacture of cleaner flours which are less likely to contain as a natural constituent the gas generating ferment.

The book is well printed on good paper and is quite free from typographical errors. It is to be commended and the author encouraged to get out a larger and more complete edition at some future time.

HARRY SNYDER



# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Analysis:** *Mikrochemische Analyse.* By P. D. C. KLEY. 504 pp. Price, \$6.00. Leopold Voss, Leipzig.
- Cement:** *Zement und Beton im Tiefbau.* By H. GAMANN. 8vo. 299 pp. Price, \$2.00. Tonindustrie-Zeitung, Berlin.
- Colloids:** *Der Kolloide Zustand der Materie.* By LEONARDO CASSUTO. 8vo. Price, \$2.00. Theodor Steinkopff, Leipzig.
- Compressed Air:** *Die Verwendung von Pressluft im Bergbaubetriebe.* By A. E. LIEVEHR. 8vo. 258 pp. Price, \$1.25. C. Steinert, Weimar.
- Concrete:** *Reinforced Concrete.* By A. A. SCOTT. 8vo. 186 pp. Price, \$1.00. Scott, Greenwood, London.
- Dynamometers:** By F. J. JERVIS-SMITH. 8vo. 267 pp. Price, \$3.50. D. Van Nostrand, New York.
- Electricity:** *Mechanics of Electricity.* By F. J. B. CORDIERO. 8vo. Price, \$1.25. E. and F. N. Spon, London.
- Ferromanganese:** *Ferromangan als Desoxydationsmittel im festen und fluessigen Zustand und das Ferromanganschmelzen.* By W. RODENHAUSER. 8vo. 127 pp. Price, \$1.75. O. Leiner, Leipzig.
- Foundry:** *Leitfaden fuer Giessereilaboratorien.* By B. OSANN. 8vo. Price, \$1.00. J. Springer, Berlin.
- Furnace Efficiency, Combustion and Flue Gases.** By J. C. PEBBLES. 8vo. Price, \$1.00. J. G. Branch Publishing Co., Chicago.
- Gearing:** *Spiral and Worm Gearing.* 8vo. Price, \$2.75. E. and F. N. Spon, London.
- Hydrogen:** *Die Konstitution des Wasserstoff Molekuels.* By P. DEBYE. 8vo. Price, \$0.50. G. Franz, Munich.
- Lignite:** *Ueber Verwertung der Lignitkohle.* By J. HUEBERS. 8vo. Price, \$0.50. Verlag fuer Fachliteratur, Berlin.
- Materials of Construction.** By A. P. MILLS. 8vo. Price, \$4.75. Chapman and Hall, London.
- Molecules:** *Probleme komplexer Molekuele.* By P. LENARD. 8vo. Price, \$1.00. G. Franz, Munich.
- Minerals:** *Die gesteinsbildenden Mineralien.* By ERNST WEINSCHEK. 3rd Ed. 8vo. 261 pp. Price, \$2.50. Herder, Freiberg.
- Optics:** *Elements of Optics.* By G. W. PARKER. 12mo. 122 pp. Price, \$0.75. Longmans, Green and Co., New York.
- Ore Analysis:** *Technical Methods of Ore Analysis.* By ALBERT H. LOW. 7th Ed. 8vo. 376 pp. Price, \$2.75. John Wiley and Sons, New York.
- Organic Chemistry:** *Experiments in Organic Chemistry.* By F. J. MOORE. 8vo. Price, \$0.50. John Wiley & Sons, New York.
- Petroleum—Nomenclature:** *Die Nomenclatur in der Erdoelwissenschaft.* By H. HOFER. 8vo. Price, \$0.25. Verlag fuer Fachliteratur, Berlin.
- Physical Chemistry:** *Practical Physical Chemistry.* By J. B. FIRTH. 8vo. 190 pp. Price, \$0.75. Methuen and Co., London.
- Soil Analysis:** *Ueber die Bedeutung und die Methode der chemischen Bodenanalyse mit starker heisser Salzsaeure.* By D. J. HISSINK. 8vo. Price, \$0.50. Verlag fuer Fachliteratur, Berlin.
- Steam Boilers and Combustion.** By JOHN BATEY. 8vo. 220 pp. Price, \$1.50. Scott, Greenwood, London.
- Steel:** *Case Hardening of Steel.* By HARRY BREARLY. 8vo. 169 pp. Price, \$2.50. Spon and Co., New York.
- Testing:** *A Short Course in the Testing of Electrical Machinery.* By J. H. MORECROFT AND F. W. HEHRE. 3rd Ed. 8vo. 91 pp. Price, \$1.50. Macmillan Co., New York.
- Textile Color Mixing.** By DAVID PATTERSON. 2nd Ed. 8vo. 140 pp. Price, \$2.00. Scott, Greenwood, London.
- Volumetric Analysis.** By A. J. BERRY. 8vo. 146 pp. Price, \$1.75. Cambridge University Press.
- Water Analysis:** *Kompendum der biologischen Beurteilung des Wassers.* By J. WILHELM. 8vo. 66 pp. Price, \$1.00. G. Fischer, Jena.

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- Alcohol:** *Estimation of Methyl Alcohol in Presence of Ethyl Alcohol.* By G. C. JONES. *The Analyst*, Vol. 40 (1915), No. 470, pp. 218-222.
- Blast Furnace:** *Progress in Blast Furnace Practice.* By A. E. MACCOUN. *Iron Trade Review*, Vol. 56 (1915), No. 22, pp. 1129-1130.
- Blast Furnace Plant Auxiliaries.** By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 6, pp. 373-378.
- Blowpipe Analysis:** *Quantitative Blowpipe Analysis in the Field.* By GEORGE DELIUS. *Mining and Scientific Press*, Vol. 110 (1915), No. 19, pp. 725-726.
- Boiler Plate:** *Tests on the Diagonal Strength of Boiler Plate.* By G. W. F. MACDONALD. *Power*, Vol. 41 (1915), No. 23, pp. 779-780.
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- Chemical Engineering in Nitro-Cellulose Manufacture.** By S. L. STADELMAN. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 6, pp. 361-366.
- Colloids:** *The Action of Certain Colloids on Ions during Electrolysis.* By A. MUTSCHELLER. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 6, pp. 353-357.
- Copper:** *Physikalisch-Chemische Studien am Kupfer.* By ERNST COHEN AND W. D. HELDERMAN. *Journal fuer Physikalische Chemie*, Vol. 89 (1915), No. 5, pp. 638-639.
- Corrosion:** *Tests for Corrosion Resistance.* By DANIEL M. BUCK. *Iron Trade Review*, Vol. 56 (1915), No. 22, p. 1124.
- Corrosion:** *Recent Progress in Corrosion Resistance.* By DANIEL M. BUCK. *Steel and Iron*, Vol. 19 (1915), No. 18, pp. 582-586.
- Cyanide Process.** By FRANK S. WASHBURN. *The Chemical Engineer*, Vol. 21 (1915), No. 5, pp. 177-184.
- Cyanide Solution:** *Assay of Cyanide Solutions.* By C. E. ROODHOUSE. *Mining and Scientific Press*, Vol. 110 (1915), No. 20, p. 760.
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- Electric Power Industry.** DAVID B. RUSHMORE. *General Electric Review*, Vol. 18 (1915), No. 6, pp. 427-439.
- Enamelling:** *Anlage und Betrieb eines Moderne Emailierwerkes.* *Die Glashuette*, Vol. 45 (1915), No. 11/12, pp. 71-72.
- Fats:** *Ueber die Bestandteile tierischer Fette.* By J. KLIMONT AND K. MAYER. *Monatshefte fuer Chemie*, Vol. 36 (1915), No. 4, pp. 281-287.
- Fatty Acids:** *Ueber die Verbindungen des Calciums und Magnesiums mit hoeheren Fettsaeuren.* By JULIUS ZINK AND RICHARD LIERE. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 36, pp. 229-232.
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- Fibrox—A New Insulating Material.** By E. WEINTRAY. *Engineering Magazine*, Vol. 49 (1915), No. 3, p. 415.
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- Gas Engine:** *History of the Large Gas Engine.* By H. HUBERT. *Iron Trade Review*, Vol. 56 (1915), No. 22, pp. 1011-1016.
- Gas Pressures:** *The Equilibrium Theory of Gas Pressures.* By R. H. JOHNSON AND L. G. HUNTLEY. *Natural Gas Journal*, Vol. 9 (1915), No. 5, pp. 240-242.
- Gas Reactions:** *Zwei Gasreaktionen.* By MAX TRAUTZ. *Zeitschrift fuer Elektrochemie*, Vol. 21 (1915), No. 7/8, pp. 118-122.
- Heat:** *The Difficulty of Measuring Heat.* By A. H. BARKER AND F. C. BRENDA. *Heating and Ventilating Magazine*, Vol. 12 (1915), No. 5, pp. 21-24.
- Industrial Research.** By L. A. HAWKINS. *General Electric Review*, Vol. 18 (1915), No. 6, pp. 416-427.
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- Irrigation:** *Transmission Losses in Unlined Irrigation Channels.* By SAMUEL FORTIER. *Engineering News*, Vol. 73 (1915), No. 22, pp. 1060-1063.
- Mercury:** *Wet Methods of Mercury Extraction.* By E. BRYANT THORNHILL. *Mining and Scientific Press*, Vol. 110 (1915), No. 23, pp. 873-874.
- Mineral Acids:** *Bericht ueber die Industrie der Mineralsaeure im Jahre 1914.* By K. RAUSCH. *Chemiker-Zeitung*, Vol. 39 (1915), No. 54, pp. 342-343.
- Palladium:** *Zur Trennung von Palladium und Zinn durch elektrolytische Abscheidung des Palladiums.* By A. GUTBIER. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 4, pp. 208-213.
- Paper:** *Practical Aspects of Paper Testing.* *Paper*, Vol. 16 (1915), No. 11, pp. 17-18.
- Rubber:** *Recent Advances in the Analysis and Evaluation of Rubber and Rubber Goods.* By PHILIP SCHNIDROWITZ. *The Analyst*, Vol. 40 (1915), No. 470, pp. 223-233.
- Rust Removal by Chemical Reagents.** By J. N. FRIEND AND C. W. MARSHALL. *Iron Trade Review*, Vol. 56 (1915), No. 22, pp. 1023-1024.
- Selenium:** *Ueber die Gewichtsanalytische Bestimmung des Selens.* By A. GUTBIER AND F. ENGEROFF. *Zeitschrift fuer analytische Chemie*, Vol. 54 (1915), No. 4, pp. 193-205.
- Steam:** *Commercial Value of Exhaust Steam.* By A. J. JOHNSTON, JR. *Engineering Magazine*, Vol. 49 (1915), No. 3, pp. 327-335.
- Sulfur Gas Reclaiming System.** By C. B. THORNE. *Paper*, Vol. 16 (1915), No. 10, pp. 11-13.
- Thermodynamics of Saturated Vapor.** By J. E. SIEBEL. *Ice and Refrigeration*, Vol. 48 (1915), No. 6, pp. 363-366.
- Zinc:** *Recent Improvements in the Metallurgy of Zinc.* *Engineering and Mining Journal*, Vol. 99 (1915), No. 21, p. 896.
- Zinc Ore:** *Electromagnetic Zinc-ore Treatment.* By L. E. IVES. *Engineering and Mining Journal*, Vol. 99 (1915), No. 23, pp. 979-980.



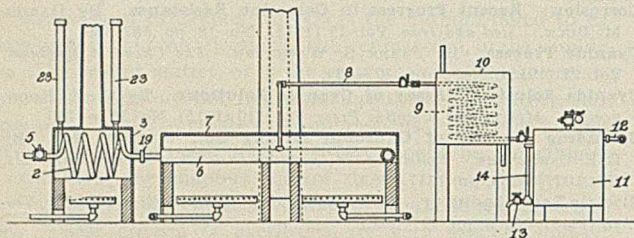
# RECENT INVENTIONS

## UNITED STATES PATENTS

By C. L. PARKER

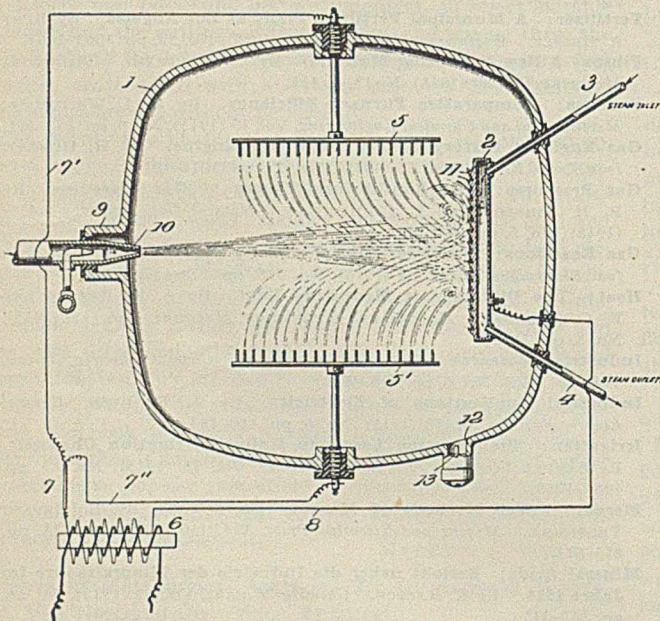
Solicitor of Chemical Patents, McGill Building, Washington, D. C.

**Treating Oil.** J. A. Dubbs, Jan. 5, 1915. U. S. Pat. 1,123,502. Finely divided particles of water are removed from emulsified oil by subjecting a body of such oil to a pressure materially above



atmospheric pressure, such pressure being produced by heating the oil to a temperature above that required for boiling water at such pressure and removing the steam and oily vapors generated during such treatment.

**Hydrogenating Fats, Oils and Waxes.** T. B. Walker, Jan. 5, 1915. U. S. Pat. 1,123,962. Hydrogenation is effected by sub-



jecting the material under treatment, in a comminuted condition, to the action of hydrogen gas under superatmospheric pressure and a catalytic body, in the presence of heat and an electric discharge.

**Magnesium Perborate.** W. Weber, Jan. 5, 1915. U. S. Pat. 1,124,081. A mixture of magnesium sulfate and sodium perborate are melted, with constant stirring.

**Electrolytically Refining Tin.** G. Michaud and E. Delasson, Jan. 12, 1915. U. S. Pat. 1,124,315. An electric current is passed from an anode of impure tin to a cathode through an electrolyte of high conductivity composed of protochlorid of tin, 100 kg.; sulfuric acid, 10 kg.; magnesium chlorid, 1 kg.; boric acid, 1 kg.; and the requisite quantity of distilled water to bring the solution up to 20° Baumé.

**Light Hydrocarbons, etc.** P. Sabatier and A. Mailhe, Jan. 12, 1915. U. S. Pat. 1,124,333. Crude petroleum, heavy pe-

troleum oils, etc., are converted into hydrocarbons distilling below 300° F. by passing their vapors over catalyzing metals in a state of division in contact with metals or alloys of metals of the nickel series maintained at a temperature varying from 300° F. to dark red and to bright red by the passage of an electric current.

**Effecting Dissociative Reactions upon Carbon Compounds.** W. O. Snelling, Jan. 12, 1915. U. S. Pat. 1,124,347. The process comprises heating a carbon compound capable of undergoing a reversible reaction in which hydrogen is one of the products and separating and withdrawing the hydrogen in an uncombined state during the progress of the reaction.

**Saturating Unsaturated Acids and Their Glycerides by Combining Them with Hydrogen.** E. Utescher, Jan. 12, 1915. U. S. Pat. 1,124,560. Hydrogenation of oil is effected by subjecting the oil to the action of hydrogen, a catalyzer and silent electrical discharges.

**Dry Fat and Oil Compounds.** M. Hamburg, Jan. 12, 1915. U. S. Pat. 1,124,611. The composition is produced by emulsifying not less than 25 parts of materials having the physical properties of oil with approximately 75 parts of highly concentrated diastatic starch conversion products without addition of a foreign emulsifying agent, and drying and granulating the resultant mixture.

**Explosive.** C. A. Woodbury, Jan. 12, 1915. U. S. Pat. 1,124,679. This is an explosive having a relatively low velocity of detonation comprising nitrate of ammonia, nitroglycerin and an absorbent, the nitrate of ammonia being in the form of relatively large globular grains.

**Extracting Potassium from Flue-Dust.** S. Peacock, Jan. 12, 1915. U. S. Pat. 1,124,798. Flue-dust containing potassium salts is treated with a solution of non-calcium phosphate to react with potassium silicates present and also with an acid to react with any potassium salts which may be mechanically held by such silicates.

**Reclaiming Rubber.** H. W. Kugler, Jan. 12, 1915. U. S. Pat. 1,124,920. Vulcanized rubber is simultaneously treated, under suitable conditions of temperature and pressure, with a carbo-cyclic amido compound, such as anilin, toluidin, xylydin, or the like and a substance capable of combining with or absorbing sulfur, such as caustic alkali solution.

**Making Arsenic and Arsenical Compounds.** G. P. Fuller, Jan. 19, 1915. U. S. Pat. 1,125,086. Arsenious acid is suspended in an aqueous solution of an alkali metal halid and subjected to electrolysis. The product of the reaction is filtered and the filtrate treated to recover its arsenical compounds.

**Copper.** W. M. Page and W. Tassin, Jan. 19, 1915. U. S. Pat. 1,125,164. Copper in a highly heated molten condition is treated with iron in excess of an amount sufficient to react with the oxygen and oxids present; the excess of iron is burned out under conditions precluding re-oxidation of the copper.

**Casein from Buttermilk.** R. Eilersen, Jan. 26, 1915. U. S. Pat. 1,126,429. Buttermilk is heated to from 40° to 65° C. to separate the whey and the curd. The curd is washed with cold water adding sufficient cold water to replace the separated whey. The casein is dissolved in an alkaline bicarbonate, separated and precipitated by a mineral acid, the precipitate being washed with cold water.



## BRITISH PATENTS

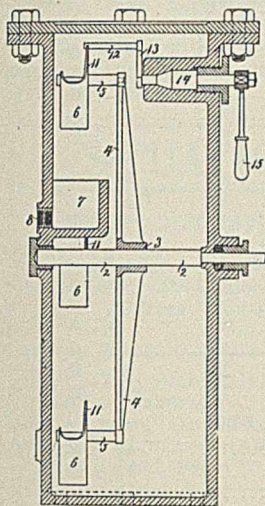
By D. GEDDES ANDERSON

Chemical Engineer and Patent Chemist, Glasgow, Scotland

The following abstracts are taken direct from the patent specifications as soon as these are published by the British patent office. The date given at the end of the abstract is the date of acceptance.

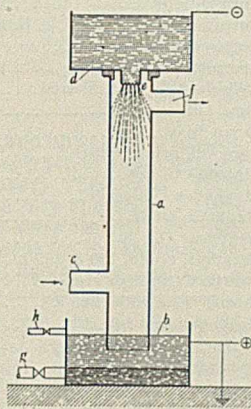
## Apparatus for Carburetting Air. H. A. Taylor, and The

British and Colonial Lighting Co., Ltd., Application, Nov. 5, 1913. Brit. Pat. 25,271. This invention relates to apparatus of the type wherein travelling pivoted buckets pick up hydrocarbon and deliver it to a carburetter. The primary feature is the adjustable bucket tipping obstruction. In the sectional view shown, the bucket 6 with lug 11 travels, filled with hydrocarbon, to the top of chamber and is there tipped by adjustable post 12 into receiver 7, from which the hydrocarbon passes to the carburetting chamber through opening 8.—Accepted Feb. 25, 1915.

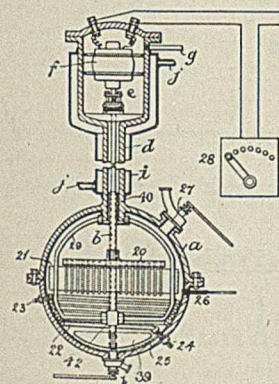


## Purification of Gases for Heating or Power Purposes. E. Howl

and F. Perry, Feb. 26, 1914. Brit. Pat. 5,051. Tar and tar fog are separated from industrial gases by subjecting the gases to a spray of electro-statically charged water. "a" is a metal tower with gas inlet "c," and gas outlet "f." "b" is a liquid sump for the collection of tarry deposits. The water in the receptacle "d" is electrified negatively and issues through suitable jets "c."—Feb. 26, 1915.



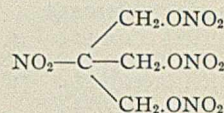
Recovery of Sulfuric Acid from Waste Pickle. E. Howl and F. Perry, March 7, 1914. Brit. Pat. 5,830. The acid liquor from operations in which iron and steel have been treated with sulfuric acid is run into lead-lined



tanks and evaporated to a concentration of 75 per cent acid. At this concentration the ferrous sulfate in the liquor is precipitated in an anhydrous form and separated with a centrifugal separator.—March 4, 1915.

Mixing Devices for the Hydrogenation of Oils. G. Calvert, March 9, 1914. Brit. Pat. 5,967. Oil and catalyst are fed in through 27, and hydrogen through "g". The co-mingling device in the container "a" comprises a propeller, 39, at the base, and rotary agitators 20 in the form of a comb; 29 is a yoke to support bearing 42 for shaft "b."—Feb. 25, 1915.

A New Explosive. F. E. Matthews, March 13, 1914. Brit. Pat. 6,447. This invention relates to a new explosive substance, nitroisobutyl glycerol trinitrate, having the chemical



For its preparation solid nitroisobutyl glycerol is brought into contact with "mixed acids" (equal vols. concentrated sulfuric and strong nitric acids) at a low temperature. The new product separates on the surface as a yellow oil. It is insoluble in water and has great stability towards heat.—March 11, 1915.

Metallic Paint. The British Patent Surbrite Co. Ltd., and E. G. Meadway, March 20, 1914. Brit. Pat. 7,087. Metallic powder, 2 lbs.; gum mastic, 320 grams; India rubber dissolved in naphtha, 2 fluid ounces; celluloid dissolved in amyl acetate, 113 fluid ounces; amyl acetate, 45 fluid ounces. The gum mastic is first dissolved in the rubber solution and this mixture added to the other ingredients.—March 18, 1915.

Accelerating the Vulcanization of Rubber. S. J. Peachey, March 24, 1914. Brit. Pat. 7,370. Vulcanization is carried out in the presence of a compound resulting from the interaction of an amine of the cyclic (aromatic or benzenoid) series, with an aldehyde of the aliphatic or of the cyclic series; or of an aldehyde of the cyclic series with ammonia. Two examples of such compounds are formaldehyde aniline, and benzylidene aniline.—Feb. 25, 1915.

Utilizing Waste Rubber. H. Gare, April 23, 1914. Brit. Pat. 10,300. Old or waste vulcanized India rubber is ground with sufficient water to bring the mass to a pasty condition and this semi-fluid mass is then molded under a pressure varying from 10 to 15 tons per pound of rubber used.—March 11, 1915.

Accelerating Vulcanization of Rubber. S. J. Peachey, May 2, 1914. Brit. Pat. 10,833. In this process the vulcanization is carried out in the presence of a small quantity of parnitrosodiphenylamine, or of the reduction product of parnitrosodimethylaniline, namely dimethyl-paraphenylenediamine.—March 4, 1915.

Cement. J. F. Goddard, June 3, 1914. Brit. Pat. 13,542. Relates to a process for making Portland cement waterproof. Plaster of Paris is allowed to set with tannic acid (1 acid to 5 plaster) and is then ground to a powder and added to the cement clinker during the grinding process. About 0.8 per cent by weight of this treated plaster is added to the clinker.—March 11, 1915.

Insecticides. Wilkie and Soames, Ltd., and W. F. Soames, July 1, 1914. Brit. Pat. 15,765. Material consists of powdered, dried soap and sulfur. It is made up with water and sprayed, or else used in powdered form.—March 4, 1915.

Antiseptic and Germicides. G. T. Morgan and G. E. Scharff, Aug. 31, 1914. Brit. Pat. 19,253. Peat tar is dried at 100° C., and distilled in suitable retorts. Three fractions are made (1) 100° C. to 200° C., (2) 200° C. to 250° C.; (3) 250° C. to 360° C. This separation leads to the segregation of the cresols in the least germicidal fraction boiling at 100° C. to 200° C. The distillates are extracted with a 10 per cent caustic soda solution and the acidic oils then set free by neutralizing with sulfuric acid.—March 11, 1915.

Improved Absorbent for Carbon Dioxide in Breathing Apparatus. E. J. Bevan and R. H. Davis, Nov. 18, 1914. Brit. Pat. 22,719. The absorption chamber of breathing apparatus, such as is used in mine rescue work, is charged with a material made by grinding cellulose with a strong solution of caustic soda; 3 lbs. of caustic soda liquor (1 of caustic to 2 of water) are ground with 2 lbs. of ground wood pulp. The resulting material resembles bread crumbs in form, and does not deliquesce.—March 11, 1915.



## MARKET REPORT—JUNE, 1915

AVERAGE WHOLESALE PRICES IN THE NEW YORK MARKET FOR LARGE QUANTITIES OF STANDARD CHEMICALS

## INORGANIC CHEMICALS

Acetate of Lime, gray.....	100 Lbs.	3.50	@	3.55
Alum, lump.....	100 Lbs.	2.50	@	3.00
Aluminum Sulfate, high-grade.....	100 Lbs.	1.25	@	1.50
Ammonium Carbonate, domestic.....	Lb.	8 1/2	@	9 1/2
Ammonium Chloride, gray.....	Lb.	6 1/4	@	6 1/2
Aqua Ammonium, 16°, drums.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3 3/4	@	—
Barium Chloride.....	Ton	80.00	@	90.00
Barium Nitrate.....	Lb.	15	@	—
Barytes, prime white, foreign.....	Ton	19.00	@	23.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.40	@	1.50
Blue Vitriol.....	Lb.	7 1/2	@	—
Borax, crystals, in bags.....	Lb.	4 1/4	@	4 1/2
Boric Acid, powdered crystals.....	Lb.	7 1/2	@	7 3/4
Brimstone, crude, domestic.....	Long Ton	22.00	@	22.50
Bromine, technical, bulk.....	Lb.	85	@	87
Calcium Chloride, lump.....	Ton	—	@	11.78
Calcium Chloride, granulated.....	Ton	—	@	14.78
Caustic Soda, 60 per cent domestic, in drums, 100 Lbs.		2.35	@	—
Caustic Soda, 70 @ 76 per cent.....	100 Lbs.	2.25	@	—
Caustic Soda, powdered or granulated, 76% 100 Lbs.		3.00	@	—
Chalk, light precipitated.....	Lb.	4 1/2	%	4 3/4
China Clay, imported.....	Ton	30.00	@	33.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	85
Glauber's Salt, in bbls.....	100 Lbs.	60	@	—
Green Vitriol, bulk.....	100 Lbs.	90	@	1.00
Hydrochloric Acid, commercial, 18°.....	100 Lbs.	1.50	@	1.75
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	2.00	@	2.25
Iodine, resublimed.....	Lb.	3.75	@	3.80
Lead Acetate, white crystals.....	Lb.	11 2/3	@	11 7/8
Lead Nitrate.....	Lb.	11	@	11 1/2
Litharge, American.....	Lb.	8 1/4	@	—
Lithium Carbonate.....	Lb.	1.00	@	1.10
Magnesium Carbonate.....	Lb.	5 1/2	@	6
Magnesite, "Calcined".....	Ton	25.00	@	30.00
Nitric Acid, 68 per cent, sp. gr. 1.42.....	Lb.	5 7/8	@	6 1/4
Nitric Acid, fuming.....	Lb.	7 7/8	@	8 1/4
Phosphoric Acid, sp. gr. 1.750.....	Lb.	28	@	31
Phosphorus.....	Lb.	35	@	90
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	20 1/2	@	—
Potassium Bromide.....	Lb.	1.10	@	1.11
Potassium Carbonate, calcined, 80 @ 85%.....	100 Lbs.	20	@	—
Potassium Chlorate, crystals, spot.....	Lb.	34	@	—
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	25	@	29
Potassium Hydroxide.....	Lb.	25	@	30
Potassium Iodide, bulk.....	Lb.	3.15	@	3.20
Potassium Nitrate, crude.....	Lb.	12	@	—
Potassium Permanganate, bulk.....	Lb.	70	@	72 1/2
Quicksilver, flask, 75 lbs.....		95.00	@	100.00
Red Lead, American.....	Lb.	8 1/2	@	8 3/4
Salt Cake, glass makers'.....	100 Lbs.	55	@	—
Saltpeter, crude.....	100 Lbs.	2.35	@	—
Silver Nitrate.....	Oz.	31 1/2	@	33
Soapstone in bags, Na <sub>2</sub> O.....	Ton	10.00	@	12.00
Soda Ash, 48 per cent. Na <sub>2</sub> O.....	100 Lbs.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	4	@	4 1/2
Sodium Bicarbonate, domestic.....	100 Lbs.	1.00	@	1.10
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 3/4
Sodium Bichromate.....	Lb.	10 1/2	@	—
Sodium Carbonate, dry.....	100 Lbs.	1.10	@	—
Sodium Chlorate.....	Lb.	15	@	17
Sodium Hydroxide, 60 per cent.....	100 Lbs.	2.25	@	—
Sodium Hyposulfite.....	100 Lbs.	1.80	@	2.00
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	2.35	@	—
Sodium Silicate, liquid.....	100 Lbs.	85	@	1.20
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	1 3/4	@	2 1/4
Sodium Sulfite, crystals.....	Lb.	2 1/2	@	2 5/8
Strontium Nitrate.....	Lb.	17 1/2	@	18
Sulfur, flowers, sublimed.....	100 Lbs.	2.20	@	2.60
Sulfur, roll.....	100 Lbs.	1.85	@	2.15
Sulfuric Acid, chamber, 60°.....	100 Lbs.	85	@	—
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	1.25	@	2.00
Sulfuric Acid, oleum (fuming).....	100 Lbs.	1.50	@	2.00
Talc, American.....	Ton	9.00	@	13.00
Terra Alba, American, No. 1.....	100 Lbs.	75	@	80
Tin Bichloride, 50°.....	Lb.	14 1/4	@	15
Tin Oxide.....	Lb.	45	@	47
White Lead, American, dry.....	Lb.	7 1/2	@	7 3/4
Zinc Carbonate.....	Lb.	10	@	12
Zinc Chloride, granulated.....	Lb.	9	@	—
Zinc Oxide, American process.....	Lb.	15	@	17
Zinc Sulfate.....	100 Lbs.	4 3/4	@	—

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	65	@	70
Acetic Acid, 28 per cent, in bbls.....	100 Lbs.	2.50	@	2.65
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	2.50	@	2.75
Acetone, drums.....	Lb.	28	@	—

Alcohol, denatured, 180 proof.....	Gal.	38	@	39
Alcohol, grain, 188 proof.....	Gal.	2.54	@	2.56
Alcohol, wood, 95 per cent, refined.....	Gal.	45	@	47
Amyl Acetate.....	Gal.	2.60	@	2.75
Aniline Oil.....	Lb.	1.00	@	1.20
Benzoic Acid, ex-toluol.....	Lb.	2.75	@	3.00
Benzol, 90 per cent.....	Gal.	90	@	—
Camphor, refined in bulk, bbls.....	Lb.	43	@	45
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	1.50	@	—
Carbon Bisulfide.....	Lb.	7 1/2	@	8
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	17
Chloroform.....	Lb.	30	@	35
Citric Acid, domestic, crystals.....	Lb.	55	@	55 1/2
Cresol, U. S. P.....	Gal.	1.40	@	1.50
Dextrine, corn (carloads, bags).....	100 Lbs.	3.10	@	3.20
Dextrine, imported potato.....	Lb.	10	@	12
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	8 1/2	@	9 1/2
Glycerine, dynamite, drums included.....	Lb.	21 1/2	@	22
Oxalic Acid, in casks.....	Lb.	23	@	25
Pyrogallie Acid, resublimed bulk.....	Lb.	1.35	@	1.55
Salicylic Acid.....	Lb.	2	@	2 1/2
Starch, cassava.....	Lb.	3 1/4	@	4
Starch, corn (carloads, bags).....	100 Lbs.	2.43	@	—
Starch, potato.....	Lb.	5 1/4	@	—
Starch, rice.....	Lb.	7	@	8
Starch, sago.....	Lb.	3 3/4	@	4
Starch, wheat.....	Lb.	7	@	7 1/2
Tannic Acid, commercial.....	Lb.	65	@	66
Tartaric Acid, crystals.....	Lb.	48	@	50

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	12 1/2	@	13
Castor Oil, No. 3.....	Lb.	9 3/4	@	10 1/4
Ceresin, yellow.....	Lb.	10	@	25
Corn Oil.....	100 Lbs.	6.26	@	—
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	38	@	39
Cottonseed Oil, p. s. y.....	Lb.	6.15	@	—
Creosote, beechwood.....	Lb.	90	@	95
Cylinder Oil, light, filtered.....	Gal.	20	@	25
Fusel Oil, crude.....	Lb.	2.40	@	2.50
Japan Wax.....	Lb.	12	@	12 1/2
Lard Oil, prime winter.....	Gal.	88	@	90
Linseed Oil, raw.....	Gal.	57	@	—
Menhaden Oil, crude.....	Gal.	37	@	—
Naphtha, 68 @ 72°.....	Gal.	—	@	12
Neatsfoot Oil, 20°.....	Gal.	93	@	94
Paraffine, crude, 120 & 122 m. p.....	Lb.	2 1/2	@	3
Paraffine Oil, high viscosity.....	Gal.	22	@	23
Rosin, "F" Grade, 280 lbs.....	Bbl.	3.80	@	—
Rosin Oil, first run.....	Gal.	—	@	25
Shellac, T. N.....	Lb.	14	@	14 1/2
Spermaceti, cake.....	Lb.	25	@	—
Sperm Oil, bleached winter, 38°.....	Gal.	70	@	—
Spindle Oil, No. 200.....	Gal.	17	@	18
Stearic Acid, double-pressed.....	Lb.	12	@	12 1/2
Tallow, acidless.....	Gal.	62	@	63
Tar Oil, distilled.....	Gal.	30	@	31
Turpentine, spirits of.....	Gal.	45	@	45 1/2

## METALS

Aluminum, No. 1, ingots.....	Lb.	29	@	31
Antimony, Hallets'.....	Lb.	44	@	46
Bismuth, New York.....	Lb.	3.00	@	—
Bronze powder.....	Lb.	45	@	3.15
Copper, electrolytic.....	Lb.	20	@	20 1/4
Copper, lake.....	Lb.	20 1/4	@	20 3/4
Lead, N. Y.....	100 Lbs.	5.75	@	—
Nickel.....	Lb.	42	@	45
Platinum, refined.....	Oz.	45.00	@	50.00
Silver.....	Oz.	49 1/8	@	—
Tin.....	100 Lbs.	40.75	@	—
Zinc, N. Y.....	Lb.	18 1/4	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	3.37 1/2	@	—
Blood, dried.....	Unit	2.65	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	30.00	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.30	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	2.52 1/2	@	10
Kainit, minimum 12.4 per cent K <sub>2</sub> O, bulk.....	Ton	35.00	@	—
Phosphate, acid, 16 per cent, bulk.....	Ton	8.00	@	9.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.25	@	—
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	200.00	@	216.00
Pyrites, furnace size, imported.....	Unit	14	@	—
Tankage, high-grade.....	Unit	2.60	@	10



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Are you interested in the manufacture of hydrogen or nitrogen or both? I can furnish you with the simplest and cheapest method possible to produce same free of carbon, so important for many industrial purposes. For particulars address "P. O. Box 217, North Diamond Str. Station, Pittsburg, Pa."

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**ENGINEERING CHEMIST AND METALLURGIST** with 25 years' experience in a special line, and owning patented improvements therein reducing cost of plant and manufacture of products of highest quality from cheaper ores by simpler methods than heretofore employed—results are obvious. Object, to secure capital or interest in established concern. Can be started with a nominal investment. For particulars address "P. O. Box 217, North Diamond Str. Station, Pittsburg, Pa."

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**SITUATIONS WANTED**

**GERMAN CHEMIST**, graduate, desires position. Experience: 2 years in Germany, 2½ years in United States. Young, efficient and inventive. Capable of research and library work. Professional references and publications on request. Address "Box 17," care This Journal, Easton, Pa.

946-7-15

**CHEMIST**, young lady, university graduate, desires position in chemical laboratory, or as teacher of chemistry. Has had five years' experience in analytical and research work. Excellent references. Address "G. L. E. M.," care This Journal, Easton, Pa.

947-7-15

**YOUNG CHEMIST**, single, university graduate, experienced in cement-, glass-, alkali-, and bleach-industry, wishes position as chemist in any branch of chemical industry. Will go anywhere. Salary no object. Address "1910, care C. F. Adams & Co., 942 Market St., San Francisco, Cal."

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**CHEMICAL ENGINEER**. College and university graduate. Varied experience in plant design, construction and operation in furnaces, electrothermics and heavy chemicals. Have directed commercial research and factory operation. Have started several new processes. First-class record. Engagement as chief chemist, superintendent or works manager. Address "Box 32," care This Journal, Easton, Pa.

959-7-15

**CHEMIST AND BACTERIOLOGIST**, Ph.D., European university graduate, twenty-one years' experience in U. S., thorough analyst and research chemist, used to supervising laboratory work, large experience in literary work and technical correspondence, linguist, is looking for permanent, remunerative position. Address "Chiffre," care This Journal, Easton, Pa.

949-7-15

**EXPERIENCED CHEMIST** wants position in California—neighborhood of San Francisco or Los Angeles preferred. Address "California," care This Journal, Easton, Pa.

956-7-15

**PAINT TECHNOLOGIST**, graduate industrial chemist with executive ability and over four years' experience, desires position as foreman or assistant superintendent in a paint and varnish plant. Age 26½, weight 168 lbs., single, healthy, willing to go anywhere but prefers the northeastern part of U. S. Excellent references from former employers. Address "W. N. C.," care This Journal, Easton, Pa.

950-7-15

**YOUNG MAN**, B.S., Michigan, 1914, desires position in chemical laboratory. Has had seven months' experience in a state experiment station and is a skilled analyst. Can furnish first-class references. Address "S. M.," care This Journal, Easton, Pa.

953-7-15

**WANTED** by 1915 B. S. in chemical engineering, graduate, Class A, eastern university, position in manufacturing plant or laboratory. Have good references and some experience as laboratory assistant. Willing to start at the bottom. Address "Box 915," care This Journal, Easton, Pa.

954-7-15

**GRADUATE CHEMIST**, age 24, with experience in the analysis of cement and cement materials, foods, drugs, fertilizers, ores, plaster, etc., and at present employed as chemist in western state food and drug laboratory, desires change to industrial chemical position with possibilities for advancement. Best of references furnished on request. Address "T. F. B.," care This Journal, Easton, Pa.

955-7-15

**CHEMIST**, Ch.B., 28, with best training in bacteriology, desires position in manufacturing plant or commercial laboratory. Four years' experience as analytical chemist. At present employed. Moderate salary where there is a chance for advancement. Can furnish excellent references. Address "Box 191," care This Journal, Easton, Pa.

957-7-15

**CHEMICAL ENGINEER**, now employed as chemist in works laboratory, with five years' analytical and research experience, both chemical and electrical, wishes a change of location and prefers work in factory or research laboratory. Excellent references. Address "M.," care This Journal, Easton, Pa.

934-7-15

**CHEMIST**, 23 years old, having advanced college training in analytical chemistry, desires position in Holyoke, Mass., or vicinity where conscientious, efficient service will bring advancement. Four years' successful experience in industrial laboratories. Able first-assistant. Special knowledge of alkali and acid, refractories and paper chemistry. Can furnish references. Address "71 P.," care This Journal, Easton, Pa.

958-7-15

**FOOD AND MILK CHEMIST**, age 24, M.S. Univ. Calif., 1915, desires at once position, preferably on Pacific Coast, in industrial work or in a health control laboratory. Thorough training in all chemical branches and bacteriology. Specialized for last two years on food work, including research on milk analytical methods. Hard work expected and salary secondary to opportunity for advancement. Address "Sig.," care This Journal, Easton, Pa.

960-7-15

**A Directory of****Chemical Equipment and Laboratory Supplies**

which we plan to make a concise Directory of the principal manufacturers of Chemical Equipment and Laboratory Supplies has been started in the Journal of the American Chemical Society.

The large number of inquiries that we receive from members of the American Chemical Society for addresses of manufacturers of special classes and makes of Chemical Equipment and Supplies, indicates the need of some such quick reference list.

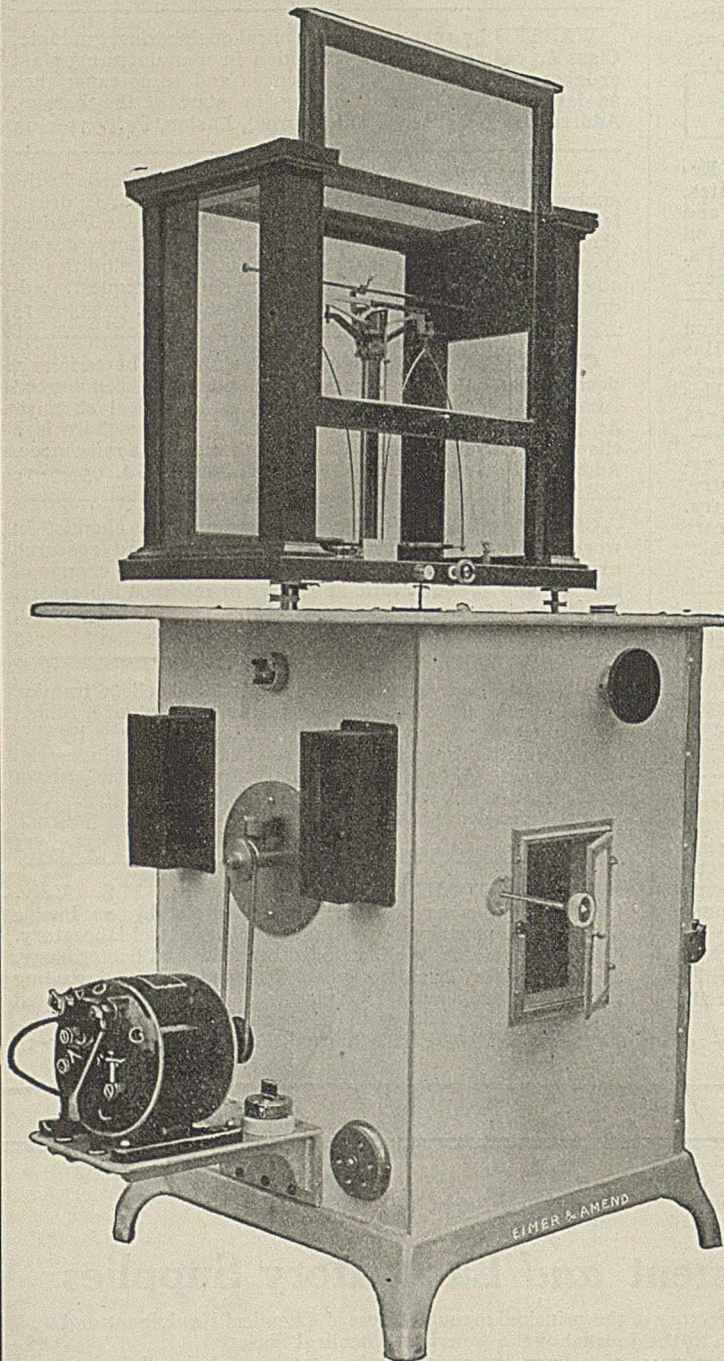
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