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EDITORIALS

SOMETHING TO THINK ABOUT AT THE SEPTEMBER MEETING

During the week of September 25th the American Chemical Society meets at New York, and the time is ripe for a consideration of the industrial side of chemistry in the United States, its prospects, and the part the American Chemical Society may play in it.

It appears that there will be a large attendance, and this is good; for the occasion is important. There will be the Chemical Exhibition going on during the same week, and on the last three days the American Electrochemical Society meets also in New York, with the usual interchange of courtesies. A part of the social entertainment will be of a joint nature. This is also favorable. The American Chemical Society is big enough to encourage as many other scientific organizations to meet with it as possible. The subject of chemistry is very much bigger than all the societies and institutes put together. And now that we have physical chemistry on the mind, in the kidney, breaking out through the skin, interleaving textbooks and controlling the operation of filter-presses, it is well to bring chemists together with those engaged in physics from every angle of attack. The contribution of papers is promising. In the ordinary sense of the word, the prospects of the meeting are very favorable. The exhibition, which some feared would be merely an advertising hurrah, proved last year to be an occasion of industrial and engineering importance, and bids fair this year to be of much greater interest than before.

But there is more than the reading of papers and seeing sights and miscellaneous entertainment to be done at this meeting, because the Society will have to determine its policy. This will take place whether any resolutions as to policy are passed or not.

A glance at chemical industry in this country shows factories of one sort or another to have cropped out all over, like measles on a baby. The great works have met the situation in most cases, with their customary intelligence. Enormous fortunes have been made and active research has been prosecuted along many lines. But there are a vast number of works, busy at the moment, when selling is easy and buying is hard, that are totally uncorrelated, and that are no more prepared for ordinary times than is the genius at the end of the line who "hired one of these here exaperts to make pitric acid" for export. The laws of this country prohibit a great deal of coöperation that is needed and wholesome. Times in chemical industry have been so hilariously prosperous that it is among the few, rather than the many, that proper provision for times of easy buying and hard selling has been made. There is a great uncoördinated chemical industry started in this country and some day before long the question will have to be settled whether we shall continue to have it here or not. If many methods and ways of to-day are continued there is only one answer possible: a good part of it will die out—for good and sufficient reasons.

We have also some bad habits. There is, for instance, a tradition of secrecy that is as absurd as it is expensive. It comes down from the days of alchemy. It is a tradition of quackery and little more. Of course, nobody cares to tell his competitors everything he knows; but in all the muggy cloud of mystery around chemical works, how much that is kept secret is of actual value? We venture the guess that it is not a tithe. The rest is just tradition, and it goes through the whole establishment. The result is disastrous. Chemical industry walks with pussy-footed tread. Cryptic utterances are in the air. Men speak in parables. The poker eye is in evidence. Everybody raises and nobody calls. Nobody knows what anybody else is making—"to a certain extent," let us say, with a view to precision. Every maker of special products is at times at his wits' ends to know where to buy something that another is anxious and willing to sell. One of the most needed things to do is to effect a method of exchange for intermediates. This must be done soon.

Another thing of equal importance is a discriminating apparatus of some sort that will help to avoid mistakes. As soon as chemical industry goes beyond the mistake-limit, just so soon will a fat measure of industrial chemistry go out of the country—for keeps. When a man in business is up against a chemical problem he is more helpless than in almost any other predicament. We can blame him all we please for his ignorance, but that will not help matters. The man wants advice and he doesn't know where to get it. The means of telling him must be invented, or the scrap-heap of defunct chemical factories will grow so fast as to make the bankers shiver.

And right here is where the American Chemical Society comes in. It is the only available medium of exchange of chemical information. It can go ahead printing papers, maintaining a catalogue of members and meeting at intervals, just as it does now; and that is an eminently respectable career. Nobody can condemn it for doing evil. But it can miss its chance. It can watchfully wait until the apple cart is upset. Or it can get busy and meet the situation in every way possible. We have mentioned two functions that it may perform and we shall content ourselves with elaborating them.

A bureau of information may be established, the business of which is to tell who makes what, so long as the maker is willing to have the fact known. It need have nothing to do with prices, for trading is not the Society's business. But technical information is its business so long as it maintains an Industrial Journal and recognizes industrial chemistry as a part of its field.

Suppose a constant series of enquiries as to buyers and sellers of rare chemicals and, in times like these, of standard goods, were to be circulated among members of the Society. They could maintain their wonted secrecy as long as they desired to. Xm might be in the market for oleum or glycol or phthalic anhydride or ethylene chloride and ask who had it for sale. Zippah might respond that he could furnish glycol. Then, when both parties are willing, the startling revelation is made to each who t'other is. Suppose they prove to be competitors, after each other tooth and nail. This would not occur often, but it might; the business end of chemistry is full of tricks. Well, Zippah could name a price that would take all the sport out of Xm's discovery. The futility of secrecy would soon show itself and manufacturers would come out into the open. Gorgonzola would tell his real name, while Xm and Zippah would prove to be honest men of business who would soon learn that all the world is not after them or their trade.

It would be gratuitous to dictate how such a bureau should be organized or operated; but if the Society wants to do it, it can.

Now we come to the second feature which is of a like nature. It is very easy to become a member of the Society and for the annual fee each receives his money's worth, if he is engaged in the active practice of chemistry. Membership does not give him a "character" or even the Society's backing as a man of science. Every member stands on the same footing, but every member is not to be recommended as a special authority in every branch of the science. The list of members does not tell anything of interest to the man who wants special information. And yet, just such information is available about many others than chemists. Every year there are published voluminous "Who's Who" books that tell what each man of supposed prominence has to say for himself. In like manner every member of the American Chemical Society could, and we venture to say substantially all those who are open to consultation would give a memorandum of his work, his achievements, the kind of work he is prepared to undertake and the places where an enquirer could find out about him. Unfaithful employees could be picked off like ripe cherries. The information about available men could be card-catalogued and this could be cross-indexed so that an industrial organization in need of advice could get a list of men who are informed, on short notice. Then a pharmaceutical manufacturer who wanted the synthesis of some drug extracted from bird's-eye maple cut in the dark of the moon, would not get a metallurgist to undertake the task.

A list of good men could be made out and such a list would grow. The knowledge that it existed would be a great encouragement to industry. Unexpected trades and lines of business would come around, and no establishment would be too big to listen to the enquiries that would have their origin in such a bureau.

Again we do not propose to give details as to how it should be organized or how it should be supported. The need of it is great enough to make it sustain itself; and the details, while full of difficulties, could be worked out. The only question now is, whether the American Chemical Society wants to undertake it or not. It can be done.

EFFECTIVE COÖPERATION BETWEEN THE UNIVERSITY AND THE INDUSTRY

During the past year a lengthy discussion of the relations between the university and chemical industry brought out interesting and helpful suggestions, but, judging from the character of the report of the Committee appointed to consider the matter, produced nothing capable of being reduced to tangible action and of bringing forth practical results. At the end of the discussion the bystander was left with the impression of the incapacity of two parties, each interested in the other's welfare, to succeed in finding common ground for action and coöperation.

Fortunately, however, one of the men who took part in that discussion was of the rare type able to reduce words to action. Convinced, as everyone has been throughout, of the desirability of essential unity in effort on the part of the chemical departments of our universities and of the industries which they serve, he has set to work to develop an effective and practicable plan of coöperation, and has himself launched the first attempt to improve the product of our universities by coördinated effort on the part both of the University, which exists to furnish the training, and of the Industry, for whom the men are trained but without whose aid the training must necessarily remain inadequate. Not only the Massachusetts Institute of Technology, but chemical education throughout the United States, and indeed higher education as a whole, are deeply indebted to Mr. Arthur D. Little of the Corporation of the Institute for the development of the School of Chemical Engineering Practice, a description of which appeared in the previous issue of THIS JOURNAL.

The scheme of Mr. Little involves the utilization of the plants of a number of selected industries as laboratories of chemical engineering for the training of men who have already substantially completed a chemical engineering course of university rank. On the other hand, this practice school is restricted to men who possess the ability and character necessary to profit thereby, and is to be followed by a year of post-graduate work allowing specialization along some specific line in chemistry or engineering. The plant experience is to be under the direction of members of the Faculty of the Institute, and is to be designed for educational effectiveness in the development of the student. This, and the fact that the students are of exclusively post-graduate grade, are the essential points in which it differs from previous experiments, and are full of promise for the success of the school.

The Institute proposes to compensate the industries for the use of their plant equipment as an educational laboratory, by the establishment and maintenance for each plant of a research laboratory for the solution of the problems of the specific industry. Such a laboratory will bring the chemical department of the Institute into most intimate touch with the problems of applied chemistry. That the return to the industries will be adequate is promised by the success not only of the research laboratories in many of our industries but of the Research Laboratory of Applied Chemistry at the Institute itself, the Director of which, Dr. Wm. H. Walker, is to be in charge of this new school. More intimate contact of the University with Industry could not possibly be attained, and the advantages of the reflex action of this contact upon both may surely be anticipated.

The Institute and the country at large owe much to Mr. Arthur D. Little for this reduction to practice of the hitherto unworked theory of coöperation between the University and Industry.

WARREN K. LEWIS

BOSTON, MASSACHUSETTS

ORIGINAL PAPERS

LABORATORY INVESTIGATIONS CONCERNING THE REDUCTION OF BARIUM SULFATE TO BARIUM SULFIDE[1]

By ARTHUR E. WELLS

Received July 3, 1916

The necessity of having more exact information than was available in the literature on the subject, concerning the reduction of barium sulfate to sulfide, arose in connection with a critical study of the Wet Thiogen Process[2] for the recovery of elemental sulfur from smelter gases. The study of this process was undertaken by the Bureau of Mines in coöperation with the Thiogen Company, forming a part of the general program of the work carried out in the Coöperative Metallurgical Exhibit Laboratory at the Panama-Pacific International Exposition,[3] which dealt with the general problem of elimination of waste in smelting operations. At the close of the Exposition this laboratory investigation was continued in the Bureau of Mines laboratory in the Hearst Mining Building, at the University of California, Berkeley.

Stated briefly, the Wet Thiogen Process involves the recovery of the sulfur dioxide from smelter gases by passing them up through absorption towers, in which a descending "mother liquor" solution absorbs the sulfur dioxide. Barium sulfide is added to the solution of sulfur dioxide and a precipitate, consisting of barium thiosulfate, barium sulfite and sulfur, is thrown out. This precipitate is filtered and the elemental sulfur, with one-half of the sulfur from the thiosulfate, is distilled, leaving a residue of barium sulfite and some sulfate. This residue is then reduced to sulfide and the barium sulfide used again for precipitation, the barium thus being kept in circulation through cycles.

In order that the barium shall be most efficient as a precipitant during these cycles, it is very necessary that the maximum reduction of the sulfite or sulfate to the water-soluble sulfide be attained in each cycle. Thus, it was very necessary to determine the conditions under which the barium sulfite or sulfate was reduced most completely to the sulfide, and considerable experimental work has been conducted on that problem. As barium sulfate must be used at the start in the initial reduction, and was present to a large extent in all precipitates after distillation, and also, as this material could be obtained in quantities much more readily than the sulfite, the greater part of these investigations were concerned with the reduction of the sulfate. This is a problem that, aside from its applicability to the Thiogen Process, is of general interest, and especially to those who are engaged in the manufacture of barium salts.

While it is true that in these investigations most of the reduction tests were conducted with a much purer grade of barium sulfate than is generally used by the manufacturers of barium salts, yet it is felt that some of the data obtained in these tests are of such general application that a brief presentation of these data may be of possible value at this time when considerable attention is being devoted to the manufacture of barium salts.

In this paper only the data concerning the first reduction of barium sulfate will be discussed. In order to fully understand the data concerning the reduction of the products from cyclic operations, it would be necessary to go into a discussion of the action of the reduced barium compounds as a precipitant in the Thiogen Process cycles, and as such discussion is reserved for another paper, the data concerning the cyclic reductions are also reserved for that paper.

In answer to several inquiries concerning what was being accomplished at the present time in the reduction of barium sulfate at various plants where barium salts were being manufactured from barium sulfate, the information was gained that although 80 or 85 per cent of the barium was readily reduced to acid-soluble compounds, yet current practices rarely reduced more than 60 or 70 per cent of the barium to water-soluble barium sulfide.

The literature verified these statements.[1]

The barium compounds found in the reduced products are classified in this discussion as follows:

I	II	III
Readily Soluble in Hot Water	Difficultly Soluble in Hot Water but Soluble in Dilute HCl	Insoluble in Acid
BaS	BaO $BaCO_3$	$BaSO_4$
BaS_x	BaS $BaSiO_3$	
BaO	Traces of $BaSO_3$	

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[1] Published by permission of the Director of the Bureau of Mines and the Thiogen Company.

[2] "Metallurgical Smoke," by Charles H. Fulton, Bureau of Mines, *Bull.* **84**, 74–77.

[3] "The Coöperative Metallurgical Exhibit at the Panama-Pacific International Exposition," by G. H. Clevenger and A. E. Wells, *Met. & Chem. Eng.*, **13** (1915), 743.

[1] "Mineral Industry," Vol. 19. Schuyler-Frazier, "Calcining Plant for Barium Sulfate." A. H. Fay, "Roasting Barytes." Maximilian Toch, "The Barium Industry in the United States since the European War," *Met. & Chem. Eng.*, **14** (1916), 47.

I—WATER-SOLUBLE BARIUM

The reduced product, ground to 100 mesh, was leached in a flask with 250 parts water, just below boiling, and filtered into a flask which was tightly stoppered while the solution was cooling. An aliquot part of the solution was then titrated with iodine, and in another aliquot part barium and sulfur were determined. As a check for the iodine value, *i. e.*, the barium sulfide content, the material was frequently treated directly in a flask with excess iodine for about 5 min., and then the excess iodine determined. In many cases there was barium oxide present in the water solution. In other products there was a slight excess of sulfur over that required for the barium to form sulfide, indicating a polysulfide. In several products of reductions at high temperatures (1050 to 1200° C.), where excess carbon was present, the presence of the carbide was indicated but was not determined quantitatively.

II—BARIUM COMPOUNDS SPARINGLY SOLUBLE OR INSOLUBLE IN HOT WATER, BUT SOLUBLE IN DILUTE ACID

In many products from the first reduction, a large portion of the oxide present was very sparingly soluble in hot water, but was soluble in dilute hydrochloric acid.

In most products of the reductions which were effected in a direct fired furnace at high temperatures and where slight sintering had taken place, a small amount of the sulfide was found to be in the water-insoluble portion. In some products, from 4 to 6 per cent of the total sulfide was found to be sparingly soluble in water. The solubility of this material was increased somewhat by finer grinding. In a typical average product from the first reduction of barium sulfate, 97 per cent of the sulfide and 40 per cent of the oxide were readily soluble in hot water, the rest being found in the acid-soluble portion. In this water-insoluble, but acid-soluble, portion was also found the carbonate in varying amounts. The products from slow reductions, at low temperatures, contained more carbonate than did those from rapid reductions at high temperatures. Very few products contained more than a trace of the sulfite or thionates.

The reduction tests here discussed will be considered under five series.

SERIES I—TESTS TO DETERMINE THE RELATIVE RATES OF REDUCTION OF BARIUM SULFATE BY HYDROGEN, CARBON MONOXIDE, AND A MIXTURE OF THESE GASES WITH OTHER HYDROCARBONS AT DIFFERENT TEMPERATURES

In these tests precipitated barium sulfate (99+ per cent $BaSO_4$) was placed in a quartz tube of about 12 mm. (0.47 in.) diameter, and heated in an electrically heated tube furnace. The barium sulfate was placed between two asbestos plugs, filling the tube for a distance of about 30 mm. (1.18 in.), but was sufficiently loose to allow the passage of gases through the material. The gases were passed through the tube at the rate of about 2 cc. per min. The data obtained probably did not represent the chemical equilibrium at any temperature. The comparative rate of reaction at different temperatures was obtained, however, as were data concerning the character of the gaseous products.

REDUCTION WITH HYDROGEN—When hydrogen was reduced as the reducing agent, there was practically no reaction at any temperature below 550° C. Around 600° C., the reaction was extremely slow, less than 5 per cent of the hydrogen passing through the plug, reacting. The gaseous product contained considerable hydrogen sulfide. At 650° C., about 15 per cent, and at 700° C., about 35 per cent of the hydrogen reacted. Between 600 and 700° C., the amount of hydrogen sulfide formed was a maximum. At 800° C., practically all the hydrogen had reacted and very little hydrogen sulfide was present in the gaseous product. In general, these data checked those of a previous investigation.[1] In the products from these reductions with hydrogen, the ratio of sulfur to barium was less than one atom of sulfur to one atom of barium.

If the reductions were effected slowly at lower temperatures (between 600° and 750° C.), the loss of sulfur was greater than if the reductions were effected more rapidly at higher temperatures (900 to 1000° C.). In one test lasting for an hour at 1000° C., 94.0 per cent of the sulfate was reduced to sulfide and 6.0 per cent to oxide. This was the maximum reduction obtained using hydrogen.

In some correlated tests, it was found that, between 700 and 900° C., water vapor reacts slowly with barium sulfide, forming sulfur dioxide, hydrogen sulfide and barium oxide. For example, through a reduced product of about 20 mesh size, containing 89 per cent of the barium as sulfide, 7 per cent as oxide and carbonate, and 4 per cent as sulfate, was passed, at 900° C., a mixture of about 16 per cent water vapor and 84 per cent nitrogen; about 1 per cent of the water vapor reacted, forming nearly two volumes of sulfur dioxide per volume of hydrogen sulfide. The reaction between water vapor and barium sulfide at other temperatures was not determined.

REDUCTION WITH CARBON MONOXIDE—With carbon monoxide the reduction was very slow below 650° C., and was fairly rapid at 750° C., about 70 per cent of the carbon monoxide reacting. With temperatures up to 900° C., however, there was present in the gaseous product some unconsumed carbon monoxide. Above that temperature the gaseous product was almost entirely carbon monoxide. In these reduced products the ratio of sulfur to barium was slightly less than 1 : 1, showing that some sulfur had been removed in the gaseous products. In this series as in tests with hydrogen as the reducing gas, the loss of sulfur was less in the cases where reduction was effected rapidly at higher temperatures (above 900° C.), than when effected slowly at lower temperatures. Thus, the products of reduction effected rapidly at

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[1] "Reduction of Sulfate of Alkaline Earths with Various Gases," L. Marino, R. University of Pisa, *Gazz. chim. ital.*, **43** [1], 416–22. *Chem. Abs.*, **7** (1913), 3202.

high temperatures contained the smaller percentages of water-insoluble barium oxide.

REDUCTIONS WITH CITY GAS—A series of 20 reductions was made, in which an excess of city gas of approximately the following composition was passed at the rate of 2 cc. per min. through the charge in the quartz tube:

C_2H_4	CH_4	H_2	CO	CO_2	N_2	O_2	TOTAL
6.4	30.4	41.4	13.4	4.0	4.2	0.2	100.0 per cent

The data obtained are given in Table I. The percentage of barium in the product present in water-insoluble, but acid-soluble, compounds was less when reductions were effected in a short period of time at temperatures above 900° C., than if effected over a longer period of time at lower temperatures; *e. g.*, compare the products obtained when the material was treated for 330 min. at 650 to 700° C., with those obtained in a reduction of 1000 to 1050° C., lasting only 60 min.

TABLE I—REDUCTION OF PRECIPITATED BARIUM SULFATE BY CITY GAS IN QUARTZ TUBE, EXTERNALLY HEATED

		PER CENT OF TOTAL Ba IN PRODUCT PRESENT AS		
Temperature ° C.	Time Min.	Water-soluble BaS and BaO	Water-insoluble but Acid-soluble BaO and $BaCO_3$	Acid-insoluble $BaSO_4$
650–700	60	2.5	4.0	93.5
	240	58.0	15.8	26.2
	330	72.5	18.2	9.3
700–750	60	8.5	6.8	84.7
	240	75.0	13.8	11.2
750–800	60	20.6	8.4	71.0
	240	88.2	11.0	0.8
800–850	60	50.8	7.8	41.4
	240	91.5	8.3	0.2
850–900	60	55.5	6.8	37.7
	240	91.8	8.0	0.2
900–950	60	65.2	6.2	28.6
	120	85.0	7.3	7.7
	240	92.5	7.5	0.0
950–1000	60	74.7	4.8	20.5
	120	91.5	6.5	2.0
	240	93.2	6.8	0.0
1000–1050	60	85.2	5.0	9.8
	120	92.0	6.5	1.5
	240	93.0	7.0	0.0

Any tendency for a reaction between the reducing gases and the reduced sulfide, resulting in the formation of water-insoluble barium compounds, is slight; *e. g.*, compare the proportion of these compounds in the products of reductions at 900 to 1050° C. for 60, 120 and 240 min.

SERIES 2—REDUCTION OF BARIUM SULFATE BY CARBON

In these tests, finely pulverized carbon, either coke or charcoal, was intimately mixed with the barium sulfate, and heated for varying periods of time at different temperatures, in crucibles or tubes placed in muffle furnaces. The theoretical amount of carbon required for the reduction is 10.3 per cent of the weight of $BaSO_4$, if the carbon is completely oxidized to CO_2, or 20.6 per cent if the carbon is oxidized only to CO. In these tests, the carbon added varied between 10 and 40 per cent of the $BaSO_4$. The temperature range was between 700 and 1250° C. The time allowed for reduction varied between 15 and 360 min.

In all but a few of the tests where the time allowed for reduction was an hour or more, the mixtures, weighing from 50 to 100 g., were placed in 10- or 20-g. fire clay crucibles and heated in a muffle furnace. The muffle had been heated to the required temperature before placing the crucibles in it, and thus the crucibles and charge were heated up quickly. When the time allowed for reduction was less than 1 hr., it was rather difficult to get satisfactorily concordant data with this size of charge and method of heating. In order to reduce the "heating up" period to a minimum, these reductions were made with much smaller charges (5 to 10 g.), in porcelain crucibles.

In Table II most of the temperatures recorded were measured near the crucibles during the period of reduction. Several, however, were measured in the charge itself, after it had come to the temperature of the muffle, but care was taken to have the heating of the muffle so regulated that the temperatures did not vary more than 15 or 20° C. either way from that desired; thus, a temperature of 700° C. means between 680 and 720° C., sufficiently close for the purposes of these investigations.

As, in these reductions, it was very important to keep the air from coming into contact with the material as far as possible, the crucibles were covered with a clay cover ground to fit. In some tests a charcoal cover about 2 mm. (0.04 in.) thick, was placed on the charge. Even with the tight covering, in some of the tests, there was a slight reversion of the sulfide to the sulfate, due possibly to a slight porosity of the crucible walls allowing air to pass through. Some of the data concerning this reversion will be given later.

In Table II are summarized the results of 76 tests made under conditions which were quite similar, so that the results are comparable. The barium sulfate used was the precipitated material. The carbon added was 20.6 per cent of the weight of the barium sulfate; it was pulverized to pass a 160-mesh screen and mixed with sulfate until the mixture looked homogeneous to the naked eye. The variables were the time allowed for reduction and the temperatures. Many of the figures given are the average of several determinations that in most cases gave concordant results.

TABLE II—REDUCTION OF BARIUM SULFATE BY CARBON

	PER CENT TOTAL BARIUM IN PRODUCT IN FORM OF:													
	Water-soluble Barium Sulfide							Soluble in Dilute HCl						
Min.	15	30	60	90	120	240	360	15	30	60	90	120	240	360
700° C.	..	12	26	28	41	65	77	..	21	37	40	54	80	93
750	..	29	35	55	59	78	..	..	38	47	69	73	93	..
800	..	51	61	63	68	82	..	..	57	70	75	85	98	..
850	..	58	69	78	85	86	..	..	65	78	87	94	98	..
900	48	65	85	87	88	..	..	54	72	94	97	99	..	..
950	..	76	89	92	95	..	..	..	80	94	97	100	..	..
1000 to 1100	75	84	96	..	..	..	..	80	89	100	..	..	..	..
1100 to 1200	96	97	..	..	..	..	..	98	100	..	..	..	..	..

In the products of reduction effected at the lower temperatures over a longer period of time, the difference between the acid-soluble barium compounds and the water-soluble barium sulfide is less in the reductions at higher temperatures for a short period of time, than in those at lower temperatures over longer periods. Most of the products contained excess carbon. Other series of tests were made to determine to what extent a decrease in the amount of carbon present in the charge affected the reduction.

When the tests were made in porcelain crucibles fitted with an ordinary porcelain cover, there was always sufficient air leaking into the crucible either to burn a small percentage of the carbon, or to reoxidize a small amount of the reduced sulfide back to the sulfate. As the data from these tests are, therefore, not quite accurate, they are not included in this paper.

Similar reductions were repeated in porcelain crucibles, when a light layer of carbon was placed on top of the charge and other precautions taken to keep the air from coming into contact with the charge during cooling, etc. Although the carbon cover did have some slight reducing action on the charge, it was decided that the data obtained were sufficiently accurate for recording in this paper, and they are given in Table III.

TABLE III—REDUCTION OF BARIUM SULFATE AT DIFFERENT TEMPERATURES IN PORCELAIN CRUCIBLES WITH VARIABLE AMOUNTS OF CARBON IN THE MIXTURES

Temp. ° C.	Time Min.	Per Cent Carbon to $BaSO_4$	Per Cent of Total Barium in Product			Carbon Consumed	
			BaS	Acid-sol.	Insol.	Per cent of Total Carbon Consumed	Per cent of $BaSO_4$ Reduced to BaS
800	60	10.5	50	58	42	69	14.5
		21.0	51	56	44	49	20.2
800	120	10.5	62	70	30	83	14.2
		21.0	66	65	32	65	20.5
850	60	10.5	66	70	30	86	13.2
		15.5	60	65	35	65	16.8
		20.5	60	70	30	58	19.8
850	120	10.3	78	85	15	97	12.9
		15.5	76	82	18	84	17.0
		20.6	74	80	20	70	19.4
900	60	10.3	80	85	15	100	12.9
		15.3	81	83	17	87	16.7
		20.6	76	80	20	72	19.4
900	120	10.3	80	86	14	100	12.9
		15.5	84	90	10	89	16.5
		20.6	83	87	13	80	19.8
950	30	10.3	80	83	17	100	12.5
		20.6	84	87	13	78	19.0
950	60	40.0	78	79	21	59	
		10.3	94	97	3	100	12.8
		20.6	95	96	4	93	20.2
		30.0	82	82	18	61	23.4
1050	30	10.3	82	86	14	100	11.2(*a*)
		15.5	96	96	2	100	16.1
		20.6	95	96	4	89	18.7
1150	20	10.3	90	90	10	100	11.5
		15.5	99	99	1	100	15.6
		20.6	99	100	0	90	18.2

(*a*) This carbon consumption factor is probably slightly low due to a slight reduction action of the carbon cover.

Later reduction tests, effected in an atmosphere of nitrogen, *i. e.*, in an atmosphere neither oxidizing or reducing, gave results that checked the abovementioned data fairly closely.

In another set of reduction tests the barium sulfate was mixed intimately with finely pulverized carbon and placed in a porcelain tube, in an electrically heated tube furnace. The tube was filled with nitrogen gas at the start, and the gases evolved were discharged through a water seal, or into caustic potash solutions. Thus, neither oxygen nor any reducing gases other than the carbon monoxide from the carbon came in contact with the $BaSO_4$. From the data in Table IV it is to be noted that the carbon efficiency was greatest when the charge contained the smallest percentage of carbon, and the efficiency decreased with an increase in the amount of carbon present. In general, somewhat higher carbon efficiency was obtained in the reductions effected at the higher temperatures than at the lower. Although the highest carbon efficiency (about 12.0 to 12.5 per cent) was obtained when the carbon present was about 10 per cent of the barium sulfate (the theoretical amount if the carbon oxidized completely to CO_2), yet with this amount of carbon the maximum reduction of the barium sulfate at temperatures up to 1000° C. was only about 80 to 85 per cent. Between 900 and 1000° C., nearly complete reduction was obtained with a carbon consumption of about 14 to 15 per cent. When the carbon was present to the extent of 20 per cent of the $BaSO_4$, the carbon efficiency was much lower, irrespective of whether the reduction was at high or low temperatures, but was slightly higher at the high temperatures than at the low.

With an excess of carbon, the reduction seemed to proceed slightly slower than with the lesser amount of carbon present. This is shown especially in the series at 850, 900 and 950° C. in Table III. However, it must be recognized that the degree of fineness to which the material is pulverized, the intimacy with which the sulfate and carbon are mixed, and the depth of material through which the carbon monoxide gas must pass before leaving the charge, are factors influencing these figures; *e. g.*, in several tests, straight barium sulfate was placed on top of the charge containing 20 per cent carbon. This barium sulfate cover was quite largely reduced by the carbon monoxide coming up from the charge proper, thus increasing the efficiency of the carbon when credited with the whole amount of barium reduced.

Summarized briefly, the data from Series 2 show that when the carbon and barium sulfate are finely pulverized and intimately mixed, and the reduction is effected in a muffle or crucible type of furnace in absence of outside air or products of combustion of fuel, and at temperatures between 850 and 1000° C., a high reduction (90 per cent or better) can be obtained when the carbon added is about 15 per cent of the barium sulfate. While the efficiency is greater with the addition of less carbon, the reduction is not so complete. With more than 15 per cent carbon, the carbon efficiency decreases, unless provision is made to utilize the carbon monoxide issuing from the charge, by passing it through another charge of barium sulfate.

TABLE IV—REDUCTION OF BARIUM SULFATE BY CARBON IN TUBE FURNACE, SURROUNDED BY ATMOSPHERE OF NITROGEN

Temp. °C	Per Cent Carbon to $BaSO_4$ in Charge	Per Cent of Total Carbon Consumed	Per Cent of $BaSO_4$ Reduced to BaS	Carbon Consumed Per Cent $BaSO_4$ Reduced
800	10	80	58	13.8
	10	100	70	14.3
	20	63	84	19.8
900	10	95	70	13.5
	10	100	74	13.5
950	10	97	75	12.9
	10	100	75	13.3
	15	90	82	16.4
	14	100	96	14.7
	15	100	90	16.7
1000	10	100	80	12.5
	15	100	90	15.6
	20	84	95	17.6

Different kinds of barium sulfate gave different results in reductions carried on under the same conditions, *e. g.*, the materials indicated in Table V, all finer than 200 mesh, were reduced at the same time under the same conditions (temperature 900° C., time 120 min.), with the results given in Table V.

TABLE V—PER CENT OF TOTAL BARIUM IN PRODUCT FROM DIFFERENT COMPOUNDS

MATERIAL	Per Cent $BaSO_4$	Water-soluble	Water-insol. Acid-sol.	Acid-insol.
Pptd. $BaSO_4$........	99.6	88	10	2
Pulverized Barytes	98.0(*a*)	78	13	9
....	92.5(*b*)	72	18	10
Pptd. $BaSO_3$ + $BaSO_4$	....	93	7	0

(*a*) The impurities were 1.4 per cent $BaCO_3$ and 0.6 per cent Fe_2O_3 + SiO_2.

(*b*) About 3 per cent Fe and 3 per cent SiO_2 were present.

Some comparative tests were made to determine the effects of iron on the reduction of barium sulfate. Four charges were made up in which iron to the extent of about 6 per cent was mixed with the precipitated barium sulfate. The iron was added to different charges as ferric sulfate, ferrous ammonium sulfate, ferrous sulfate, and ferric oxide. Two charges of the pure precipitated barium sulfate were reduced under the same conditions (temp. 850° C., time 120 min.).

PER CENT OF TOTAL BARIUM PRESENT IN COMPOUNDS (AVERAGE OF 4 TESTS)

MATERIAL	Water-soluble	Water-insoluble Acid-soluble	Acid-insoluble
Pure $BaSO_4$............	80	10	10
$BaSO_4$ with 6 per cent Fe	68	17	15

REOXIDATION OF BARIUM SULFIDE TO SULFATE

It has been stated that barium sulfide, when at red heat, is readily reoxidized to the sulfate. The data from several of the crucible reduction tests were found to be of no value since adequate precautions had not been taken to prevent the oxygen from getting into the crucible. An example of the effect of small air leakages into the crucible is given below. These results were obtained when reducing pulverized barytes (98 per cent $BaSO_4$) with 20 per cent willow charcoal at 1000° C.

PER CENT BARIUM IN PRODUCT PRESENT IN COMPOUNDS

TIME. Min.	Water-soluble (BaS)	Water-insoluble Acid sol. Comp.	Insoluble ($BaSO_4$)	FIT OF COVER
60	94	6	..	Tight
	76	3	21	Loose
120	56	4	40	Tight
	35	3	62	Loose

That the reoxidation product is the sulfate and not the oxide, is shown in the above and also in some special tests made to determine the product of oxidation of barium sulfide. In these tests, material containing 95 per cent of the barium as BaS was heated in the air for varying periods of time at different temperatures. In most cases practically all the sulfide was reconverted to the sulfate, and only small amounts of oxide were formed. The maximum conversion to oxide was about 7 per cent and was obtained when the material was heated to 800° C. for 2 hrs.

SERIES 3—BARIUM SULFATE, MIXED WITH CARBON, MADE INTO BRIQUETTES AND REDUCED IN A SHAFT FURNACE HEATED BY OIL

Precipitated barium sulfate was mixed with lampblack carbon from the local oil gas works, and the mixture pressed into the form of cupels, 1 in. (2.5 cm.) in diameter, and 1$^1/_4$ in. (3.2 cm.) high. These cupels were dried and then charged into a small shaft furnace, 12 in. (30.5 cm.) in diameter and 30 in. (76.2 cm.) high, which was heated to about 950–1100° C. by an oil flame, the products of combustion or excess gases passing through the shaft and maintaining strongly reducing conditions in the shaft. The furnace was kept filled with briquettes during a test, more briquettes being added at the top as the reduced product was withdrawn below. The time the briquettes were in the furnace varied between 1$^1/_2$ hrs. and 3 hrs. During an average run of 6 hrs., about 80 kg. of these briquettes were reduced. The best average product obtained from any of the days' runs contained 82.5 per cent of the barium as sulfide, 13.8 per cent as oxide and carbonate, and 3.7 per cent as insoluble sulfate. The best product from any charge during this run contained 87 per cent of the barium as sulfide: during this run the maximum furnace temperature was 1150° C.; the average carbon monoxide content of the gases in the shaft of the furnace was 4 per cent.

In this shaft furnace, several runs were also made with briquettes of pulverized commercial barytes (92.5 per cent $BaSO_4$), and lampblack carbon. These briquettes were 2$^1/_2$ in. (6.36 cm.) long, 2$^1/_2$ in. (6.35 cm.) in diameter and weighed about 0.81 lb. (370 g.), each. With these briquettes, very unsatisfactory reductions were obtained, even though the temperature of the furnace was raised to 1100° C., and broken pieces of coke were charged with the briquettes. The best products contained only about 70 per cent of the barium as sulfide. Also, unless these large briquettes were broken up and chilled immediately on being removed from the furnace, they retained their heat for a long time, and the barium sulfide to a great extent oxidized back to the sulfate.

One charge of reduced briquettes weighing about 25 kg., and containing at the time of withdrawal from the furnace about 70 per cent of the barium as sulfide, was allowed to stand unbroken in an iron container for about 15 hrs. At the end of this time, the briquettes in the center of the container were still glowing. The outside cooled briquettes contained less than 15 per cent of the barium as sulfide, the rest having oxidized back to sulfate.

SERIES 4—REDUCTION OF BARIUM SULFATE IN THE MULTIPLE HEARTH ROASTING FURNACE

DESCRIPTION OF FURNACE—The multiple hearth furnace used for these reduction tests was one designed by Mr. Utley Wedge and loaned to us for these investigations (see Figs. I and II). The furnace was 24 in. inside diameter and 34 in. high, *i. e.*, between bottom of the cast-iron drying hearth to top of bottom hearth. Beneath the bottom hearth was a calcine pit, 12 in. deep. Above the drying hearth were placed the driving gears, roller bearings, etc. The total height over all was 6 ft. The walls of the furnace were of specially moulded fire brick, 8 in. thick, containing openings for gas burners, pyrometer tubes, gas sample tubes and mica windows, or peepholes. Outside the brick walls of the furnace was placed a covering of magnesia board 1$^1/_2$ in. thick; this magnesia was covered with a layer of asbestos cement $^1/_8$ in. thick, with a thin layer of Portland cement on the outside.

To a revolving center column inside the furnace were attached three cast-iron hearths 22 in. in diameter. Thus, there was an annular space 1 in. wide between these hearths and the furnace walls. Between these movable hearths and below the lowest one were placed three stationary hearths resting on shelves provided on the brick walls. The opening at the center of these hearths was 6 in. in diameter, leaving an annular space 1 in. wide between the stationary hearths and the center columns. The total effective hearth area was 16.5 sq. ft.

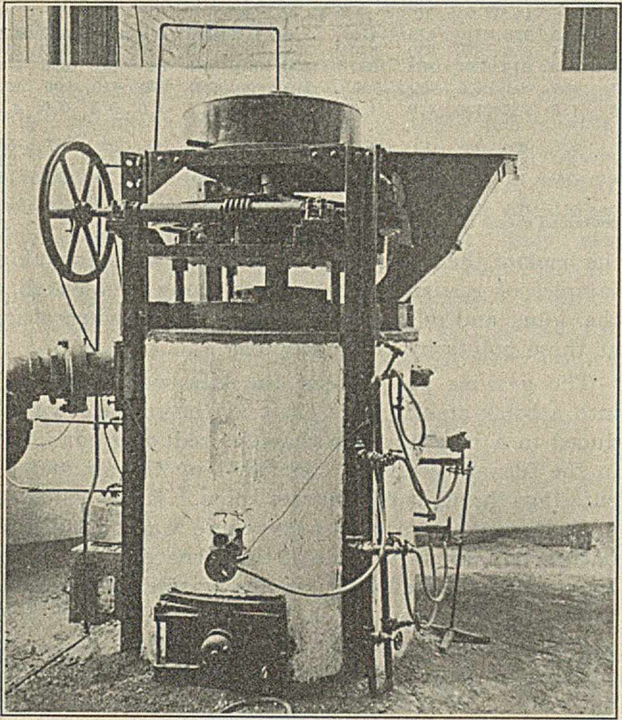

FIG. I—MULTIPLE HEARTH ROASTING FURNACE
Loaned by Mr. Utley Wedge

Rabbles were attached to ribs cast on the under side of the hearths, these rabbles stirring and moving the ore across the hearths immediately below. The ore on the cast-iron drying floor was moved by rabbles revolving with the center column. From the drying floor the ore fell to the center of the top movable hearth, and was moved by the rabbles suspended from the stationary drying hearth, to the outside of this revolving hearth, falling on to the second hearth, a stationary hearth. It was then moved by rabbles attached to the first movable hearth, to the center of the stationary hearth, and fell on the third hearth, a moving hearth. The ore was thus moved through the furnace in a manner similar to that in a regular, large size, multiple, roasting furnace.

The cast-iron hearths lasted for many tests when the temperatures were not over 800° C., but when temperatures above 900° C. were maintained they warped and cracked and had to be replaced after eight or nine 12-hr. runs.

Bristol pyrometers were inserted through the walls of the furnace for measuring the temperature on the first, third and fifth hearths. Gas samples were also drawn from the furnace at these hearth levels. Peepholes were provided at several points for observing the charge in the furnace. Movable brick plugs were provided in the walls of the furnace, which gave access to the interior for cleaning off the hearths. At times these movable plugs were found to be convenient, as some charges had a tendency to ball up in front of the rabbles.

The furnace was heated by oil fuel or by city gas. In most of the tests, the latter fuel was used. The gas was burned through Méker burners, using 20 lbs. air pressure at the burners.

It is not considered that the fuel consumption in this furnace furnished data for calculating the fuel which would be required in a standard furnace of this type, if properly designed to prevent radiation losses, etc. The center revolving column was water-cooled. The cooling water removed from $^{1}/_{5}$ to $^{1}/_{3}$ of the total heat supplied to the furnace by the combustion of the gas. In most of the reduction tests, the furnace was operated only under a very slight draft, just enough to allow the products of combustion, etc., to be removed from the furnace.

SUMMARY OF REDUCTION TESTS IN MULTIPLE HEARTH FURNACE

In Table VI are summarized briefly 20 tests made in this furnace; the variables were:

(1) *Length of time the material was in the furnace*—This was controlled by the rate at which the charge was fed and by the speed of revolution of the center column. Rate of feeding was varied between $2^{1}/_{2}$ and 9 kg. per hr. Length of time the material was in the furnace varied between 2 and $3^{1}/_{2}$ hrs.

(2) *Furnace temperatures*

TEMPERATURE	1st Hearth	3rd Hearth	5th Hearth
Minimum	180° C.	560° C.	840° C.
Maximum	485	905	920
Average	360	800	850

(3) *Reducing conditions*—In all cases there was excess city gas used above that required for the combustion, to maintain the proper temperatures. In the 20 tests here summarized, no free oxygen was allowed in the furnace. The carbon monoxide content of the gases taken from the furnace on the third and fifth hearth ranged between 0.5 and 5 per cent. The fuel gas consumption was between 3 and 6 cu. ft.

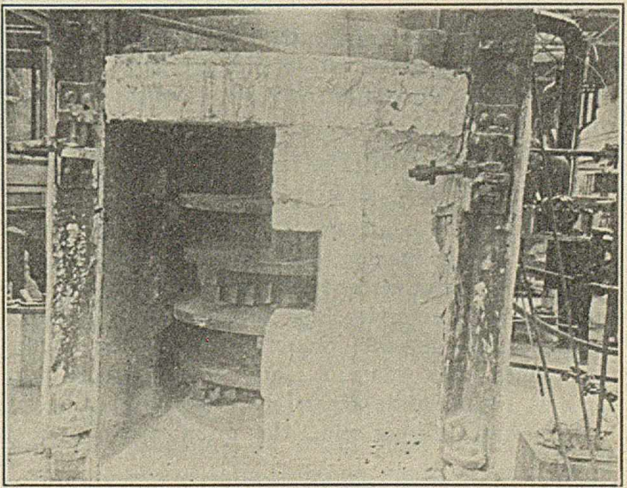

FIG. II—MULTIPLE HEARTH ROASTING FURNACE, SHOWING HEARTHS AND RABBLES

Table VI—Reduction of Barium Sulfate (or Barytes) in Multiple Hearth Furnace by Excess H_2, CO, or Hydrocarbons Entering Furnace through Burners

Barium Compound Used	Precipitated Barium Sulfate (99+ % $BaSO_4$) Intimately Mixed with Carbon Used								Pptd. Barium Sulfate (99+ % $BaSO_4$)					Pulverized Commercial Barytes As used in Paints by W. P. Fuller Co.						
Character of Carbon Used:	Lampblack			Pulverized Coke					No Carbon Used					Pulv. Coke		L.-B.	P. C.	No Carbon		
Test No.:	1	2	3	4	5	6	7	8	B-3	B-4	B-5	B-6	B-7	C-1	C-2	C-3	C-4	D-1	D-2	D-3
Per cent Carbon to $BaSO_4$ in Charge	20	16	20	25	25	17	18	15	0	0	0	0	0	20	20	20	20	0	0	0
Rate Charge to Furnace, Kg. per hr.	8.9	5.0	3.5	3.5	3.5	2.8	3.0	3.5	$3^1/_3$	$3^1/_3$	$3^1/_3$	3	3	3.5	3.5	3.5	3.0	3	3	3
Rate Gas Consumption, Cu. ft. per min.	5.2	5.0	5.0	3.7	4.6	3.5	3.5	4.5	4.8	5.1	4.8	5.0	4.5–5.0	3.8	4.5	5.0	4.2	5	5	5.5
Time of Material in Furnace, Hrs. (approx.)	2	2.30	2.45	3	3	3.30	3.15	3	3	3	3	2.30	2.30	2.45	2.45	3	3	...	...	...
Duration of Test, Total hrs.	8	9	12	9	9	10	10	12	14	14.30	9	12	12	12.30	8	6	7	10	11	10
Average Temperature (° C.): Top hearth	180	270	300	270	420	370	370	460	470	300	510	475	470	370	410	380	410	480	410	420
3rd hearth	560	590	640	570	760	810	790	890	895	830	880	830	890	760	790	760	780	850	820	810
5th hearth	810	860	880	890	895	880	885	890	900	890	890	885	895	870	895	890	865	890	880	900
Maximum Temperature of 5th hearth	840	880	890	895	905	905	910	900	905	905	900	900	900	910	900	900	890	910	900	905
Average % CO in Furnace Gases (3rd hearth)	4.5	5.0	4.7	1.6	2.0	0.5	0.5	2.0	1.8	3.5	1.0	4.0	4.0	0.5	1.0	2.5	1.0	0.8	2.0	4.2
Analyses of Product of Test:						(a)	(b)													
Per cent of Total Ba, Water-soluble	18	71	75	55	77	80	76	77	69	69	60	72	68	51	65	68	68	53	67	68
Acid-soluble	35	88	93	78	92	98	94	90	84	87	73	83	81	59	75	89	80	64	75	82
Insoluble ($BaSO_4$)	65	12	7	22	8	2	6	10	76	13	27	17	19	41	25	20	20	36	25	18
Max. % Ba, Water-soluble in Hourly Samples	43	73	79	67	78	82	80	...	...	...	...	...	...	60	68	70	...	70	72	...

(a) Note maximum reduction. (b) Products from all tests except 7, and 7 contained excess carbon.

per min. The main efforts in these tests were to obtain the maximum reduction rather than the highest efficiency of the reducing agent, carbon or gases.

It is to be noted from Table VI that with precipitated barium sulfate, the highest reductions were obtained when the material was mixed with carbon, either as pulverized charcoal or lampblack, and when the higher temperatures were maintained in the furnace. Under these conditions the percentage of excess-reducing gases present in the furnace could be reduced to a very low figure. The pulverized commercial barytes was more difficult to reduce than was the precipitated barium sulfate.

When the maximum temperature in the furnace was above 850° C., the material was slightly sintered into balls about $^1/_8$ in. in diameter, like cement cinder. These slightly cindered balls formed in the first reductions were easily broken up, and the material was pulverized readily for subsequent use as a precipitant in the solutions.

It is to be regretted that reduction tests at higher temperatures, *i. e.*, above 900° C., could not have been made with this type of furnace. However, we were not equipped with refractory hearths to withstand higher temperatures over longer periods of time.

SERIES 5—REDUCTION OF BARIUM SULFATE IN CEMENT KILN

Through the courtesy of the Chemistry Department of the University of California, we were given the use of a small cement kiln in the chemistry building of that university, for further work at higher temperatures on the reduction of barium sulfate. The cement kiln was 12 ft. long, 19 in. outside diameter and 10 in. inside diameter. The number of revolutions was 1.15 per min., the pitch was 1 : 18 (see Fig. III).

In the tests at this furnace, city gas or oil fuel was used for heating. The lower end of the kiln was closed by a sheet-iron plate covered with asbestos. Through this plate a gas burner was inserted, the gas being blown in with air under low pressure. A small gate was provided in this sheet-iron plate to allow drawing out the reduced product intermittently.

The charge to the furnace was fed in by hand at the back of the furnace. Provision was made for taking samples of gas at several points along the length of the kiln, and also for measuring the temperatures at these points by thermocouples.

The gaseous products of the kiln were discharged into a brick stack. The draft at the furnace was reduced to a minimum, so that the reducing conditions in the furnace could be controlled by the air and gas entering through the burner pipe. Even with the draft reduced to a minimum, there was considerable barium sulfate carried out of the furnace by the gases. In one test, when oil was used and was being discharged through the burner by a high air pressure directly along the center line of the kiln, the loss of barium sulfate was very high, about 30 per cent. When this oil and air mixture was discharged at right angles with this center line striking against the sides of the kiln, the loss was greatly reduced.

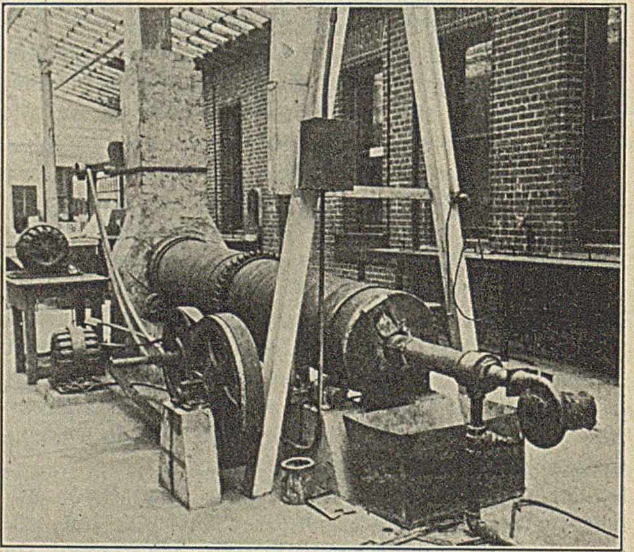

Fig. III—Cement Kiln
Chemistry Building, University of California

In these reduction tests, the temperature at the hottest part of the furnace was as high as 1100° C., and averaged 1050° C. For over half of the furnace the temperature was above 850° C. The average time the charge was in the furnace was $2^1/_2$ hrs.

The average rate of feeding the charge to the furnace was 15 kg. per hr., ranging between 10 and 20 kg. per hr. The best reductions were obtained when the furnace was kept well filled with the charge.

The material used was finely pulverized barytes (98+ per cent $BaSO_4$) (material used in paints by W. P. Fuller Co.), as large quantities of the precipitated barium sulfate could not be obtained. Six tests were made using city gas and one using oil for fuel. The main object in these tests was to obtain a high reduction of the barium to the water-soluble sulfide; high efficiency of the reducing agent was a secondary consideration. One test (5–7) below, however, was conducted for the purpose of obtaining a higher fuel efficiency than the others. This test showed that almost as high a reduction could be obtained with much less fuel consumption. None of these tests furnished conclusive data for calculating the fuel that would be required for effective reduction in a commercial sized kiln.

TABLE VII—REDUCTION OF COMMERCIAL PULVERIZED BARYTES IN CEMENT KILN

CHARACTER OF C USED	Pulverized Coke		Pulverized Charcoal		None	Pulv. Coke	Coke
TEST NO.	5–1	5–2	5–3	5–4	5–5	5–6	5–7
Per cent C to $BaSO_4$ in charge	20	15	20	16	0	18	13
Rate Charge: Kg. per hr.	10	10	15	15.2	12.5	16	18.7
Gas Consumption, Cu. ft. per min.	5.4	5.6	6.1	6.3	6.2	oil(a)	3.8
Duration of Test. Total hrs.	25	10	5	5	4	2	4
Av. Temp. (°C.): Exit Gases	450	460	420	400	510	...	370
Av. Temp. Middle of Kiln	850	880	880	860	900	...	840
Max. Temp. in Kiln (approx.)	1050	1050	1100	1050	1100+	1360	1050
Av. per cent CO in Furnace Gases (middle)	3.8	4.2	3.1	4.2	6.2	...	1.5
ANALYSES OF PRODUCT OF TEST:					(b)		
Per cent of Total Ba:							
Water-soluble	89	87	90	89	69	84	82
Acid-soluble	98	97	98	98	78	96	90
Insoluble ($BaSO_4$)	2	3	2	2	22	4	10

(a) Product of Test 5–5. Clinkered and unreduced $BaSO_4$ left in interior of the clinker.
(b) Rate of oil consumption, 3 gals. per hr.

SUMMARY

I—The data obtained in the five series of reduction tests outlined above indicate that the maximum reduction of barium sulfate to sulfide was obtained at the higher temperature, *i. e.*, around 1000° C., and when the reductions were effected in an indirect fired furnace, *e. g.*, in the muffle furnace, 15 or 16 per cent carbon gave the highest fuel efficiency consistent with completeness of reduction of the barium to the sulfide.

II—In reductions effected in a direct fired furnace (a cement kiln, multiple hearth roasting furnace, or a shaft furnace where hydrogen, hydrocarbons, or where the products of combustion of the fuel, water and carbon dioxide, were brought into contact with the sulfate or sulfide) there were formed a larger proportion of barium compounds insoluble in water, than were formed in a furnace indirectly fired. Thus, although the barium compounds in the best products from a direct fired furnace were 90 to 95 per cent soluble in acid, yet the barium present as the water-soluble sulfide was not more than 85 to 87 per cent of the total.

III—By effecting the reductions rapidly at high temperatures, *i. e.*, above 1000° C., the proportion of these water-insoluble barium oxides and carbonates was less than that formed in reductions at lower temperatures over a longer period of time.

IV—Below 750° C. the reduction by carbon or reducing gases was too slow to be considered commercial.

BUREAU OF MINES, WASHINGTON

THE THERMAL DECOMPOSITION OF THE ETHANE-PROPANE FRACTION FROM NATURAL GAS CONDENSATE

By J. E. ZANETTI AND E. H. LESLIE

Received August 3, 1916

In a previous paper[1] one of us presented the results obtained by the thermal decomposition of the propane-butane fraction from natural gas condensate. As a continuation of that work it seemed desirable to study the lower fraction, that containing chiefly ethane and propane, which fraction can likewise be found on the market and is used mainly for lighting and oxygen welding. This fraction comes in cylinders under 500 to 1000 lbs. pressure, and owing to the great difference in boiling points between ethane and butane, —93 and +1°, is little contaminated by butane. At 750 lbs. and the temperature of 25° the vapor pressure of butane as calculated from Burrell and Robertson's formula[2]

$$\log P = -1633/T + 1.75 \log T - 0.01094\,T + 7.590$$

is 1545 mm., a little above 2 atmospheres. Since the pressure in the cylinder used was 750 lbs. above atmospheric, at 25° the amount of butane present in the issuing gas would be about 4 per cent. If we consider that the vapor pressure of the butane must be considerably diminished by the fact that it is dissolved in the liquid ethane and propane, the amount of impurity in the gas from this source becomes small. The very high pressure in some of these cylinders would indicate that there is also some dissolved methane in the liquid ethane. The critical temperature for ethane is +34° and the critical pressure 50.2 atmospheres. As at 25° the pressures are often above the critical, the only other hydrocarbon present would be methane. This matter is dwelt on at present as it further bears out the observation made by one of us in connection with the propane-butane fraction that the *aromatic hydrocarbons obtained from these fractions are built up from aliphatic compounds of lower carbon content than benzene.* There is no possibility of aromatics having been obtained here by the splitting off of the benzene ring from phenyl paraffins as no such compound is known that would boil at the temperature of liquid ethane, under atmospheric pressure, or conversely under the pressure of liquid ethane at ordinary temperature. If such compound were present in this gas its vapor pressure would be so small in comparison with that of ethane and propane that it would constitute but a minimal fraction of the issuing gas and it could in no way account for the yield of tar obtained in these experiments—2.5 cc. of tar

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[1] THIS JOURNAL, **8** (1916), 674.

[2] *J. Am. Chem. Soc.*, **37**, 2190.

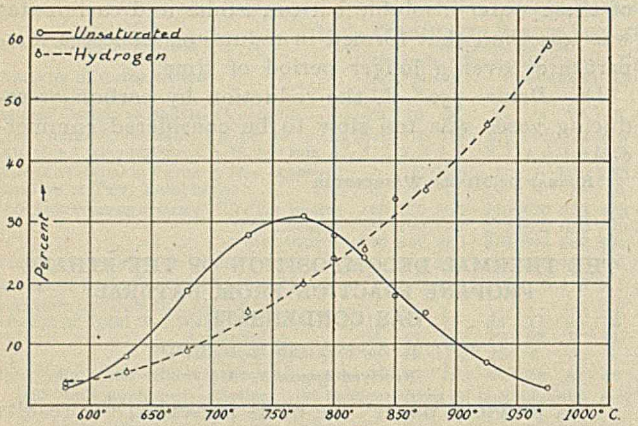

Fig. I—Decomposition of Ethane-Propane Mixture
No Catalyzer

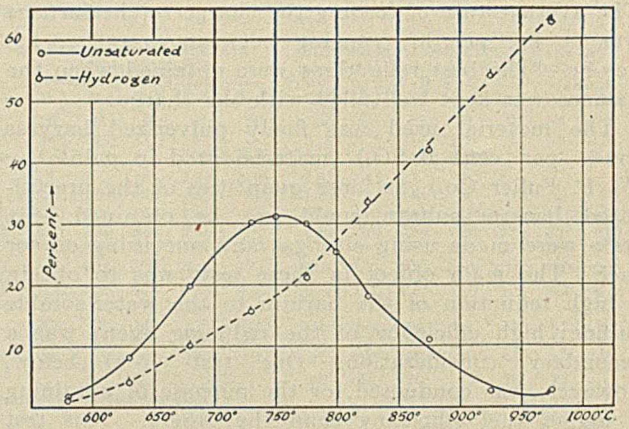

Fig. II—Decomposition of Ethane-Propane Mixture, Using Copper as Catalyzer

(*liquid*) per cu. ft. of *gas* used. The cylinder of gas used showed a pressure of 750 at 25° which pressure remained constant, within the limits of accuracy of the gauge used, during these experiments. Analysis of the gas showed it to be composed chiefly of ethane and propane. No CO_2 was present and only less than 0.5 per cent "unsaturated."

The apparatus and method of procedure were exactly as described in the case of the propane-butane fraction. The gas was passed at a measured rate through a heating chamber, the tar "fog" formed precipitated electrically and samples of the gas analyzed for "unsaturated" and hydrogen. The results of these analyses are plotted in Fig. I. As in the case of the butane-propane fraction, the percentage of "unsaturated" increases gradually to a maximum in the neighborhood of 750°, decreasing again above that temperature to a minimum at about 950°. The content of hydrogen increases slowly at first, a marked increase in its rate taking place above 750°. The beginning of the decrease in "unsaturated" formation and of the increase in hydrogen formation are coincident, as noted in the case of the propane-butane fraction with the appearance of the tar "fog."

The "unsaturated," as shown by fractionation of the bromides, consisted chiefly of ethylene and propylene with small amounts of butene. The presence of butenes, which occurred in a very small amount, is doubtless due to the decomposition of the butanes, which, as pointed out above, must occur in the gas in small amounts.

The tar formation occurred at about 750°. The yield was very much smaller than in the case of the butane-propane fraction, amounting to only 2.5 cc. per cu. ft. of gas used. This might be expected from the fact that the average molar weight of the gas is much smaller than in the other fraction. How much of this aromatic formation is contributed by the ethane and how much by the propane is a question which we cannot discuss at the present moment. That the ethane does contribute to some extent can not be doubted since Bone and Coward[1] have found it to be the case, though only to a slight extent. The very small percentage of the lower boiling aromatics and the unusually high one of naphthalene is worthy of notice. Only about 3 cc. out of 20 cc. of tar came over below 125° and about 1 cc. more below 200°. The rest was naphthalene and pitch. The naphthalene formed choked the condenser coil several times during a run and could be noticed in large flakes at the end of the quartz tube when cleaning out the apparatus between experiments.

The effect of copper as catalyzer was not marked in any way. The results when plotted (Fig. II) were, both for the "unsaturated" and for hydrogen, very similar to those obtained without a catalyzer. The aromatic formation proceeded in much the same way.

With iron as catalyzer (Fig. III) the same sharp drop in the unsaturated content at about 710° was noticed as with the propane-butane fraction, the hydrogen content increasing very rapidly as the "unsaturated" decrease. No aromatic formation was noticeable beyond the formation of a slight amount of "fog." Much carbon was deposited on the catalyzer necessitating its frequent renewal.

EXPERIMENTAL

MATERIAL—The material was a "liquid gas" from West Virginia in a steel cylinder under 750 lbs. pressure at 25°. The results of the explosion with oxygen are given in Table I. Analyses I and II were made at the beginning, III and IV at the end of the experiments presented. The gas had in addition 0.4 per cent "unsaturated" and about 0.5 per cent hydrogen. There was no CO_2.

Table I—Analysis of Gas

Analysis:	I	II	III	IV
Volume gas	12.3	12.3	11.7	12.2
Contraction	34.4	34.0	32.0	33.9
Volume CO_2	29.9	29.6	30.9	31.7

APPARATUS AND PROCEDURE—The apparatus and procedure were the same in all respects as used for the propane-butane fraction and their description is unnecessary. The rate of gas flow through the chamber was the same, 0.45 cu. ft. per hr.

GAS ANALYSIS—The gas analysis was conducted over water. For the determination of the "unsaturated," bromine was used. The hydrogen was determined by combustion over copper oxide. The results are given in Table II.

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[1] *J. Chem. Soc.*, **93**, 1197.

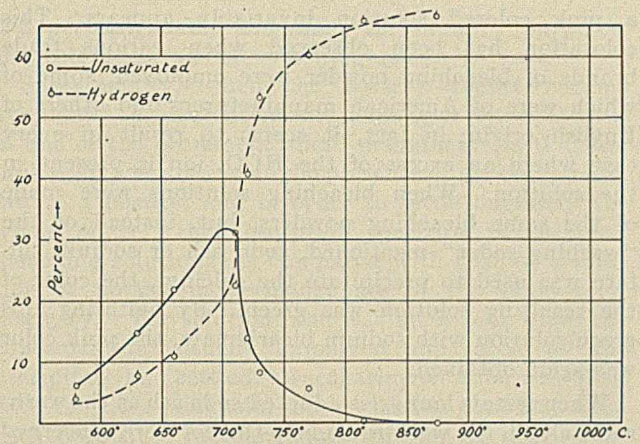

FIG. III—DECOMPOSITION OF ETHANE-PROPANE MIXTURE, USING IRON AS CATALYZER

THE "UNSATURATED"—The gases coming between 800 and 850° were passed into bromine till the latter became colorless. After drying, 25 cc. were distilled and the following fractions collected: 5 cc. below 127°; 9 cc., 127–132°; 5 cc., 132–142°; 5 cc. residue. On allowing the residue to stand a small amount of crystals separated out. Pressing from the mother liquor and crystallizing from alcohol they were obtained in the form of small, transparent, prismatic crystals melting at 116°.

AROMATICS—The tar obtained was quite fluid and after filtering showed a specific gravity of 1.075. Twenty cc. were distilled in a small flask. Three cc. came over below 125°, 1 cc. below 200°. Above that, naphthalene began to solidify in the condenser. The distillation was continued under reduced pressure, about 8 cc. coming over and solidifying to a yellowish mass of crystals. On crystallizing from alcohol they gave a melting point of 79°. The residue solidified in the flask, forming a black pitch with a strong odor resembling anthracene. Nitrobenzole was obtained from the fraction boiling below 125°, but no nitrotoluols could be obtained from it.

TABLE II—ANALYSIS OF GASEOUS PRODUCTS WITH AND WITHOUT CATALYZER

NO CATALYZER			COPPER AS CATALYZER			IRON AS CATALYZER		
Temp. ° C.	Unsaturated Per cent	H Per cent	Temp. ° C.	Unsaturated Per cent	H Per cent	Temp. ° C.	Unsaturated Per cent	H Per cent
580	2.8	3.4	580	1.7	1.3	580	6.1	3.6
630	7.8	5.8	630	8.1	4.0	630	14.9	7.9
680	18.9	8.8	680	19.9	10.1	660	22.0	10.9
730	28.0	15.3	730	30.2	15.6	710	31.2	22.5
775	31.0	19.6	750	31.5	....	720	14.2	40.9
800	27.9	24.0	775	30.0	21.2	730	8.3	53.4
825	24.2	26.1	800	25.4	....	770	5.7	60.3
850	18.0	34.0	825	18.2	33.5	815	0.3	65.8
875	15.2	35.3	875	11.0	42.0	875	0.0	66.6
925	7.2	46.4	925	2.6	54.0			
975	3.0	58.8	975	2.8	62.7			

SUMMARY

I—It has been shown that mixtures of ethane and propane decompose at high temperatures, giving ethylene, propylene and other "unsaturated," hydrogen and aromatics.

II—The percentage of "unsaturated" increases with increasing temperatures to a maximum in the neighborhood of 750°, then decreases with increasing temperatures. The aromatic formation begins at about 750° C. and is coincident with an increase in the rate of hydrogen formation.

III—The action of copper and iron as catalyzer has been studied. Iron prevents aromatic formation and favors the decomposition of the hydrocarbons into carbon and hydrogen.

Further work upon these topics is now in progress in this laboratory.

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY
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THE SOLUBILITY OF LEUCITE IN SULFUROUS ACID

By J. SCHROEDER

Received May 19, 1916

Leucite belongs to a class of potash-carrying silicates that has received considerable attention as a possible source of potash.[1] It is a metasilicate of aluminum and potassium having the formula $KAl(SiO_3)_2$ or $K_2O,Al_2O_3{\cdot}4SiO_2$. On this basis its theoretical composition is: Silica, 55.0 per cent; alumina, 23.5 per cent; and potash, 21.5 per cent. From this it is evident that in potash content it is one of the richest minerals known.

Leucite occurs in the more recent volcanic rocks as embedded crystals, grains, or aggregates of grains. It is identified especially with the lavas of Mt. Vesuvius and other localities in Italy, though its occurrence is by no means restricted to these localities. In North America it is found in Lower California, New Jersey, Arkansas, British Columbia, and especially in several places outlying from the Rocky Mountains, notably the Leucite Hills of Wyoming. These hills are situated in southwestern Wyoming from 10 to 15 miles north of Bitter Creek, which is an eastern tributary of Green River and is followed by the Union Pacific Railroad.

The Leucite Hills consist of a number of conical peaks of lava protruded through the beds of rocks forming the plateau of the surrounding neighborhood. Each peak consists of a lava sheet, presenting an abrupt wall from 50 to 150 ft. high. These deposits are described in detail by Schultz and Cross.[2]

The leucite rocks of this neighborhood are of a yellowish gray color and often, if not always, of a pronounced cellular structure. The porosity, however, does not reach the pumice stage. The leucite inclusions are microscopic crystals 0.035 mm. in diameter. The chemical composition of the rocks as indicated by the analyses of the United States Geological Survey is about as follows: Silica, 53 per cent; alumina, 11 per cent; ferric oxide, 3 per cent; magnesia, 6.5 per cent; lime, 4.5 per cent; soda, 1.5 per cent; and potash, 11 per cent.[2]

To ascertain the possibility of recovering this potash by leaching, solubility tests were made with sulfurous acid. A sample of leucite rock from Batuku, Celebes, East Indies, containing 9 per cent potash, was obtained through the courtesy of Dr. J. P. Iddings of the United States National Museum. This was ground and separated, by sifting, into portions of different fineness and these portions shaken over night with a solution of sulfurous acid. The latter was prepared by passing sulfur dioxide through water to approximate satura-

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[1] Cushman and Coggeshall, THIS JOURNAL, **4** (1912), 821.

[2] U. S. Geol. Survey, *Bull.* **512**.

tion at room temperature. The total quantity of material dissolved was found by filtering the solution through a Gooch filter and weighing the residue, and the potash was determined by the chlorplatinic acid method. The quantity of sample used was 0.5000 g. and the volume of the solvent 200 cc. The determinations showed the following results:

FINENESS OF SAMPLE	PER CENT OF POTASH DISSOLVED On basis of sample	On basis of K_2O present	TOTAL MATTER DISSOLVED
0.5 to 0.25 mm.	3.7	41.7	16.4
0.25 to 0.10	5.1	57.0	18.8
0.10 to 0	6.7	75.2	25.8
0.10 to 0	6.8	76.4	26.2
0.5 to 0(*a*)	4.7	52.2	26.7

(*a*) This sample consisted of a mixture of the first three grades of fineness in the ratio of 5, 36 and 58 per cents.

From these results it is evident that potash may be dissolved from leucite rocks by means of sulfurous acid. This shows a possibility of an important industrial application since it indicates that smelter fumes, containing sulfurous acid gas, may be used directly for recovering potash from leucite. Of course it is known that sulfuric acid may be used for that purpose, but there is a demand among operators of smelters for a method of using sulfurous acid gas that does not involve the expensive installation required to convert it into sulfuric acid. It happens also that the leucite of the Leucite Hills occurs in a region accessible in a general way to the smelters of Utah, Colorado and Montana. It may be possible to devise methods whereby smelter fumes can be passed over or through the leucite rocks, in the presence of water, and the potash thus gradually leached out, perhaps with the minimum of installation and manipulation. It is recalled that the Wyoming leucite rocks are porous, somewhat resembling pumice. This fact may operate to facilitate the percolation of the material and the leaching of the potash. It is observed, furthermore, that the dissolution in sulfurous acid is selective. Thus, while other materials are dissolved from the rock, the potash is dissolved in the greatest relative proportion.

It has been shown that the quantity of potassic rocks in the Leucite Hills region is very great, the potash therein contained being estimated by Schultz and Cross at 197,349,617 tons. That large quantities of sulfurous acid gas are available at the western smelters is of course well known.

BUREAU OF SOILS
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A NOTE ON THE CAUSE OF THE PINK COLOR OBSERVED IN CERTAIN HYPOCHLORITE BLEACHING SOLUTIONS

By H. G. ELLEDGE

Received May 17, 1916

When sodium hypochlorite bleaching solutions are prepared for use in laundering, by treating a solution of calcium hypochlorite, or bleaching powder, with a solution of the so-called neutral washing powder,[1] after the calcium carbonate has settled out, a pink colored solution invariably appears. This coloration has been observed when various trade brands of bleaching powder were employed, some of which were of American manufacturers and others of English origin; in fact, it seems to result in every case where an excess of the HCO_3 ion is present in the solution. When bleaching solutions were made of the same bleaching powders, but, instead of the "washing sodas" mentioned, soda ash or sodium sulfate was used to precipitate the calcium, the color of the resulting solution was green. By agitating this green solution with sodium bicarbonate, the pink color was again obtained.

When certain laundries adopted soda ash as the wash-room alkali, the wash-room help thereof were concerned about the absence of the pink color which, through habit and also because of the influence of the sales agents of certain alkali companies, they had come to regard as an index to the bleaching qualities of the solution. Owing to this condition, the writer was requested by the Allegheny County Laundrymen's Exchange to explain the origin of the coloration and to ascertain definitely whether there was any difference in the bleaching properties of the green and pink solutions. As was to be expected, it was found that equal volumes of the solutions, when made up with identical weights of the same bleaching powder, gave the same values for available chlorine. Among others, bleaching tests on hemp strings indicated that one solution was as satisfactory as the other for laundry bleaching.

The writer was led to conclude that the color of the pink solution was attributable to the presence of traces of sodium permanganate, the manganese being derived from the bleaching powders used. This conclusion was reached after certain experimental work, of which the following is illustrative: There were made up two solutions of sodium hypochlorite of the same strength.[1] To one of them a small amount of manganous sulfate was added; this produced no change in color. Then to each of the solutions, 10 g. of sodium bicarbonate were added; after thoroughly shaking and settling, the solutions both assumed a pink color, but the one to which the manganous sulfate had been added possessed a much more intense color. By color comparisons, it was estimated that 0.02 per cent to 0.04 per cent of manganese in the bleaching powders would be sufficient to produce this color.

It was early suggested that the pink coloration might be caused by the presence of small amounts of sodium ferrate. Therefore, solutions were prepared as above, and to one of them, ferric chloride was added; then, to both solutions sodium bicarbonate was added, as above. After the precipitates had settled, no difference could be observed in the intensities of the pink color of the different solutions. These and other experiments led to the conclusion that the color was due to traces of manganese, which, by the catalytic action of the bicarbonate on the hypochlorite, was oxidized to

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[1] These sodas are usually of about the following composition: normal sodium carbonate, 46.3 to 36.1 per cent; sodium bicarbonate, 37.7 to 50.0 per cent; and water, 16.0 to 13 per cent. See Faragher, THIS JOURNAL, **6** (1914), 641. The observations of Faragher have been confirmed and extended by the writer.

[1] The solutions were prepared by making a paste of 10 g. of bleaching powder and water, adding thereto 10 g. of soda ash, and, after thoroughly shaking in a flask, making the volume up to 250 cc. This is the strength usually adopted in the laundry for stock solutions.

the permanganate, and that, for laundry purposes, this coloration was of no consequence.

Subsequently, when the writer's report became available,[1] the contention was made by a representative of one of the prominent alkali manufacturers that the pink color was due not to the presence of permanganate, but of a ferrate; and in order to settle definitely the whole matter, the absorption spectrum of the pink bleaching solution was compared with that of a solution of potassium permanganate of the same color intensity. The solution used was made four times the concentration[2] usually employed and, after all the precipitate had settled, a saccharimeter tube was filled with the clear pink solution. A similar tube was filled with potassium permanganate solution of same color intensity and the absorption spectra were compared; they were found to be identical. To compare the two more carefully, the two absorption spectra were brought in view at one time, by means of the comparison mirror, and the positions of the lines were shown to be exactly the same.

No attempt is made here to account for the presence of the trace of manganese in the bleaching powder, but the writer feels that he has offered positive evidence that the color of the pink bleaching solutions is due to the presence of sodium permanganate, and not of sodium ferrate, as some have maintained.

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ON THE USE OF CERTAIN YEAST NUTRIMENTS IN BREAD-MAKING[3]

By Henry A. Kohman, Charles Hoffman, Truman M. Godfrey, Lauren H. Ashe, and Alfred E. Blake

Received June 7, 1916

The work in bread-making at the Mellon Institute was begun in 1911 through the establishment of the Ward Fellowships and the results will now be published in a series of contributions.

One of the important problems studied in our bread investigations was the effect of certain mineral salts (such as are commonly found in natural waters) upon the fermentative activity of the yeast in bread-making. It was found necessary by the Ward Baking Company (who operate bakeries in several cities) to change the quantity of yeast as well as the fermentation period of their dough batches in the different cities, in order to produce a standard product, or nearly so, even though all the raw materials used were identical (being purchased through a central office). Upon investigation it was found that variations in the activity of the yeast were due to the differences in the mineral content of the waters used for making the bread in these cities. In the work reported in this paper the effect of mineral salts found in natural waters upon the fermentative power of the yeast, as well as the quantity of yeast necessary for leavening purposes, has been given particular attention and close investigation. The mineral substances contained in flour, milk, yeast and other raw materials for bread were investigated in detail also, using a large variety of combinations and proportions.

Of the large number of substances investigated, those that have a really significant effect upon the fermentation in bread are surprisingly few. The salts of the mineral acids, such as the chlorides, nitrites, nitrates and sulfates, exert practically no influence except when combined with a cation which in itself has an effect. The carbonates are especially common in natural waters and as a class are objectionable in bread, since they neutralize the acids of the dough and thus interfere with the progress of the fermentation. More particularly, the carbonates of magnesium and the alkali metals should be considered as being detrimental to the fermentation of the yeast.

The salts of potassium, particularly the phosphates, were expected to exert a decided influence on the fermentation of bread, because these compounds constitute such a large proportion of the ash of yeast and are mentioned so frequently in connection with alcoholic fermentation. However, the potassium salts were found to influence the fermentation of bread only very slightly, while the phosphates had no noticeable effect. This is to be explained, no doubt, by the fact that the ash of flour is rich in these salts, consisting of about one-third potash (K_2O) and one-half phosphoric acid (P_2O_5), which abundantly supplies the yeast.

Because of their common occurrence in natural waters, the salts of the alkaline earth metals were studied in detail, with surprisingly interesting results. The calcium salts, especially, are of common occurrence in water and it is around these that the most interesting results presented in this paper center.

Besides the water problem, the utilization of stale bread was indicated as an important problem for research. One of the proposed methods for using stale bread comprised the cooking of the crumbs and then digesting with malt. The starches were thus transformed into sugars and the gluten remained in flakes which could be separated by filtration. From this gluten residue, by digesting with concentrated HCl in the ordinary way, glutamic acid hydrochloride was recovered in considerable quantities. The effect of the glutamic acid upon the parent substance, gluten, in bread was found to be a decidedly beneficial effect both upon the dough and upon the yeast.

AMMONIUM SALTS

Like many other acids, glutamic acid matures or ages the dough and, in addition, increases the gas production of the yeast. This accelerating effect upon the yeast was observed in bread and likewise in fermenting cane sugar, dextrose, and malt extract. In fermentation of this kind other acids failed to increase the fermentation as did glutamic acid hydrochloride, so we were led to believe that it was not a matter of acidity but that glutamic acid hydrochloride owes its accelerating effect to its nitrogen content. With this idea in mind, we conducted baking experi-

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[1] The conclusions were reported by bulletin to the Allegheny County Laundrymen's Exchange on April 17, 1916.

[2] The solution of sodium hypochlorite was prepared with 40 g. of commercial calcium hypochlorite, 40 g. of soda ash, and 40 g. of sodium bicarbonate, made up to a volume of 250 cc. with distilled water.

[3] A paper presented in abstract by Henry A. Kohman at the Urbana Meeting of the American Chemical Society, April 19, 1916.

ments with other nitrogenous substances. Ordinary peptone, such as is used for culture media, as already known, accelerates alcoholic fermentation greatly but this substance is expensive and, accordingly, attention was directed toward cheaper materials which would accomplish a similar result. The salts of ammonium were found fully as efficient as peptone.

Before giving the experimental data, it should be said that during the course of this investigation, which extended over a period of several years, the conditions were changed from time to time; consequently, the results of any particular series of baking experiments can not be compared strictly with those of another. Every precaution was taken, however, to maintain the same conditions throughout each series, so that the individual loaves could be compared closely with the control and with each other. In each series of experiments the loaves were scaled, moulded, proofed and baked together. Therefore, when accelerators were added the loaves naturally had not all risen to the same height when they were placed in the oven, as they do in commercial baking practice. Consequently, the volumes given in the tables are an expression of the rate of fermentation rather than of the relative lightness or degree of expansion that may be obtained. For example, when there was, say, a 10 per cent increase in volume noted with the use of an accelerator, it does not mean that the expansion was increased but merely that the rate of fermentation was increased by that amount. If the two loaves had been brought to the same degree of maturity and proofed to the same height in the pans, as is customary in baking practice, both loaves would have conformed to the standard size. In many bread laboratories, also, it is customary to proof all the loaves to the same height, especially when the volumes are taken to represent the expansion, as is the case in testing flours. In the experiments of this paper, however, all the loaves of each series were baked simultaneously, so the volumes should be interpreted as indicating the rate of the fermentation rather than the expansion of the loaves.

The following series of experiments will serve to illustrate the effect of ammonium sulfate upon the yeast in bread-making. A kilogram of flour was used in each batch.

BREAD No.	Grams $(NH_4)_2SO_4$	LOAF Cc.	VOLUME % Increase	Cc. Gas in $7^1/_2$ hrs.	Per cent Gas Increase
646	0.0	1630	0.0	292	0.0
647	0.5	1790	0.8	311	6.5
648	1.5	1865	14.4	310	6.5
649	2.5	1870	14.7	329	12.6
650	3.5	1930	18.4	328	12.6
651	4.5	1900	16.5	338	15.7

Besides increasing the gas production and improving and securing a more uniform loaf volume, the ammonium sulfate improved the texture and the general uniformity and appearance of the bread. The gas production was estimated by taking a small portion (50 g.) from each dough and collecting the gas evolved over a saturated solution of calcium chloride in Bunsen gas holders.

In a cane-sugar medium, ammonium sulfate also greatly increased the fermentative power of yeast. A series of seven fermentation experiments was made, using 68 g. of water, 1.2 g. of yeast and 6 g. of sugar, with varying amounts of ammonium sulfate. The results were as follows:

Experiment No.	1	2	3	4	5	6	7
Grams $(NH_4)_2SO_4$...	0.0	0.25	0.5	1.0	2.0	4.0	8.0
Gas, cc. in $6^1/_2$ hrs...	291	358	364	392	447	457	155
Per cent increase....	0.0	230	25.1	34.8	53.7	57.2	—46.8

While readings were taken every half hour, the total gas produced will serve to illustrate the accelerating action of ammonium sulfate. It will be noted that 8 g. has a marked retarding action.

Early in the research it was observed that the increased fermentation, due to ammonium sulfate, matured the doughs in a much shorter time. Bread fermented $3^1/_2$ hrs. with the use of ammonium sulfate was practically as mature as the control bread in $4^1/_2$ hrs. Obviously, then, this salt can be used for the production of bread in a shorter time. On first thought, one might infer that this action would be taken advantage of in increasing the output of a bakery; this, however, is not the case. The oven capacity, more than anything else, governs the productive power of a bakery. Although a short fermentation period is highly desirable in the bake shop, there is a limit beyond which it is not safe to go. Unforeseen delays are frequent in the daily operations, and since these often occur when the dough is already working, over-fermentation is the result. The shorter the fermentation period, the greater will be the over-fermentation when delay occurs. In our opinion, according to present practices, the fermentation period should not be less than $4^1/_2$ to 5 hrs. for hard wheat flours, excepting, of course, in special cases in which it is necessary to produce bread in a very short time to meet rush orders. In general, the increased fermentation due to the addition of ammonium sulfate can best be utilized by reducing the amount of yeast that is ordinarily required. The following series of baking experiments serves to illustrate the value of this salt in the diminution of yeast requirement:

		VOLUME OF LOAF (Cc.)		
BREAD No.	GRAMS YEAST	Fermented: $3^1/_2$ hrs.	$4^1/_2$ hrs.	$5^1/_2$ hrs.
193 (control)	12.0	1695	1735	1745
198	9.0 (25% less)	1805	1815	1875
194	8.4 (30% less)	1665	1755	1795
196	7.8 (35% less)	1655	1705	1805
197	7.2 (40% less)	1645	1695	1795

It is obvious that the amount of yeast that can be saved by the use of ammonium sulfate depends upon the length of time the dough is fermented. In a $4^1/_2$-hr. dough ($4^1/_2$ hrs. is the time adopted in many bakeries for straight doughs), 30 per cent of the usual amount of yeast can be saved, while the saving in yeast in a $5^1/_2$-hr. dough is 40 per cent. Various processes are in use in different bakeries and the length of the fermentation period ranges from $3^1/_2$ hrs. to 6 or even 8 hrs. in straight doughs and from 5 to 10 or 12 hrs. in the sponge-dough process. The fact that the ammonium salt accelerates the activity of the yeast most toward the end of the fermentation period is considered significant. It is then that gas production is most essential, for it causes the loaves to "spring" or "kick," which is very desirable and necessary for the production of a loaf with a fine close texture, good color and flavor. Especially is the "spring" desirable in the special types of loaves which are cut lengthwise, for it opens and ventilates them properly and gives to the top of the loaves a fine shredded appearance that is inviting and appealing to the sight and taste. In referring to good color here, it must be borne in mind that excessive fermentation will destroy such good color, as is reasonable to expect, dependent on the grade or quality of flour used, while proper fermentation will save or spare it.

Other ammonium salts than the sulfate may be used with equally good results. We have employed the chloride, phosphate, biphosphate, tartrate, oxalate, nitrate, acetate, formate, iodide, and sulfocyanate, and have observed no pronounced differences. However, for economic reasons, the sulfate and chloride are considered most suitable for commercial purposes. Because of its alkaline properties, ammonium carbonate can not be used successfully, as is shown by the following baking experiments:

Bread No.	1653	1654	1655	1656
Gram $(NH_4)_2CO_3$	0.0	0.24	0.5	1.0
Loaf volume, cc.	1505	1560	1530	1445
Per cent increase	0.0	+3.3	+1.6	—3.9

In small quantities, the volume remains practically unchanged, while it is diminished by 1 g. or more. Alkalies are very detrimental in bread and this, no doubt, explains the inefficiency of ammonium carbonate. Moreover, it was observed that ammonium carbonate imparted an objectionable odor to the bread. The carbonate may be used successfully only when sufficient acid is used to neutralize its alkalinity.

Ammonium fluoride accelerates the fermentation quite as much as other ammonium salts if used in small quantities; but in larger quantities it retards fermentation to a marked extent, as is evident from the following series of experiments:

Bread No.	847	848	849	850	851	852
Grams NH_4F	0.0	0.1	0.2	0.4	0.8	1.6
Loaf volume, cc.	1690	1850	1955	2080	1930	1400
Per cent increase	0.0	10.0	15.7	23.1	14.1	—17.1
Acidity	0.14	0.13	0.14	0.13	0.15	0.14

Evidently ammonium fluoride can not be used in as large quantities as ammonium sulfate, for, with the latter, the maximum acceleration was not exceeded even when 4.5 g. were used, while with the fluoride the maximum effect was obtained with less than 1 g.

In small quantities, however, the acceleration by ammonium fluoride is more pronounced, in equal weights, than that by ammonium sulfate, the explanation of which, no doubt, lies in the great difference in the molar weights. The inhibiting effect characteristic of ammonium fluoride in large quantities was also noted with hydrofluoric acid. Three doughs of the usual size were made with respectively 1, 2 and 4 cc. of hydrofluoric acid solution and none of them rose. Sodium fluoride is not so detrimental, as may be seen from the following results:

Bread No.	1338	1339	1340	1341	1342	1343
Grams NaF	0.0	0.1	0.2	0.4	0.8	1.6
Volume, cc.	1515	1555	1525	1485	1475	1505
Per cent increase	0.0	+2.6	+0.6	—1.9	—2.6	—0.6

The diminution in volume observed in this series is not significant.

CALCIUM SALTS

The results of our experiments with calcium salts, which have already been mentioned in connection with their occurrence in natural waters, will now be taken up in detail. Their effect will be given both when used alone and in conjunction with other salts. The effect of calcium chloride is indicated in the following table:

Bread No.	609	610	611	612	613	614
Grams $CaCl_2$	0.0	0.5	1.5	2.5	3.5	4.5
Loaf volume, cc.	1830	1935	2040	2070	2090	2110
Per cent increase	0.0	5.7	11.4	13.1	14.2	15.3
Gas	348	361	380	393	391	385
Per cent increase	0.0	3.7	9.1	12.9	12.3	10.6

There was a decided increase in volume and gas production with the increase in the calcium chloride content of the doughs. The texture, flavor, and general appearance of the bread were improved, as well. The loaf volume was increased considerably more than the gas production, which would indicate that calcium chloride has an effect upon the gluten of the dough as well as upon the yeast. In the light of some experiments conducted by Hardy upon the effect of electrolytes on the strength of wheat flour, this seems highly probable.

The effect of calcium chloride upon the fermentation of cane sugar is shown in the table below. In each of the six experiments, 100 g. of water, 10 g. of sugar, and 2 g. of yeast were used.

Experiment No.	1 (control)	2	3	4	5	6
Grams $CaCl_2$	0.0	0.5	1.0	2.0	4.0	8.0
Gas in $6^1/_2$ hrs.	344	391	408	418	429	281
Per cent increase	0.0	+13.6	+18.6	+21.5	+24.7	—18.2

The accelerating effect of calcium chloride in bread, like that due to ammonium salts, can best be taken advantage of by reducing the amount of yeast ordinarily used. As with the use of ammonium salts, the amount of yeast that can be saved depends upon the length of the fermentation period. In a $4^1/_2$-hr. dough, about 25 per cent of the yeast can be saved.

The effect of other calcium salts is very similar to that of the chloride. The results given below with calcium bimalate indicate that it is equally effective.

Bread No.	573	574	575	576	577	578
Grams calcium bimalate	0.0	0.5	1.5	2.5	3.5	4.5
Loaf volume, cc.	1770	1850	1970	2005	2020	2110
Per cent increase	0.0	4.5	11.3	13.3	14.1	19.2

The increase in volume is even greater than with calcium chloride. However, as calcium bimalate is slightly acid, the two salts are not strictly comparable.

The sulfates of calcium in the following series of experiments, in which $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot {}^1/_2H_2O$ were compared in molar quantities, increased the volume rather less than the chloride, especially with the larger quantities.

BREAD No.	Grams $CaSO_4.2H_2O$	Grams $CaSO_4.{}^1/_2H_2O$	LOAF VOLUME Cc.	LOAF VOLUME % Increase
3916 (control)	0.0	0.0	1670	0.0
3917	0.5	0.0	1710	2.4
3918	0.0	0.422	1723	3.2
3919	1.0	0.0	1726	3.4
3920	0.0	0.844	1796	7.6
3921	2.0	0.0	1863	11.5
3922	0.0	1.688	1826	9.4
3923	4.0	0.0	1830	9.6
3924	0.0	3.376	1853	11.0
3925 (control)	0.0	0.0	1676	0.4

In the following series of experiments the sulfate and chloride were compared carefully, using small quantities:

Bread No.	Grams Salts	Loaf Volume Cc.	% Increase
1060	0.0	1830	0.0
1061	1 $CaCl_2$	1915	4.6
1062	1 $CaSO_4.{}^1/_2H_2O$	1945	6.2
1063	2 $CaCl_2$	2045	11.7
1064	2 $CaSO_4.{}^1/_2H_2O$	2065	12.6

In each case it will be noticed that the sulfate gives a slightly larger loaf volume. In small quantities, then—say, about 2 oz. per 60 lbs. of water, or approximately 160 lbs. of bread—the sulfate gives equally good, if not better results than the chloride. In practice there is used not more than 2 oz. per 160 lbs. of bread and as calcium chloride, owing to its extremely hygroscopic nature, can not be used satisfactorily, because it can not be conveniently shipped or kept in the dry state, the sulfate is preferable for commercial use.

The nitrate and phosphates of calcium have also been used successfully. Of the phosphates, $Ca(H_2PO_4)_2$ and $CaHPO_4$ are most suitable, as the normal salt is both alkaline and difficultly soluble.

Since both calcium and ammonium salts accelerate fermentation and improve bread, experiments were made with both salts in conjunction with bread-making. The results of one series of experiments were:

Bread No.	Gram $(NH_4)_2SO_4$	Grams $CaCl_2$	Loaf Volume Cc.	% Increase
548 (control)	0.0	0.0	1800	0.0
549	0.5	0.0	1800	0.0
550	0.5	0.5	1985	10.1
551	0.5	1.5	2050	13.9
552	0.5	2.5	2065	14.7
553	0.5	3.5	2115	17.5
554	0.5	4.5	2120	17.7

Thirty per cent less yeast was used with these salts. It will be seen that in conjunction with ammonium sulfate calcium chloride gives a further increase in the loaf volume. Since this was found to be true, a series of experiments was made to determine how much yeast could be saved by the use of both salts in bread. The results were as follows:

Bread No.	Grams $CaCl_2$	Gram NH_4Cl	Yeast Used	Loaf Volume Fermented: $3^1/_2$ hrs.	$4^1/_2$ hrs	$5^1/_2$ hrs.	Mean Loaf Vol.	Per cent Increase in Vol.
555 (control)	0.0	0.0	Normal	1915	1820	1890	1875	0.0
556	0.0	0.5	30% less	2000	1920	2070	1995	6.4
557	2.0	0.5	30% less	2130	2270	2365	2255	20.2
558	2.0	0.5	40% less	2000	2165	2195	2120	13.1
559	2.0	0.5	50% less	1965	2060	2270	2095	11.7
560	2.0	0.5	60% less	1800	1880	2055	1910	1.8

With both salts, as with the use of an ammonium salt alone, the amount of yeast that can be saved depends upon the fermentation period employed. After $3^1/_2$ hrs. fermentation, only 50 per cent of the normal amount of yeast could be saved without a sacrifice in loaf volume, while after $4^1/_2$ hrs. 60 per cent could be saved. After $5^1/_2$ hrs. fermentation, the batch with 60 per cent less yeast produced a loaf volume that was decidedly larger than the control, indicating that still more yeast could have been saved.

The fact that the gas production is greatly increased toward the end of the fermentation period by the yeast nutriments, was observed also by collecting the gas from 60-g. portions of two doughs over a saturated solution of calcium chloride in Bunsen gas holders. The following data will serve to illustrate this point:

Gas Produced during Various Periods

Time	9:40	10:40	11:40	12:50	1:50	2:50	3:50	Total
Control	0	55	67	85	89	74	77	447 cc.
1643	0	28	43	62	73	75	80	361 cc.

It will be noticed that dough 1643 (with 50 per cent of the usual quantity of yeast, 1 g. of $CaCl_2$ and 0.5 g. of $(NH_4)_2SO_4$) evolves gas only about half as rapidly as the control in the initial fermentation, but that after 6 hrs. it exceeds the control in the rate of gas production. This is indeed significant, for it is at the end of the fermentation period when the dough has been moulded into loaves that active production of gas is required and most needed. If the yeast weakens when the dough is in the proof box or oven, the bread will not have the "spring" necessary to produce a well-risen loaf with a good shape and texture.

In this connection, it should be mentioned that others have experimented with ammonium salts in connection with research on flours. J. T. Willard and C. O. Swanson[1] found that ammonium chloride produced a beneficial effect on the baking qualities of flour, while the phosphate had no effect, and the tartrate and acetate had a detrimental effect upon the texture. The application of ammonium chloride or other ammonium salts to effect economies in yeast in connection with bread-making are not mentioned in the report of those investigators.

A. J. J. Vandervelde, L. Bosmans, F. Le Perre, J. Mason and A. Revigu[2] state that ammonium chloride and nitrate have only a slight action and that calcium nitrate exerts a very unfavorable action. In our opinion, the quantities used were excessive, and, moreover, such discrepancies in the literature on bread are not uncommon and are to be explained, no doubt, by inaccuracy in experimentation and by the fact that so many factors, such as temperature, age of dough, strength of flour, stiffness of dough, etc., affect the results; consequently, they are often misinterpreted and important results are sometimes overlooked.

The fact that the initial fermentation with yeast nutriments with a reduction in the usual amount of yeast is much slower than that of a normal dough has an interesting economic significance. It is well known that during the normal fermentation of bread there is a considerable loss of dry material, due to the decomposition of the constituents of the dough into volatile products. These losses as determined by various investigators are: Voorhees,[3] 4.3 per cent; Heeren,[3] 1.57 per cent; Fehling,[3] 4.21 per cent; Croeger,[3] 2.14 per cent; Jago,[4] 2.50 per cent; and Snyder and Voorhees,[5] 2 to 6 per cent or even 11 per cent, in cases of prolonged fermentation.

One of us, in a previous paper,[6] demonstrated that the losses in bread-making depend to a large extent upon the amount of fermentation which the dough undergoes. In a normal fermentation the losses were found to be 5.15 per cent, while with the same flour

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[1] Kansas Agr. Exper. Sta., *Bull.* **190**, 248–251; *Exp. Sta. Record* March, 1912, 356.

[2] *Rev. gén. chim.*, **16**, 123, 136.

[3] U. S. Dept. Agr., Office of Experiment Stations, *Bull.* **35.**

[4] Jago, "The Science and Art of Bread-Making," p. 361.

[5] U. S. Dept. Agr., *Bull.* **67**, 11 and 28.

[6] Kohman, This Journal, **4** (1912), 20–30 and 100–106.

the total losses were only 1.81 per cent, when the loaves were placed into pans at once upon mixing. The bread obtained in this way was decidedly poor, as is always the case when it is very much underfermented, and it was made in this way merely to detect any difference in losses due to fermentation. In salt-rising bread the losses were found to be only 0.44 per cent. This difference in the losses in the two types of bread was explained as follows: (1) Yeast produces 1.04 parts of alcohol for every part of carbon dioxide, both of which are largely driven off during the process of baking, while in salt-rising bread there is no alcohol produced. (2) It is necessary to ferment yeast bread in the sponge and dough stages from 5 to 8 hrs., and, as it is allowed to rise in loaf form in the pans but one hour or less, only a small part of the total gas produced is actually used in aeration, while salt-rising bread is made into loaves and placed in the pans immediately upon mixing the dough and very little gas is lost. (3) The gases produced by yeast consist of carbon dioxide, while those produced by the salt-rising bacterium consist of about $^{1}/_{3}$ carbon dioxide and $^{2}/_{3}$ hydrogen, which is only $^{1}/_{22}$ as heavy as the former.

The fact that the losses in ordinary bread are dependent upon the amount of fermentation led us to suspect that with the use of yeast stimulants the decomposition of sugar would be less than in a normal dough, because the initial fermentation is much slower and the total gas production is less. With this idea in mind, we made three normal doughs and three with a reduction of 50 per cent in the usual amount of yeast and with 0.5 g. ammonium sulfate and 1.2 g. calcium chloride in 1000 g. of flour. The gas evolved in the usual time from 50-g. portions of the doughs was collected in Bunsen gas holders, and from the total weight of gas produced the quantity of sugar decomposed was calculated, assuming that the carbon dioxide evolved represented 45 per cent of the loss in sugar. The results of these experiments are given below:

BREAD NO.		CC. GAS FORMED		PER CENT LOSS IN SUGAR Calculated on Flour	
Controls	1135	396	Av. 403	4.25	Av. 4.33
	1137	404		4.34	
	1139	409		4.39	
NH_4Cl and $CaCl_2$	1136	333	Av. 345	3.58	Av. 3.70
	1138	353		3.79	
	1140	348		3.94	
				DIFFERENCE	0.63

It will be noticed that the consumption in sugar is considerably higher in the control dough than in the one with added salts. The difference represents the saving in sugar that is effected by the use of ammonium and calcium chlorides in bread.

USE OF POTASSIUM BROMATE

In connection with the use of these salts as yeast nutriments in bread-making, with special reference to the losses, mention will be made briefly of potassium bromate as used in conjunction with them. The functions of the latter salt will be more fully treated in a subsequent paper, inasmuch as it is not a yeast nutriment but acts upon the dough, imparting to it very desirable properties.

In the fermentation of bread, a twofold object is accomplished; namely, the maturing, or aging, of the dough, and the aeration of the bread. The former is accomplished during the fermentation period, which takes from 4 to 6 hrs. in the best practice, and the latter during the proofing period, which requires from $^{1}/_{2}$ to 1 hr. After the dough is sufficiently matured, or aged, it passes through the dividing and moulding machines, which press out practically all of the gas. Then it is put into pans and allowed to proof, and only the small fraction of the total gas which is produced while the bread is in the pans actually functions in aerating the bread. The effect of the potassium bromate upon the dough is essentially an aging, or maturing, effect and is characterized by the exceedingly small quantities required. The following series of experiments will serve to illustrate the changes in loaf volume with increasing quantities of potassium bromate:

Bread No.	4547	4548	4549	4550	4551
Gram potassium bromate	0.000	0.015	0.030	0.060	0.120
Loaf volume, cc.	1735	1785	1755	1605	1375
Per cent increase	0.0	+218	+1.1	—7.4	—21.3

The maximum volume occurs with 0.015 g. per batch of 1000 g. of flour, and it will be noticed that with 0.06 and especially with 0.120 g. there is a marked diminution in volume. This influence upon the loaf volume is not due to any change in the rate of fermentation or gas production, but to the pronounced aging, or maturing, effect of the salt upon the dough itself. Similar changes in volume are effected by varying the amount of fermentation to which the dough is subjected. Up to a certain point, the gas-retaining power of dough and the loaf volume are increased by fermentation; then the dough becomes "rotten," *i. e.*, it no longer retains the gas well and, accordingly, the volume is greatly reduced.

A desirable quantity of potassium bromate—say 0.015 g. per batch of dough containing 600 g. of water—ages the dough so decidedly that 25 or 30 per cent of the usual amount of yeast can be saved without imparting to the bread any of the characteristics of underfermentation, such as heaviness, dark color and coarseness in texture. In fact, the bromate in these quantities improves the bread with respect to texture even though the yeast is reduced by 25 per cent. This pronounced effect is attributed to the oxidizing power of this salt, for it has been found that by passing oxygen through the dough a similar maturing action is obtained, but to a lesser degree. This is probably due to the condition of the oxygen—in one case we have molecular oxygen and in the other we have nascent oxygen—the nascent oxygen being more powerful than the molecular, and, therefore, would have a greater maturing action on the dough. The effectiveness of the nascent oxygen is indeed surprising, for the quantity of the potassium bromate is so small that the total available oxygen is less than 1 cc. per loaf of bread.

When potassium bromate is used in addition to ammonium and calcium salts, it effects a saving in yeast of 25 to 30 per cent of the amount required without it. For instance, when 50 per cent of the usual amount of yeast can be saved with the yeast stimulants, the saving may be increased to 65 per cent with the addition of potassium bromate.

The aging, or maturing, effect of potassium bromate upon the dough, without increasing the rate of fermentation or the sugar consumption by the yeast, results in a much greater saving in sugar than that due to the yeast stimulants alone.

To determine this saving, three normal doughs were made and three with 0.5 g. ammonium sulfate, 1.2 g. calcium chloride, and 0.015 g. of potassium bromate in 1000 g. of flour and 35 per cent of the usual quantity of yeast. The gas evolved from 50 g. portions of the doughs was used as the basis for calculating the losses in sugar due to fermentation. The results of these experiments may be thus summarized:

Bread No.		Cc. Gas Formed		Per cent Loss in Sugar Calculated on Flour	
Controls	2237	415	Av. 440	5.64	Av. 5.98
	2238	452		6.15	
	2239	452		6.15	
New Process	2240	225	Av. 266	3.62	Av. 3.62
	2241	...		..	
	2242	267		3.62	
				Difference	2.36

The results of a similar series of experiments are tabulated below; these show the losses at the end of 5, 6 and 7 hrs., respectively.

Bread No.		Gas in Cc. 5 hrs.	Gas in Cc. 6 hrs.	Gas in Cc. 7 hrs.	Cc. Gas between 6th & 7th hrs.	Loss in Sugar Per cent 5 hrs.	Loss in Sugar Per cent 6 hrs.	Loss in Sugar Per cent 7 hrs.	Diff. in Loss between New & Old Process 5 hrs.	Diff. in Loss between New & Old Process 6 hrs.	Diff. in Loss between New & Old Process 7 hrs.
Controls	2251	309	373	435	62	5.26	6.34	7.44			
	2252	310	375	440	65	5.26	6.38	7.50			
	2253	312	379	442	63	5.30	6.42	7.50			
Average		310	375	439	64	5.27	6.38	7.48			
New Process	2254	184	250	322	72	3.12	4.25	5.44			
	2255	177	239	302	63	3.00	4.07	5.10			
	2256	178	240	309	69	3.02	4.07	5.25			
Average		180	243	311	68	3.04	4.13	5.26	2.23	2.25	2.22

Six hours' fermentation is the approximately normal period in the best baking practice, 5 hrs. in the dough state and 1 hr. after the bread is made up into loaves. The range between 5 and 7 hrs. fermentation will cover most variations in baking processes, due to the requirements of different flours and the type of bread desired. It is clear from the results cited above that the losses increase as the fermentation proceeds and that they are uniformly lower in the new process. The differences in the average losses between the two processes are 2.23, 2.25, and 2.22 per cent in 5, 6 and 7 hrs., respectively, which is practically a constant. This is to be explained by the fact that after 5 hrs. the rate of fermentation in the two processes is practically the same. The difference in decomposition of sugar occurs mostly in the initial stages of the fermentation before the nutriments greatly accelerate the activity of the yeast.

In another series of experiments, the losses were determined by direct weighing, as had previously been done by one of us,[1] and also by collecting the gas. Both batches were set with 1000 g. of flour, and, after mixing, were divided into two equal portions. One-half was used for the determination of the losses by weighing and from the other half three portions of 40 g. each were taken by collecting the gas. The results given in the following table represent the mean of the three results obtained:

Bread No.	Moisture-Free Material Put into Batch	Dry Bread	Loss Grams	Loss Per cent	Per cent Loss by Gas Collection 3:30 P.M.	Per cent Loss by Gas Collection 4:00 P.M.
2340 (Control)...	494.78 g.	458.7 g.	36.08	7.21	6.12	6.59
2341 (New Process)..	493.75 g.	469.7 g.	24.05	4.81	3.98	4.38

The losses[1] were calculated from the gas collected at 3 : 30 o'clock, when the bread was put into the oven, and again at 4 : 00 o'clock, when it was taken out. The fermentation was completely arrested between the two times, of course, and the results obtained by direct weighing can more strictly be compared with those calculated on the gas at 4 : 00. Rather lower results were obtained by collecting the gas than by direct weighing. The solution of gas in the liquid of the dough may in part account for this and it is also suggested that the losses may not be due entirely to the decomposition of sugar by the yeast. However, the agreement is fairly close, showing that most of the material lost is due to the destruction of sugar by the yeast.

Sugar analyses were made of breads prepared with and without added salts and the results afford additional confirmation of the destruction of sugar by the yeast. Three batches were made, one each by the two processes with the regular amount of sugar and one by the new process with 2.25 per cent less sugar (calculated on the flour), which represents the difference in sugar consumption by the two processes, as determined by collecting the gas. The results follow:

Hrs. Fermentation	Per cent Sugar in Bread Calculated on Flour: Control Normal Sugar (25 g.)	With Added Salts Nor. Sug. (25 g.)	With Added Salts 2.25% less Sugar
5	1.70	3.41	2.70
6	1.56	3.02	1.96
7	1.37	2.66	1.63

It will be noticed that with the normal amount of sugar and added salts the bread is much richer in this substance than the control, while if 2.25 per cent less sugar is used in the batch, the bread is slightly richer in sugar than the control bread.

To confirm the reduction in the destruction of fermentable material in bread by the use of the new process, gas-collection experiments were conducted in a large bakery where it is in operation. Three portions of 50 g. were taken from each of the two doughs (1600 lbs.) set by the new and old process, respectively. The losses, representing the mean of the three determinations, were as follows:

Per cent Loss Sugar New Process	Per cent Loss Sugar Old Process	Per cent Sugar Saved	Time Hours
0.24	0.39	0.15	1½
0.43	0.69	0.26	2
0.55	0.97	0.42	2½
0.69	1.27	0.58	3
0.82	1.58	0.76	3½
1.10	1.96	0.86	4
1.38	2.36	0.98	4½
1.64	2.68	1.04	5
1.84	3.13	1.29	5½
2.25	3.48	1.23	6
2.49	3.85	1.36	6½
2.81	4.18	1.37	7
3.03	4.35	1.32	7¼

The difference in the destruction of sugars in these

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[1] Kohman, *Loc. cit.*

[1] It is assumed that the carbon dioxide represents 45 per cent of the sugar destroyed by the yeast.

experiments was 1.37 per cent at the time the bread was removed from the oven, which was considerably less than that obtained in the laboratory. This, we think, is due to the fact that less yeast in proportion to the dough batch is required in the bakery. It is common practice to use about twice as much yeast in laboratories as is required in bakeries to mature dough in the same time. This is to be explained in part, at least, by the fact that a batch of 1600 lbs. rises from 3 to 6° C. in temperature, due to the fermentation, while a small batch containing 1000 g. of flour remains practically constant in temperature. The authors have frequently observed a difference in temperature of 5 to 6° C. between the center and outside of a large dough batch. This is attributable, no doubt, to the evaporation of water on the surface of the dough, as the temperature of the room is the same as that of the dough at the time of its setting; naturally, then, the cooling effect will be much more pronounced in the case of a small dough. The small amounts of dough (50 g.) taken for collecting the gas from the large mass of 1600 lbs. in the bakery, would be especially subject to this cooling effect. Hence, we are inclined to regard the results obtained in the laboratory as nearer the truth than those obtained in the bakery, particularly when it is common knowledge that much higher proportions of yeast are required in laboratory batches.

The curves in Fig. I illustrate graphically the losses in bread-making due to the destruction of sugar. By means of the curves, the losses can be calculated at any desired time, which is impossible in determining the losses by direct weighing. In connection with the determination of the losses in bread-making, it should be mentioned here that the method involving the collection of the gas given off from an aliquot portion of the dough batch is novel.

An attempt was made to estimate the consumption of the sugars in bread by making sugar determinations upon the dough at intervals as the fermentation proceeded. Such determinations were made upon large-scale doughs set both by the old and new processes. Sugar determinations were also made upon sample loaves of bread that were taken from the batches at intervals and allowed to rise to the usual height in the pans and baked. The results are given in the following table:

PER CENT SUGAR CALCULATED ON FLOUR

Dough				Bread			
Time	Old Process	Time	New Process	Time	Old Process	Time	New Process
9 : 50	5.21	9 : 30	4.72	12 : 00	5.32	1 : 10	4.82
11 : 50	5.67	11 : 40	5.16	1 : 10	5.14	2 : 25	4.58
1 : 55	5.22	1 : 30	5.44	3 : 20	4.12	3 : 50	4.35
3 : 30	5.13	3 : 05	5.29	5 : 00	3.47	4 : 45	4.22
5 : 05	4.27	4 : 55	4.88				

It is interesting to note that for several hours there is an *increase* in the sugar content of the dough, the old process reaching a maximum about 2 hrs. after the dough is set and the new one at about 4 hrs. In the light of this fact, it is evident that sugar analyses upon dough can not serve as an index to sugar consumption by the yeast. The results are of interest, however, in demonstrating the activity of diastatic enzymes. In the new process the sugar content is higher at the end of the fermentation period than at the beginning, showing that the production of sugar is greater than the consumption; in the old process, this does not obtain, as there is nearly 1 per cent less sugar at the end. The difference in the sugar content between the two doughs at the beginning is due to the fact that less sugar is regularly used in the new process.

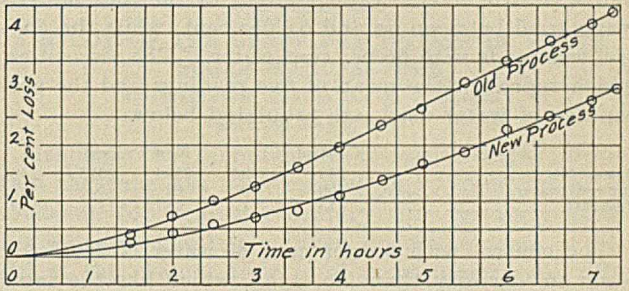

FIG. I—LOSS IN BREAD-MAKING CALCULATED FROM CO_2 EVOLVED

The curves in Fig. II present graphically the changes in sugar content of the doughs during the fermentation period. As the curves cross, it is demonstrated clearly that although 1 per cent less sugar was used in the new process, the bread baked after the usual fermentation period was actually about 1 per cent richer in sugar than that made by the old process.

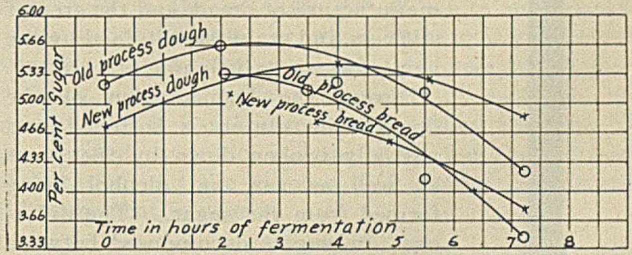

FIG. II—CHANGES IN SUGAR CONTENT

The economic saving possible by the proper use of nutrient salts, in the advent of a rather general adoption, sums up to surprising figures. Take, for example, the saving in sugar on the average flour production of the State of Kansas—say 20 million barrels, or nearly 4 billion pounds. A saving of 2 per cent on this amount is 80 million pounds; and it is mainly sugar that is decomposed and thus lost in bread-making. The economies in the yeast are greater than those in the sugar. Even a moderate use of such a process means a considerable saving to the country and is a step towards conservation of resources. At the present time, this process is used commercially in the manufacture of more than a million loaves daily.

A further advantage incident to this process of bread-making was observed in the increased stability and stiffness of the dough. To one familiar with doughs this is easily discernible to the touch; it was also determined more accurately and with numerical data by means of the dough viscosimeter (see Fig. III).

The viscosimeter consists essentially of a cylinder having a graduated piston which forces the dough through an aperture at the bottom. The stiffer and more tenacious the dough, the slower is the descent of the piston. The time that elapses while the piston descends the distance between two chosen marks is determined by means of a stop-watch. This reading in seconds represents comparative viscosities of the doughs. In the study of flours, the authors have found the viscosimeter very valuable.

Five doughs were made, four by the new process and a control. The water content of the four doughs was varied between 60 and 63 per cent, while the control was made with 60 per cent water. The viscosities, which represent the mean of five readings and the percentage of water used, are tabulated below:

	Control	New Process			
Bread No.	2391	2393	2394	2395	2396
Per cent water	60	60	61	62	63
Viscosity	13	21	18	17	9

The control with 60 per cent of water is decidedly lower in viscosity than No. 2393, which has the same amount of water. It will be noticed, further, that to obtain a dough of normal stiffness and stability, from 2 to 3 per cent more water may be added, another evidence of the conservation of flour in the dough batch from the use of these yeast foods. The resistance to softening of flour during the progress of the fermentation is of great significance in the manufacture of bread, and the greater stiffness and stability obtained by the new process is a valuable feature.

During the fermentation of the dough, the gluten is softened and partially broken down by the yeast as well as gas and alcohol being formed from the sugar. The difference in sugars decomposed between the old process and the new process is about 2 per cent when figured on the flour used. By using the new process, we are thus able to decrease the quantity of flour used by 2 per cent and still have a dough of the same stiffness. This probably accounts for the fact that in the bakery we can use 1.5 per cent more water or are able to decrease the amount of flour 2 per cent and still have a dough of the desired or usual stiffness.

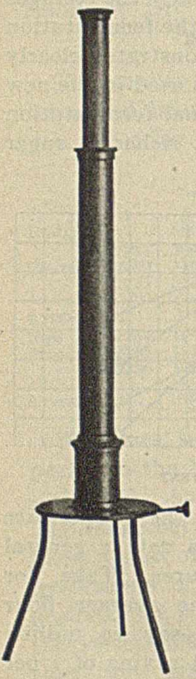
Fig. III

The new process has been used for breads of various types, such as pan breads, Vienna and French breads; also, for rye, Graham and whole-wheat breads. Likewise, it has been used with spring, winter and Kansas flours, and the different grades of flour, and has been found to be universally applicable.

In connection with the different grades of flour, it should be said that the process can not be used to give bread the appearance of being made from a higher grade of flour than is actually employed. The improvement in color with the use of the new process is due to the improvement in texture and can not be regarded as a bleaching process. The grayish color of the lower grades of flour remains in the bread made by the new process just as it does in the usual process. By any process, the color of the crumb is improved by fermentation up to a maximum and in the new process the same changes are noted; much less yeast, however, is required to accomplish the desired results.

The practical application of the new process has met with success and it is now in operation in a large number of bakeries. A number of these are under the direction of one superintendent, who claims that the process has been of material aid in standardizing the manufacture and maintaining uniformity of the bread in the different localities. As already stated, certain differences were noticed in the bread in a chain of bakeries, although all the raw materials were identical. These have been practically overcome by the new process, which virtually standardizes the water used for the baking purposes. This would be expected, because the required nutriment is supplied by means of these salts used as yeast food, and the addition of further mineral matter, either through the water or otherwise, has less and less effect as the quantities increase. It is a general rule that, in the addition of nutriments or activators in steps, the first portion added has a correspondingly greater effect than the succeeding portions.

For the sake of convenience and accuracy in the use of these salts, they are in practice mixed with flour and salt, so that it requires 8 oz. of the mixture for 60 lbs. of water, or approximately 160 lbs. of bread. An average bakery batch (1200 to 1500 loaves) contains about 480 lbs. of water, which requires 4 lbs. of the yeast food, a quantity that may be conveniently weighed with accuracy. The product has also been prepared as a liquid, in which case the salts are dissolved in water, so that 8 oz. of the solution for 60 lbs. of water deliver the required amount. For the dry product the sulfate of calcium is preferred, while in the solution the chloride is used. The use of either product introduces about 2 oz. of a calcium salt, a little less than 1 oz. of ammonium chloride and 0.02 oz. of potassium bromate into the batch for 60 lbs. of water used or for 160 lbs. of bread. In practice, the yeast food is first dissolved in the water used in the dough batch.

It is but natural to inquire: What becomes of the chemicals during the fermentation and baking of the bread? The purpose of the ammonium salt, as already stated, is to supply the nitrogen required by the yeast and it is of interest to know whether any of it remains in the bread.

The following table, showing the analyses in public laboratories of five commercial breads of greater Boston, will answer this question.

RESULTS (PER CENT) OF ANALYSES OF VARIOUS BREADS

Bread No.	Moisture	Ash	Lime (CaO)	SO_2	Ammonia (NH_3)
I	40.12	1.16	0.026	0.037	0.0053
II	40.19	1.04	0.029	0.016	0.0044
III	41.29	1.14	0.019	0.022	0.0037
IV	38.31	0.93	0.017	0.014	0.0011
V	41.06	1.05	0.015	0.019	0.0069

Bread No. I was made by the new process and it will be observed that it is not as high in ammonia as No. V, made without yeast nutriments. None of the breads has an ammonia content that is at all significant.

Additional analyses in our own laboratories confirm the above results.

It will be noticed, also, that No. II is higher in lime than No. I. The state of combination of the calcium in the bread is scarcely subject to question. It has been shown by Teller[1] that the phosphoric acid in flour exceeds by ten times the calcium and it may be safely said that, even by the use of the new process, the bread contains several times as much phosphoric acid as is required to combine with the calcium. Under these conditions, the potassium phosphate of the wheat undoubtedly interacts with the calcium sulfate, as it does in wort,[2] in accordance with the following equations:

$$KH_2PO_4 + CaSO_4 = CaHPO_4 + KHSO_4$$
$$2K_2HPO_4 + 3CaSO_4 = Ca_3(PO_4)_2 + K_2SO_4 + 2KHSO_4$$

It is known[3] that the calcium requirements of the body can be supplied by inorganic as well as by milk calcium. Abderhalden[4] has demonstrated that the complicated organic substances of our foods are replaceable by the simplest structural materials and that these are built up into various tissue substances. It should be mentioned in connection with the use of calcium salts in bread that Rudolph Emmerich and Oscar Loew[5] advocate the use of calcium salts in bread from a purely dietetic standpoint. In fact, the deficiency of calcium in our food is indicated clearly in *Experiment Station Record*, **20**, 68. A detailed discussion of this subject, with special reference to white bread, was published recently by one of us.[6]

The increased lime content of bread by the use of the new process is a very happy coincidence, even though incidental. Unfortunately, in modern methods of milling, the greater part of the mineral constituents of wheat is lost to white flour. As indicated by Teller,[7] seven-eighths of the phosphoric acid and eleven-fourteenths of the potash and lime of wheat are found in the stock feed; consequently, a partial restoration of the lime in white bread must be considered highly desirable.

CONCLUSIONS

I—By the use of minute quantities of ammonium and calcium salts and potassium bromate in bread, from 50 to 65 per cent of the usual amount of yeast can be saved.

II—Incident to the economy in yeast thus effected, there is a saving of about 2 per cent of fermentable carbohydrates, calculated upon the total flour used, due to the greatly diminished consumption of these by the yeast.

III—The proper use of nutrient salts for the yeast gives greater control over the dough batches and aids in the production of better and more uniform bread, regardless of the locality.

IV—The added salts conserve the inherent qualities of the dough and consequently maintain its stability and strength to a far greater degree than by the old process.

V—The finished loaves are improved in quality, flavor, texture, bloom and uniformity.

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[1] Ark. Agr. Expt. Sta., *Bull.* **42**, 70.

[2] Matthews' "Manual of Alcoholic Fermentation," pp. 194 and 195.

[3] *Biochem. Z.*, **9**, 185–207.

[4] *Wien. med. Woch.*, **63**, 177.

[5] *Z. Hygiene*, **77**, 311–28.

[6] Kohman, *Bakers' Review*, **31** (1914), 61–62.

[7] Ark. Agr. Expt. Sta., *Bull.* **42**.

A STUDY OF THE SYRUP PRECIPITATE IN WHITE SUGAR MANUFACTURE

By Charles E. Coates and L. C. Slater

Received May 9, 1916

Although the manufacture of white sugar direct from the cane has been carried on to some extent in Louisiana for nearly a century, for certain reasons this industry has lately taken on a new lease of life and at the present time is of great importance. To such a degree is this true, that most of the larger Louisiana sugar houses are now equipped for the direct manufacture of white sugar without the intervention of the bone-black refinery and in many instances have installed apparatus which has proven valuable in the manufacture of beet sugar.

The experience of the last few years, however, would indicate that there are not only different chemical difficulties to overcome, but also certain mechanical differences in the manufacture of white granulated beet sugar and cane sugar, which make special detailed attention to the latter exceedingly necessary. For instance, leaving aside the important question of clarification, it has become evident that filtration of the clarified cane juice is imperative, but the method of filtration and the number of filtrations are points still somewhat in dispute.

Some sugar houses allow the clarified juice to settle and pass the decanted, clear juice through bag filters. Occasionally the filtered juice is filtered again before final evaporation, but ordinarily it passes direct to the effects, where it is evaporated to a Brix of from 50 to 55°. There is considerable difference of opinion as to the proper subsequent treatment of this syrup. Sometimes a little sulfur dioxide or phosphoric acid is added to restore the initial acidity, but usually the syrup is passed into tanks, where it is allowed to settle from 2 to 4 hrs., gradually falling in temperature during that time. When the syrup is finally drawn from the tanks, there is always to be found a precipitate, which is separated as well as possible by decantation. In certain houses the attempt has been made to filter the syrup through leaf presses. This gives a bright filtrate, but the process, being tedious and expensive, is ordinarily dispensed with, though something is always removed from the syrup. If what it removes does no harm in the subsequent manufacture of white sugar from the cane it is evident that syrup filtration could be safely omitted and the cost of manufacture lessened.

The syrup precipitate is probably not present in the solid form in the freshly evaporated syrup, inasmuch as it will form in the course of several hours in syrup which has been previously filtered, hot, through paper.

It is not easy to get a satisfactory sample of the precipitate, which is gummy and difficult to obtain in a state of purity, but owing to the courtesy of two factories the writers succeeded in obtaining samples for preliminary investigations.

In Factory No. 1, the process of clarification was as follows: The juice was obtained by 9 rollers and a crusher, about 5 per cent maceration being employed. The extraction was relatively low, being 77 per cent on the weight of the cane. The purity of the juice was fairly high for Louisiana, being about 83. Sulfur dioxide was run into the raw juice until the acidity was raised to the equivalent of 4 cc. of $N/10$ potassium hydroxide for every 10 cc. of juice, phenolphthalein being used as an indicator. Slaked lime was next added until the acidity was reduced to 1 cc. The juice was then heated, passed through a continuous settling apparatus and the clear juice filtered over sand. The filtrate was not particularly bright. The juice was next passed to the effects and concentrated to a Brix of about 53°. It was then run to the settling tanks, where, in the course of a few hours, a gelatinous precipitate settled. These settlings were removed, as far as possible, by decantation and it is this precipitate which is the subject of this study.

In Factory No. 2 there were also 9 rollers and a crusher, with a saturation of about 10 per cent and extraction of about 79. The juice had a purity of about 84.5. It was sulfured to an acidity of 9 cc., which was exceedingly high (in the writers' judgment, considerably too high), then limed back to an acidity of 1 cc. and passed through heaters to a continuous settling apparatus. The clear juice was passed through bag filters and thence to the feed tanks for the effects, where phosphoric acid was added until the acidity was raised to 1.4 cc. It was then passed to the triple effects where it was evaporated to a Brix of about 53°. The syrup was then heated to boiling with live steam and slowly passed through a battery of inclined, continuous separators, being about 4 hrs. in transit. During this time a precipitate settled at the bottom of the separators, which precipitate is the second one included in this study.

Both of these factories made white sugar. It will be noted that in the first factory no phosphoric acid was used in the clarification. In the second factory, phosphoric acid was added to the clear juice after it had passed through the bag filters. Ordinarily, when phosphoric acid or sodium phosphate is used it is added before the juice is filtered. This precipitate seems, however, to occur normally in the syrup at all sugar houses. It forms quite slowly, usually taking several hours before it can be noticed. In one instance a perfectly bright, bag-filtered syrup stood 5 hrs. in a test tube before the precipitate became evident, though it eventually deposited a fairly large quantity. As stated, in order to get rid of this precipitate, the syrup is sometimes filtered through some form of leaf filter press but after a time the filter cloths get hard and crack, thus necessitating a considerable expenditure for filter cloth. Moreover, the gelatinous nature of the filtrate makes filtration slow, so that many factories prefer to omit syrup filtration entirely.

The sample of the settlings obtained from Factory No. 1 was filtered through paper and washed with cold water until the filtrate was practically without optical rotation. The precipitate was then removed, shaken several times with cold water and refiltered, the filtrate finally running clear. The same process was repeated with the settlings from Factory No. 2. The results are indicated in the following tables of analysis. For the sake of clearness, each set of analysis will be followed by the comments bearing on it specifically.

TABLE I

	Factory No. 1	Factory No. 2
Total amount of wet precipitate	71.5 g.	....
Total amount of air dry	....	32 g.
Water	45 per cent	13 per cent
Total amount of dry matter	39.3 g.	27.7 g.

It was impossible to estimate just how much of the original syrup this precipitate represented. In No. 2, however, we received a 50 l. carboy of the settlings from which we secured 27.7 g. dry precipitate. Taking the specific gravity of the syrup at 1.25, 50 l. equals 62,500 g. The precipitate therefore is about 0.04 per cent of the settlings and as these represent a much larger amount of juice, it is probable that the percentage of precipitate in the unfiltered syrup would be less than 0.01 per cent. The precipitate is so voluminous that the amount present seems much greater than it really is.

The dry precipitate was pulverized, extracted with ether and ignited, the loss in weight on ignition being taken as organic matter. The ether extract proved to be largely, if not entirely, cane wax.

TABLE II

	Factory No. 1	Factory No. 2
Ash in percentages	58	75.6
Organic matter in dry ppt	42	24.4
Ether extract	..	2.6

The excess of ash in No. 2 over No. 1 proved to be mainly calcium phosphate as shown in Table III, due to the use of phosphoric acid in clarification in one case and not in the other.

Part of the precipitate was ashed, boiled with concentrated hydrochloric acid, and evaporated to dryness. The silica was filtered off and the filtrate made alkaline with ammonia. The ammonia precipitate was filtered off and weighed. In each case considerable copper was found in the filtrate.

TABLE III

PERCENTAGES IN ASH	Factory No. 1	Factory No. 2
SiO_2	75.3	53.7
Ammonia precipitate ($P_2O_5.CaO.Fe_2O_3.Al_2O_3$)	5.3	34.5
CaO in filtrate	8.0	4.1
Cu	11.3	1.2
Total P_2O_5	0.6	13.5
(SO_4)	4.0	0.0

The large excess of silica in No. 1 may have been due to the use of sand filtration. It seems to have been present as colloidal silicic acid. The large amount of copper in No. 1 was doubtless due to an imperfect sulfur stove, which delivered the gas hot and probably with an excessive amount of SO_3: the resulting sulfuric acid seems to have attacked the various copper coils in the subsequent flow of the juice and syrup. As a matter of fact the copper was found badly pitted at the end of the campaign. Just how the copper was finally precipitated is not clear, especially since 50 g. of the mother liquor from the settlings gave no test for copper when ashed. In No. 2 where the sulfur stove was working well, the amount of copper in the precipitate was small, although there was an excessive amount of sulfur dioxide added in the sulfuring. This view is borne out by the fact that there was a fair amount of SO_4 (probably as $CaSO_4$) in No. 1, which was absent in No. 2.

In discussing the sulfitation process for white sugar making, the objection has been raised in Java that the sulfurous acid corrodes the coils. This has not been the Louisiana experience. When such corrosion does appear in excess it has been ascribed by some to sulfuric, rather than to sulfurous acid. This does not seem very probable, in our opinion. It might be noted here, however, that the coils used in sulfitation and the effect tubes as well are uniformly made of copper in Louisiana. In one instance brass tubes were substituted for copper tubes in a quadruple effect, evaporating juice of about 5 cc. initial acidity. These brass tubes corroded badly, though the writers understand brass has been successfully used in alkaline clarification in the beet sugar houses.

In Table III, the ammonia precipitate in Sample No. 1 proved, on analysis, to be mainly oxides of iron and aluminum together with what phosphoric acid was present. The excessive iron content was probably due to the poor sulfitation. In Sample No. 2 the precipitate contained little iron. Since in tricalcium phosphate the ratio of $(CaO)_3$ to the (P_2O_5) is 168 to 141, the precipitate is probably tricalcium phosphate with a little iron and aluminum phosphate and possibly some calcium silicate. As no sulfuric acid was present, it is evident that the excess calcium in the filtrate must have been originally present as insoluble salts of some organic acids.

After filtering off the first settlings through paper, the filtrate from No. 2 was corked and heated on a water bath in order to sterilize it. After an hour or so, a second precipitate separated out. This was filtered off, washed until the washing showed no optical activity, dried and analyzed with the following results:

TABLE IV

Total Amount of Dry Precipitate	Ash	Organic Matter	SiO_2 in Ash
1.6 g.	67.8 %	32.2 %	26.4 %

The filtrate from the SiO_2 gave a heavy precipitate with ammonium hydroxide which proved to be tricalcium phosphate. The filtrate from this in turn contained a quantity of calcium. The determinations of calcium and phosphoric acid were accidentally lost, but it will be noticed that in addition to the calcium phosphate there was also an excess of calcium which must have been present as calcium silicate, or as calcium salts of organic acids. Why this precipitate formed at all is not clear. The syrup stood a couple of days before it was heated and was perfectly bright. The flocking of the precipitate took place as soon as the temperature of the water bath was reached. A possible inference from this might be that when syrup is run into settling tanks and allowed to stand, the precipitate will form faster and more completely if the syrup is kept hot.

In order to get some clue as to the nature of the organic matter present in the precipitate, the following tests were made, the calculations being reduced to the basis of dry matter. The polariscope readings are in degrees Ventzke, for 10 g. of dry matter in 100 cc. reading in a 20 cc. tube. Reducing sugars were determined by weighing the reduced copper.

The moist precipitate was shaken thoroughly with cold water and filtered.

TABLE V

	Factory No. 1	Factory No. 2
Direct reading	....	—0.4°
Invert reading	....	—0.3°
Reducing sugars	Trace	0.0 per cent

Some of the moist settlings were boiled 6 hrs. on the water bath with frequent shakings, cooled and filtered from the insoluble precipitate. The filtrate gave the following figures:

TABLE VI

	Factory No. 1	Factory No. 2
Direct reading	—0.3°	—0.5°
Invert reading	—0.4°	—0.6°
Total solids in solution	1.7 per cent	3.9 per cent
Ash in same	0.4 per cent	2.0 per cent
Reducing sugars	Absent	0.03 per cent
Reducing sugars when hydrolyzed as for dextrin	....	0.11 per cent

From the composition of the aqueous extracts in Tables V and VI, it may be inferred that the organic matter of the settlings contained little or no soluble sugar, gums or dextrins, but that a fairly constant quantity of a levo-rotatory substance was present, which was not a sugar. The residues from the water extracts were washed into a beaker with dilute hydrochloric acid, heated on the water bath for 3 hrs. and filtered from the insoluble residue. This filtrate was made neutral with sodium hydroxide and filtered from the resulting precipitate. The results were as follows:

TABLE VII—HYDROCHLORIC ACID DIGESTION

	Factory No. 1	Factory No. 2
Polariscope reading	0.0°	0.0°
Reducing sugars	0.182 per cent	0.256 per cent

This digestion effected only a slight hydrolysis as indicated by the slight increase of reducing sugars, which may have come from fragments of fiber.

TABLE VIII—SODIUM HYDROXIDE PRECIPITATE

PERCENTAGES	Factory No. 1	Factory No. 2
Ammonia precipitate	....	19.0
CaO in filtrate	....	2.4
Total CaO, in ammonia precipitate	....	6.1
Total P_2O_5, in ammonia precipitate	....	4.0

This precipitate was redissolved in hydrochloric acid and aliquot portions analyzed.

The ratio of the P_2O_5 and the total CaO to the total ammonia precipitate, makes it probable that more than half the calcium was present as a salt of some organic acid.

The residue insoluble in dilute hydrochloric acid was washed, dried at 110° C., extracted in ether, and ashed.

TABLE IX

PERCENTAGES	Factory No. 1	Factory No. 2
Organic matter	Present	16.8
Ash	Present	83.2
Ether extract	Present	5.1
SiO_2 in ash	96.5	98.1

The ether extract was recrystallized from hot alcohol. It proved to be a saturated alcohol of high molecular weight, m. p. 81° C. It was clearly cane wax, probably present in a fine emulsion and carried down by the coagulated silicic acid. In ashing the residue there was an odor somewhat like that of burning feathers, but there was not enough material at hand to carry the investigation further.

As mentioned before, the filtrate from No. 2 settlings gave a second precipitate on being heated (see Table IV). Part of this precipitate was heated on the water bath for several hours with dilute hydrochloric acid and filtered from the insoluble residue which was almost entirely silica. The filtrate was made alkaline with sodium hydroxide which gave a precipitate as before. This was filtered off, redissolved in hydrochloric acid and analyzed. The filtrate from the sodium hydroxide precipitate showed neither optical activity nor the presence of reducing sugars, but showed 4.2 per cent CaO. The precipitate proved to be nearly pure tricalcium phosphate. A rough proximate analysis of Precipitate 2A would be as follows:

TABLE X

SiO_2	25 per cent
Tricalcium phosphate	40 per cent
Calcium salts of organic acids	35 per cent
Gums and sugars	Absent

In every instance the filtrate from the sodium hydroxide precipitate in 2A was colored, the alkaline solution being strongly purple; in neutral solution, it was bright green, in acid, light reddish yellow. The color change was exceedingly sharp. It was thought at first that this coloring had been developed by hydrolysis, possibly of some member of the complex anthocyan group, which is known to be present in the rind of the cane. The coloring matter was very soluble in water, but when the solution was evaporated to dryness, it proved to be insoluble in chloroform, ether, alcohol-ether, alcohol or methyl alcohol and was different in many ways from anthocyan. The residue was heated with concentrated hydrochloric acid and then with concentrated caustic soda in order to destroy any traces of carbohydrates which might have been present. What was left proved to be largely a copper salt, which seems to have been transformed by the sodium hydroxide into some soluble alk-oxide or protein compound. The original color was doubtless due to this copper compound together with possibly a small amount of an unknown natural indicator. There was not enough of the substances to permit of an extensive investigation, but the high coloring power may not be without significance in white sugar manufacture.

Comparatively little work has been done on the syrup precipitate. Prinsen-Geerligs[1] gives an analysis of it in his book on cane sugar. Geerligs concludes that the precipitate is practically identical in composition with the scale from different evaporating vessels and that it can not be removed by filtration owing to its gummy nature. On comparing the analyses of the precipitates from Factories Nos. 1 and 2, it was noticed that they were quite different from each other and from that analyzed by Geerligs, who found but 27 per cent silica. Here the silica ran 75 per cent and 54 per cent. The character of the precipitate clearly differs as the method of clarification differs. With the sulfitation method as practiced in Louisiana it was found quite possible to filter the syrup on a large scale. If a little kieselguhr was thrown into the press first so as to coat the cloths, the precipitate could be washed from the cloths without much difficulty and a leaf press working with a head of about 6 ft. give a perfectly bright filtrate. But even when working under most advantageous conditions the process proved expensive and was frequently omitted when there was any pressure upon the filtering capacity of the house. Numerous experiments were made with a view to improving the filtering quality of the precipitate, mainly by the addition of phosphoric acid or a phosphate in order to precipitate the calcium salts. The factory practice showed no particular improvement under this procedure, which may be readily understood by noting the composition of precipitate (Table IV). Here the filtered syrup stood for several days at about 12° before it was heated on the water bath, but when heated there was a heavy precipitate of tricalcium phosphate and silicic acid. Clearly these substances, though insoluble in the ordinary sense, were held possibly in colloidal solution by the heavy syrup. This being the case, the addition of phosphates can not be expected to bring down the theoretical amount of calcium in the short time available in factory practice.

In Factory No. 1, using no phosphates, the precipitate was, essentially, 40 per cent organic matter, 30 per cent silica, the remainder being calcium phosphate, copper, iron and aluminum salts. In Factory No. 2, using phosphates, the precipitate was 25 per cent organic matter, 30 per cent silica, 25 per cent calcium phosphate, the remainder being copper, iron and aluminum salts. The copper seems to have been completely precipitated from the syrup.

The organic matter present in the precipitate does not yield reducing sugars by hydrolysis and is probably mainly a calcium salt of organic acids.

Taking into account the exceedingly small weight of the syrup precipitate in spite of its apparent volume, and considering also the fact that nothing in the precipitate would affect materially the finished product, the practice of filtering the syrup would hardly seem to do sufficient good to warrant the increased expense. The best procedure is to allow the hot syrup to settle for at least 4 hrs. and as the precipitate forms most completely and settles most quickly at high temperatures, it is well to have the settling tanks sheathed to prevent radiation as far as possible. The clear syrup can be decanted and the bottoms run back to the limed juice where the amount of the precipitate is not sufficient to interfere with the subsequent bag filtration.

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[1] "Cane Sugar and Its Manufacture," **1909**, p. 211.

A CONTRIBUTION TO THE CHEMISTRY OF LAUNDERING

I—THE RESULTS OF RELATIVE SURFACE TENSION MEASUREMENTS OF SOLUTIONS OF SOAP AND OF SOLUTIONS OF SOAP AND VARIOUS ALKALIES[1]

By H. G. Elledge and J. J. Isherwood

Received May 3, 1916

During the course of an investigation of the various wash-room reagents which are employed in power laundries, the senior author was called upon to make a comparative study of various alkalies and alkaline mixtures marketed under trade names.

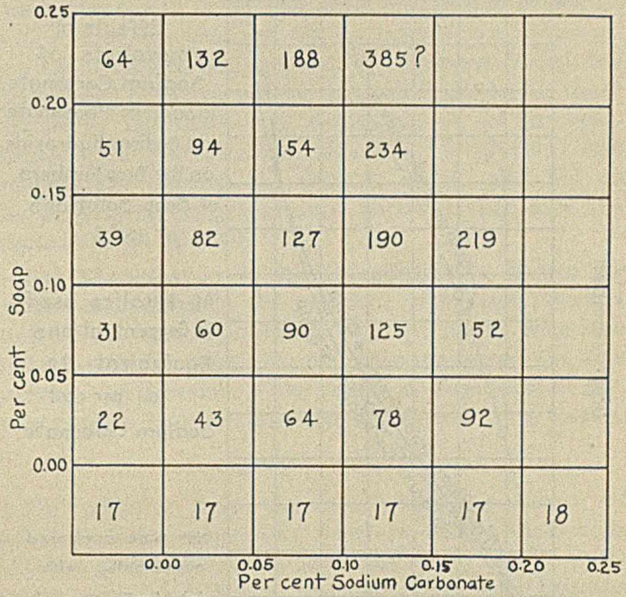
Among those examined were found sodium carbonate, mixtures of sodium carbonate and bicarbonate, mixtures of sodium carbonate and borax, trisodium phosphate, mixtures of disodium phosphate and borax, and a mixture of 3 per cent soap, 6.3 per cent caustic soda, 8.7 per cent soda ash, 36.3 per cent sodium silicate and sodium aluminate, and 45.7 per cent water. Under various trade names, these materials were sold to the power laundry trade, each with extravagant claims as to its excellence above all others. To the purchaser who desired to know the composition thereof, they were usually composed of a "sodium base" and mystery in equal proportions.

The mystery was really resolved by *a priori* knowledge, to the satisfaction of the writers. Herbert Jackson[2] had shown that the values of the alkaline salts of weak acids—sodium carbonate, trisodium phosphate and borax—were equal when chemically equivalent weights were considered, and that sodium bicarbonate was either valueless or, within the limits of his observations, one-fiftieth of that of the others mentioned. It seemed desirable, however, to secure more evidence of a quantitative nature. Then, too, it was regarded as important to obtain quantitative data regarding the suitable proportions of alkali and soap to be used, and to demonstrate clearly to launderers that because of the hydrolysis of soap in dilute solutions, the use of a certain quantity of alkali in excess of that required to precipitate the calcium and magnesium salts, is indicated by reasons of economy. These considerations induced the work reported in this communication.

The apparatus used was that described by H. W. Hillyer.[3] This apparatus consists of a 5 cc. capacity dropping pipette with capillary stem, which terminates with a perfectly *plane* surface, 10 mm. in diameter, upon which the drops form in a bath of kerosene. The reservoir containing the kerosene is equipped with an overflow in such a manner that the drops of the aqueous solution sink to the bottom and are discharged, leaving the kerosene undisturbed, throughout the experiment. A glass beaker was used for a water bath to control the temperature. Acknowledgment is hereby made for Dr. Hillyer's courteous advice on the construction of the apparatus and for his communication of certain precautions regarding the necessary manipulation in counting the drops.

A 0.4 per cent solution of soap was made with distilled water and a good grade of commercial chipped soap, which, upon analysis, was found to be free from excess of alkali. A 0.5 per cent solution of sodium carbonate was made up from calcined sodium bicarbonate and distilled water. Solutions of trisodium phosphate, sodium hydroxide and sodium bicarbonate were made equivalent to a 0.5 per cent sodium carbonate solution, in order to facilitate the preparation of the solutions to be tested.

A field was plotted, with soap solutions as ordinates, in 0.05, 0.10, 0.15, 0.20 and 0.25 per cent, and the alkalies as abscissa in units of 0.10, 0.15, 0.20 and 0.25 per cent. Solutions of the percentages indicated by each intersection were then prepared and the drop number was read for the temperature of 100° C. The results obtained are indicated in Fig. I.



64	132	188	385?		
51	94	154	234		
39	82	127	190	219	
31	60	90	125	152	
22	43	64	78	92	
17	17	17	17	17	18

FIG. I—Drop Numbers for Soap and Sodium Carbonate Solutions.

Lampblack is a substance very comparable to street dirt. It is composed of finely divided particles of carbon, associated with various hydrocarbons which may be condensed on them. The same description is applicable to the smoke resulting from furnaces wherein bituminous coal is used. By placing weighed amounts of lampblack on filter papers of uniform texture, treating them with equal volumes of the various solutions of alkali and soap, and weighing the filter papers with the residue of lampblack that was not washed through, we were able to show more or less quantitatively, that solutions of the highest drop numbers would, under standard conditions, carry through a filter paper (S. & S. No. 589) the greatest amount of lampblack. Water and the solutions of alkalies used would not take any of the lampblack through. It was therefore concluded that solutions giving the highest drop number have the greatest detergent value with respect to unsaponifiable dirt.

This conclusion lends support to the contention of a number of investigations since the theory of

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[1] Presented at the Urbana Meeting of the American Chemical Society, April 20, 1916.

[2] "Cantor Lectures," **1907**.

[3] *J. Am. Chem. Soc.*, **25** (1903), 511, 524, 1256.

Chevreul has been disproved, that alkaline solutions are in no sense detergents in the absence of free fatty acids or soap.[1] Water solutions of sodium hydroxide, sodium carbonate and trisodium phosphate, in the concentrations studied, showed very little changes in drop numbers with alterations in concentration. Within the limits of error of our observations, the changes in surface tension were about the same for chemical equivalents of the three solutions mentioned. The data for all are about as shown for sodium carbonate in the bottom row of Fig. I. Along with the facts mentioned, these results show that within the field examined the greater the quantity of alkali added to a soap solution, the better the detergent properties. This is limited in practice by the harmful effects on fabrics of large concentrations of the hydroxyl ion; Faragher has shown that these effects are almost negligible in the case of sodium carbonate and cotton, up to a 1 per cent solution of sodium carbonate, provided careful rinsing is employed. This figure is from 5 to 10 times the amount usually employed in power laundries.

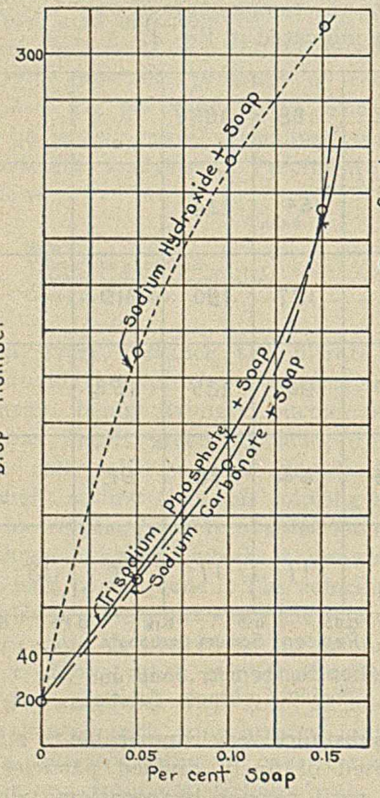

FIG. II
Effects of Equivalents of Sodium Carbonate, Trisodium Phosphate and Sodium Hydroxide on the Drop Numbers of Soap Solutions at 100° C.

All Alkalies used in Concentrations Equivalent to 0.1 per cent Sodium Carbonate.

Not to be compared numerically with data in Fig. I

In Fig. II there are shown the effects of equivalents of sodium carbonate, trisodium phosphate and sodium hydroxide on the drop numbers of soap solutions at a temperature of 100° C. Because of a change in the dropping pipette, these data are not to be compared numerically with those presented in Fig. I, but they show that the values of equivalent weights of sodium carbonate and trisodium phosphate are equal, while that of sodium hydroxide is different within the field studied. The case of sodium hydroxide is of no practical interest, because it is, for obvious reasons, seldom used in power laundries. These facts indicate that, of the alkaline salts of weak acids, one is as efficient as the other as a wash-room reagent, excepting, of course, sodium bicarbonate, which, in cold solutions, does not affect the drop number of soap at all. This conclusion is in harmony with the findings of Jackson, cited above.

From the foregoing data, one is able to eliminate all of the mystery in the "trade name" washing sodas mentioned. This is a preliminary report on work being conducted in the Mellon Institute of Industrial Research for the Laundrymen's National Association of America, and it is the intention of the authors to study further the field outlined above as to the effect of these solutions on the breaking strength of cloth.

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[1] See Faragher, Rogers and Aubert's "Industrial Chemistry," 2nd Ed.; Hillyer, *Op. cit.*, and Jackson, *Op. cit.*

NOTES ON SOME PHYSICAL CHARACTERISTICS OF PIGMENTS AND PAINTS

By HENRY A. GARDNER

Received August 4, 1916

HIDING POWER OF PIGMENTS

The opacity or hiding power (covering ability) of a paint pigment depends upon its fineness, refractive index, and oil absorption. These physical properties are responsible for the fact that a coat of white lead in oil hides a dark surface better than a coat of silica in oil.

FINENESS—Paint pigments, if produced in sufficiently large size particles, would be more or less transparent like a lump of glass, since all such products allow the light to be transmitted in varying amounts. If any one of them, however, is broken down and powdered, the finely divided particles reflect the light in all directions and only a small amount of light is transmitted; the powdered substance thus appears opaque. Therefore, it may be stated that *the opacity of pigments increases with fineness of division.* With some pigments, however (produced by the fume process), there may be a point beyond which increasing fineness may result in a lowering of opacity.

REFRACTION—The refractive index of a pigment determines the amount of light that will be transmitted by it. The higher the refractive index, the greater the reflection and consequent hiding power. A layer of white lead will reflect more light than a layer of finely ground silica, since the refractive index of the lead is higher than the refractive index of silica. When either of these pigments are ground in water, the same phenomenon holds true, but both are less opaque than in dry form because water has a higher refractive index than air. *As the refractive index of the vehicle approaches that of the pigment, opacity diminishes*, an optical condition being produced by the film around the particles, that allows the passage of light, thus decreasing the reflection. When turpentine is used as a binding medium, the pigments show the same relative differences in hiding power, but both are less opaque than when in water, since turpentine is more highly refractive than water. When linseed oil is used as a medium, still less opacity is shown by the resulting paints, as linseed oil has a greater refractive index than turpentine. The resulting silica paint will now be practically transparent, since the refractive index of the medium is substantially the same as that of the pigment. The lead paint, however, will still be opaque, since white lead has a refractive index greater than that of the oil.

OIL ABSORPTION—*Opacity increases inversely with the amount of oil absorbed by the pigment.* This is shown by comparing the hiding power of lead and zinc whites. These pigments have substantially the same refractive index and theoretically should hide equally. As a matter of fact, however, a workable lead paint has greater hiding power, since it may be produced by grinding 70 parts of lead in 30 parts of oil, while a workable zinc paint will contain 50 parts of zinc and 50 parts of oil. More light will pass through a film of the zinc paint than through the lead paint, on account of the greater quantity of oil present in the former. This accounts for the difference in the hiding power of the two paints. The preponderance of oil in the zinc paint, however, accounts for the much greater durability of those paints which contain zinc oxide in combination with lead pigments, since abundance of oil is recognized as a necessity in exterior paints.

It is apparent from the above considerations that the hiding power of a white pigment is measurable by determining its physical characteristics. Various methods for determining fineness and oil absorption have been in use, but no method has apparently been adopted for determining the refractive index of pigments. It occurred to the writer that some application of the petrographic microscope might be made for this purpose. A series of pigments were therefore prepared and submitted to test, the readings being made by Dr. Frederick E. Wright, of the Carnegie Geophysical Laboratory of Washington. Small particles of the pigment under observation were rubbed up with media of known refractive indices, covered with glass, and submitted to examination. Some of the readings are shown below:

Quartz silica	1.55	Basic carbonate—white lead	2.0
Barium sulfate	1.6	Basic sulfate—white lead	2.0
Zinc oxide	1.9+	Zinc sulfide	2.2 to 2.37

OPAQUE ADSORPTION PIGMENTS

One of the most interesting pigments examined was lithopone. Difficulty was experienced in getting an exact reading, as it consists of a submicroscopic mixture of aggregated particles. It is possible that the average refractive index might be considered as being between 1.9 and 2.0. This pigment is prepared by the resulting interaction of chemically equivalent amounts of zinc sulfate and barium sulfide solutions. The precipitated pigment is calcined, quenched, washed and dried. It consists of approximately 70 per cent barium sulfate and 30 per cent zinc sulfide. When barium sulfate, which has a refractive index of 1.6, and zinc sulfide, which has a refractive index of 2.2 to 2.4, are *mixed* in the above named proportions, a pigment is produced which is deficient in hiding power. It is apparent, therefore, that the precipitation process of preparing these pigments produces some physical change which is of great importance. It is the writer's opinion that the effect is due to adsorption of the zinc sulfide by the barium sulfate particles. Microscopical examination indicates that each particle of finely divided barium sulfate is coated over by adsorbed particles of opaque zinc sulfide. Experiments have been made with varying strengths of barium sulfate and zinc sulfide liquors in varying amounts, to determine whether it would be possible to produce even more opaque types of lithopone by increasing the amount of the zinc sulfide present. When lithopones are made containing as high as 50 per cent zinc sulfide, the hiding power has not been found substantially greater than that of lithopone which contains from 28 per cent to 38 per cent of zinc sulfide. Below 28 per cent of zinc sulfide, the hiding power of the pigment decreases. It is, therefore, between the limits of 28 per cent and 38 per cent zinc sulfide that the greatest hiding powers are obtained, and the increased hiding power of lithopone containing 38 per cent is hardly greater than that shown by those containing the theoretical equivalent of 30 per cent. Rapidity of precipitation, strength of solution, and temperature control are factors which also aid in the production of fine grained particles that give the pigment great opacity.

The phenomenon of surface adsorption shown by certain lake bases in the presence of organic coloring matters is also interesting, and explains why the highly colloidal pigments are often preferred for this purpose. A measure of the degree of dispersion of pigments might be based on their color adsorption values.

SUSPENSOID PIGMENTS

The adhesive properties and cementing values of paint pigments apparently increase with approach to colloidal form. That all paint pigments are to some extent colloidal, is the assumption of the writer as the result of some recent tests. These were first suggested by some previous experiments in which a number of white pigments were ground in clear linseed oil. After standing for a year, the oil upon the surface of the settled paints was examined and found to be much higher in ash than the original oil. This condition could easily be accounted for in the case of the lead and zinc paints by the presence of dissolved metallic linoleates formed by reaction between the pigments and the free fatty acid of the oil. No explanation, however, was offered as to the cause of the high ash in those paints made of silica, barium sulfate and other pigments which it was thought could exert no chemical effect upon the vehicle. A sample of the oil from one of the inert pigments (blanc fixé), after standing in a bottle for a further aging period, became viscous and thick, later on developing a peculiar cloudiness. Examination showed that the pigment had probably been held in colloidal suspension and previous to its precipitation had effected a change in the oil that had caused the gelatinous condition. As a result of these observations, the writer prepared a series of paints by grinding in a clear linseed oil a number of standard white pigments, including basic carbonate- and basic sulfate-white lead, zinc oxide, lithopone, and china clay. After settling for a period of two weeks, the clear oil was removed from each paint. The oils were examined under the ultramicroscope by Dr. E. C. E. Lord, of the U. S. Office of Public Roads, and the writer. Particles were visible but apparently in a quiescent state. This condition was undoubtedly due to the viscosity of the oil media which exerted a cohesive force upon the particles, binding them together in aggregates and thus impeding their motion so that the Brownian movement was not observable. These liquids, however, after dilution with 4 volumes of redistilled 90° benzol (disperse free) were again examined. The viscosity of the media thus being reduced, great rapidity of motion of the particles was shown. This Brownian movement was observed in every liquid and indicated that all of the above pigments may contain particles that act as suspensoids in oil. A sample of the original oil used in making the paint was also examined and although Brownian movement was observed therein, the number of particles present was not comparable to those shown by the oils removed from the paints. The particles present in the original oil were probably due to the "foots" present, regarding which reference is made below.

For the sake of convenience, the writer has given the name of "Linosols" to pigment suspensoids, since paint pigments are almost universally used in conjunction with linseed oil. When a condition is produced by these pigments, whereby the oil assumes the state of a gel, as in the case of the blanc fixé pigment mentioned above, the product of reaction might be called a "Linogel." The precipitation of the blanc fixé which was first visible as a cloudiness in the oil might possibly have been caused by absorption of oxygen by the oil, and would then be comparable to the precipitation of silica when carbon dioxide is absorbed by a sol of hydrated silicic acid. The term "Linoxygel" might, therefore, be more acceptable for such a product.

Experiments were then made with the same series of pigments ground in various oils, including a heavy bodied linseed oil of very high viscosity. In the latter, separation of the pigment from the oil, even after standing for two months, was only partial. After the paints were diluted with 4 volumes of benzol, only the coarser particles subsided, the liquid above remaining cloudy and suggestive of a true colloidal condition—the subdivided particles no longer showing any tendency to settle. Even after standing five weeks, the same cloudy condition was observed. It was apparently impossible to clarify the turbid liquid by sedimentation, even with the aid of a high-speed centrifuge. Attempts were then made to precipitate the Linosols. It was found that by mixing two of the cloudy paints (zinc oxide and silica), a fairly clear liquid could be produced. The explanation of this phenomenon might be that the pigments being oppositely charged had neutralized each other and thus disturbed the disperse phase, resulting in precipitation.

COLLOIDAL COLOR PIGMENTS

In order to study the condition of finely divided colored pigments, several were selected, including Prussian Blue, Chrome Green, Chrome Yellow, Ultramarine Blue, Lampblack, and Paranitraniline Red. These were ground in the same type of oil that was used with the white pigments, and treated in the same fashion. The clear liquid shown after settling was diluted with 4 volumes of benzol (disperse free) and examined. It is of interest to record the fact that the oil obtained from the settled Para Red pigment was only slightly colored, but when benzol was added, it became a bright, clear red. It is probable that part of the pigment present as a suspensoid was brought into actual solution by the solvent power of the benzol upon the organic coloring matter present in the pigment, thus accounting for the increase in color. When the liquids were examined under the ultramicroscope, Brownian movement was exhibited by each, the green and blue being most active and apparently containing many times the number of particles present in the others. Comparing the blue roughly with a counted solution of colloidal asphalt, it is probable that 1 cc. of the liquid contained over a hundred million particles.

Many of the particles or aggregates in the oil from the Chrome Green were colored crimson, orange, green, and blue. The colors were apparently permanent and did not change as would be the case if due to refraction. Since it is supposed that ultramicroscopic particles simply reflect light and therefore do not show colors, the above result is interesting and should warrant some extended work on the subject.

PREFERENTIAL ADSORPTION EFFECTS

The effect shown by carbon black is worthy of study. This pigment is supposed to be one of the most inert to linseed oil. It is probable, however, that it is really one of the most active in some ways. The great surface which its particles present, on account of their extreme fineness of division, probably gives to it very high adsorptive properties. The purest pigment obtainable by burning oil may be free of other solids and yet, according to F. P. Ingalls,[1] contain only from 80 to 90 per cent of carbon, the balance consisting of carbon monoxide, carbon dioxide, hydrocarbon compounds, nitrogen, oxygen, and water, all of which have been adsorbed by the carbon particles during the process of manufacture. That these substances are firmly locked to the particles is apparent, since vacuum treatment of the pigment fails to remove them. When ground in oil, however, the writer believes that the gas is removed from the pigment and the oil is adsorbed in place thereof by a preferential adsorption action of the pigment. Clifford Richardson has shown, for instance, that asphalt particles have the power of adsorbing some of the heavier constituents of a liquid by preferential adsorption. The present writer has similarly noticed that some finely divided pigments may adsorb the heavier constituents of an oil medium. This may be shown by dissolving a very heavy bodied linseed oil in benzine and grind-

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[1] Private communication.

ing it with lithopone. After a period of time, a reaction will be effected, whereby the oil is adsorbed by the settled pigment, leaving a clear, oil-free benzine floating on top. Very strongly oxidized and bodied oils may even show precipitation upon standing after being mixed simply with benzine. It is a question, therefore, whether any true solution of the oil has originally taken place. It is very likely that the apparent miscibility of the benzine is due in this instance to a sponge-like process of imbibition which might be compared to the absorption of benzol by rubber, or the swelling of gelatin in water (these effects, however, are illustrative of emulsoids). The preference shown by pigment particles for various liquids is aptly illustrated in the manufacture of pulp lead. The white lead, which contains a large amount of moisture, if agitated with linseed oil will immediately unite with the oil, and the water will be thrown out, floating on the surface of the paste paint. Other pigments and liquids may show a similar reaction. When zinc oxide or lithopone, for instance, are ground in alcohol and subsequently agitated with linseed oil, the oil will immediately unite with the pigments and the alcohol will be found floating on the surface of the paste. It is probable that these reactions have been made possible by a lowering of surface tension by the introduction of the oil.

SUSPENSOIDS IN OIL AND VARNISH

The "foots" present in linseed oil offers another example of what might be termed a "Linosol." When freshly crushed from the flaxseed, the oil will be apparently clear. If heated to 100° C., it will become cloudy and a large precipitate will form. This is referred to as "foots" and consists of mineral matter —lime, silica, phosphoric acid, etc.—admixed with albuminous matter. The mineral matter is present in the raw oil as a suspensoid[1] and is agglomerated and precipitated when the albumen is coagulated by the heat. The aging of oil may accomplish a somewhat similar effect, but sufficient tankage space is not always available to the crusher, and, therefore the raw oil is often marketed immediately after it has been produced. In the writer's opinion, such oil is not fit for use in high-grade paints, and the grinder should demand a better product. If the crusher should heat the raw oil to 100° C. and then centrifuge it, this method might take the place of tanking and would, at the same time, accomplish the destruction of fat-splitting enzymes[2] which might be present in the oil.

Varnish constitutes another organic product that may contain mineral suspensoids. Tanking of clear, newly made varnish always results in a slow precipitation of "foots." Centrifugal force will bring about the result more rapidly. It is gratifying to note that the centrifuge has become a part of the equipment of every modern varnish plant, and its use in this industry is bound to be more extended in the future. E. E. Ayres[3] has recently commented upon the clarification of pyroxylin varnishes by centrifugal action, and has mentioned the remarkable effect of a precipitant such as tricalcium phosphate. Similarly it is probable that the addition of certain mineral matter to freshly made varnishes, just previous to centrifuging, may effect more rapid and permanent clarification.

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[1] "Refining Vegetable and Animal Oils," Chas. Baskerville, *J. Franklin Inst.*, June, 1916.

[2] "Changes Occurring in Oils and Paste Paints, Due to Autohydrolysis of the Glycerides," H. A. Gardner, *J. Franklin Inst.*, May, 1914.

[3] "The Application of Centrifugal Force to Suspensions and Emulsions," E. E. Ayres, *J. Soc. Chem. Ind.*, June, 1916, p. 676.

COUMARONE RESIN AND ITS USES

By CARLETON ELLIS AND LOUIS RABINOVITZ

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Resinous bodies obtained by the polymerizing action of sulfuric acid on indene (C_9H_8) and coumarone (C_8H_6O) occurring in the fraction of coal-tar naphtha boiling between 160 and 180° C., are found in the market under the name of coumarone resin. Various attempts have been made, with some measure of success, to substitute these polymerization products for certain of the natural resins. This paper aims to give a brief review of the subject and a résumé of some experimental work carried out by us on coumarone resin.

Coumarone (or cumarone) resin was obtained by Kraemer and Spilker, during their investigation on indene and coumarone in coal-tar naphtha,[1] by the action of strong acids, particularly sulfuric, on coumarone; they called the product *para coumarone.* Somewhat later[2] they subjected this resin to a more thorough investigation and found that when pure coumarone which has been diluted with benzol is treated with a moderate amount of sulfuric acid, the greater part of the coumarone is converted into a resin soluble in benzol, while a lesser portion is transformed into a body insoluble in benzol and is carried down by the sulfuric acid, from which it may be removed by treatment with water.

The investigations of these chemists show that polymerization begins with an acid strength of 80 per cent (monohydrate). With this strength of acid the soluble resin is obtained almost exclusively. As the concentration of the acid is increased more and more of the insoluble resin forms. Increase in the proportion of the acid acts in a similar manner. With acid of 95 per cent strength applied in sufficient amount to a 2 per cent solution of coumarone in benzol the insoluble resin is formed almost quantitatively. When using 50 per cent of acid, calculated on the coumarone taken, about 25 per cent of soluble resin is formed while with four times the amount of acid no insoluble resin is formed.

Indene behaved very much like coumarone, only in that case the resinification was accompanied by a rise in temperature. The coumarone resin was found to melt between 107 and 108° C.

By the treatment of coumarone with a relatively large proportion of sulfuric acid,[3] at first a soft pasty mass was obtained which soon hardened to a brittle and infusible body, insoluble in all solvents. Kraemer

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[1] *Ber.*, **23** (1890), 78, 3276.

[2] *Ibid.*, **33** (1900), 2257.

[3] *Ibid.*, **23** (1890), 81.

and Spilker were unable to state whether this body corresponded in composition to that of coumarone. It had a specific gravity of 1.25 at 19° C. Its molecular weight was four times that of coumarone and on heating the resin decomposed between 300 and 350° C.

Indene was found to give a resin similar to that obtained in the case of coumarone and the product was obtained by them in various modifications, of differing melting points and molecular weights. From pure indene they obtained a resin which melted at 210° C. By treating the purified fractions that came over at 155–158° C. with sulfuric acid and steam distilling the solvents, they obtained a crude indene resin which was in many respects very similar to the coumarone resin.[1]

Later Kraemer and Spilker analyzed the insoluble and infusible modification of coumarone resin and found that sulfur which they previously had noted and had regarded as a mere impurity was in fact chemically combined.[2]

In 1890 Kraemer and Spilker[3] called attention to the industrial possibilities of "para coumarone" or "coumarone resin." They noted that it formed a coating for wood and metal surfaces which on account of its resistance to acids and alkalies possessed certain advantages over the ordinary resin solutions and varnish coatings employed for this purpose.

Wendriner, who has done a considerable amount of work on coumarone resin, describes a process for the manufacture of a light-colored resin, as well as a white solvent naphtha, from coal-tar naphtha distilling at 160–180° C., by removing first the acidic and basic constituents of the oil with 3 to 5 per cent by volume of 60° Bé. sulfuric acid under constant agitation and then treating the naphtha with 0.25 to 0.4 per cent by volume of concentrated sulfuric acid in a thin stream until the temperature rises to 110–120° C. After this treatment the acid is removed from the oil and the latter containing the dissolved resin is neutralized, dried and distilled from the resin with superheated steam. A less pure coumarone resin is prepared by treating solvent naphtha in the presence of its acidic and basic impurities with 0.5 per cent instead of 0.25 by volume of concentrated sulfuric acid.[4] Wendriner modified the process by omitting the use of 60° Bé. acid and carrying out the polymerization under cooling and under slow introduction of concentrated acid. He mentions that care should be taken to use an amount of concentrated acid equal to 0.25 to 0.4 per cent by volume of the naphtha treated and that the temperature should not rise above 40–50° C. The advantages of this process are: A saving of 3 to 5 per cent of 60° Bé. sulfuric acid; avoidance of the danger caused by heating of the volatile naphtha; a product in appearance somewhat resembling a light Congo resin melting between 80–100° and having a color varying from yellow to amber, depending on the care exercised in carrying out the reaction. According to Wendriner it is important to avoid sulfonation which has an influence on the color and boiling point of the naphtha yielded by the operation.

Knüppel[1] states that a hard brittle resin is obtained by blowing air through para coumarone and para indene for 3 to 5 hrs. at a more or less high temperature. According to Knüppel, the product is not tacky, dries with a high lustre and increases the drying power of the varnish prepared from it.

Fehringer[2] prepares a bronzing liquid or bronze powder varnish by dissolving coumarone resin in benzine, gasoline, benzol, chlorethylene or a mixture of these solvents.

Varnishes are prepared from cellulose esters by dissolving them in methyl alcohol, acetone oils, ketones or the like, with the addition of polymerization products of coumarone or indene, dissolved in benzol, alcohol or like solvents.[3] The resulting varnish is stated to be oily, lustrous, to dry uniformly, forming a very elastic coating which is stable in air and light. For instance, 1 part by weight of coumarone resin is dissolved in 5 parts benzol and added to a liquid consisting of a solution of 3 parts of collodion and 0.5 part of acetone oil, 10 parts each of alcohol and ketones: the resulting composition is diluted with 30 parts alcohol, 30 parts benzine and 10 parts methyl alcohol. Or, 1 part of coumarone resin is dissolved in a mixture of 2.5 parts each of fusel oil and tetrachlorethane; this solution is added to a mixture of 60 parts acetone and 30 parts methyl alcohol; 40 parts of acetyl cellulose are dissolved in this liquid. (See also U. S. Patent 1,185,514, May 30, 1916, to Lehmann and Stocker.)

Eichler[4] describes the simple preparation from the polymerization products of coumarone of a primer and varnish which is impervious to water vapors, caustic alkalies, ammonia and efflorescence. For example, para coumarone is melted and compounded with a solvent while heat is applied, whereupon the varnish is formed. The consistency of the varnish of course depends upon the quantity of solvent employed. Usually equal parts by weight of the resin and solvent are used. The primer and varnish may also be added to ordinary varnish to render the latter more impervious to water and more resistant to alkali. Benzine, gasoline, benzol or turpentine are good solvents for the resin. Eichler[5] also refers to the application of coumarone resin in linseed-oil varnishes in lieu of ordinary varnish resins.

Lender and Koch[6] note that coumarone resin may be used in a varnish base for the manufacture of varnishes, enamels and paints and as a binder in the manufacture of linoleum, lincrusta and oil cloth. They state that all objections encountered in the preparation of paints or varnishes by incorporating Chinese wood oil with ordinary resins are overcome, if in place of these the

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[1] *Ber.*, **33** (1900), 2257.

[2] *Ibid.*, **34** (1901), 1888.

[3] *Ibid.*, **23** (1890), 81.

[4] German Patents 270,993 and 281,432; *J. Soc. Chem. Ind.*, **1914**, 474; *Chem. Abs.*, **1914**, 2248; **1915**, 2001; *Z. angew. Chem.*, **27**, 2582.

[1] German Pat. 253,437, 1912; *Z. angew Chem.*, **25** (1912), 2506.

[2] *Chem. Abs.*, **1915**, 3369; U. S. Patent 1,157,768, Oct. 26, 1915.

[3] *Ibid.*, **1915**, 1850; German Patent 281,265, 1913.

[4] U. S. Patent 1,133,432, March 30, 1915.

[5] U. S. Patent 1,133,433, March 30, 1915.

[6] U. S. Patent 1,019,666, March 5, 1912.

polymerization products of coumarone and indene, namely, para coumarone and para indene, are employed. A varnish of this type is prepared as follows: 10 kg. of Chinese wood oil are heated to 220–240° C. and a quantity of the polymerization products of coumarone and indene to suit the conditions of use, generally an equal weight, is added; the product is a homogeneous mass which is hard when cold. This material is the base from which varnish, lac, enamel or similar coating material are made. This base is then heated and mixed with a suitable solvent such as liquid hydrocarbons, *e. g.* benzine, benzol, ligroin, turpentine, etc., and also chlorinated hydrocarbons. The amount of solvent used is dependent upon the consistency of the product desired and the use to be made of it. It may be thinned at will. To the mixture of the base and solvent may be added any desired coloring matter and the varnish or paint is stated to dry rapidly to a brilliant elastic coating impervious to liquids and unattacked by gases. It is unusually resistant to water, acids, heat and cold. A varnish paint or other similar product of this character is claimed to have a wider range of use than any other similar product or any product consisting of Chinese wood oil and ordinary resins, especially as it does not become tacky and does not set or liver by the addition of such pigments as lead or zinc compounds.

Lender[1] states that a varnish can be prepared from indene or coumarone, or both, with or without the addition of vegetable or animal oil, by heating with sulfur or sulfur chloride under pressure or at ordinary pressure, and dissolving the product in a volatile solvent.

PROPERTIES OF COUMARONE RESIN

Bottler,[2] who has investigated the properties of commercial coumarone resin, states that the resin of commerce varies widely in character. Some varieties which he examined were solid and more or less brittle, others were soft and pasty. A rough and ready method for the determination of the hardness of a resin according to Bottler is to scratch the surface of the resin with a needle. On soft resins the needle traces a smooth and even line. On hard resins the line is rugged and rough.

Some of the coumarone resins, Bottler notes, were of a dark brown color, sometimes even black while others varied from a yellow-brown to a brown color. They occurred in lustrous non-transparent lumps having a shiny fracture. Some of the samples gave a light yellow, others a dark brown powder. They possessed a tar-like odor. The yellow and brown resins in powder form attracted moisture from the air on standing over night. In some cases it was found necessary to use a spatula to remove the powdered material from the mortar. Their melting point varied over a considerable range. Some of the yellow-brown and brown varieties melted at 55, 60 and 65° C. The darker varieties generally melted higher, softening at about 85° C. and melting completely at 98, 100 and 108° C. They fused more easily than various natural resins. The fused material usually solidified very quickly to a resin of the original color.

A sample of brown coumarone resin, made in this country, was examined in this laboratory and found to melt completely at 65° C.

ACTION OF ALKALIES

A 5 per cent sodium carbonate solution, a 1 and a 5 per cent solution of sodium hydroxide and 10 per cent ammonia water did not affect coumarone resin. Only on prolonged warming with 5 per cent caustic was the resin somewhat acted upon, and the solution shows signs of frothing. At any rate no saponification took place.

SOLUBILITIES OF COUMARONE RESINS, ETC.

SOLVENT	HARD COUMARONE RESIN (BOTTLER)	COLOR OF SOLUTION
Alcohol	Slightly soluble	Light yellow
Absolute alcohol	Easily soluble	Yellow
Carbon tetrachloride	Completely soluble	Yellow to brown
Trichlorethylene	Completely soluble	Yellow
Benzine	Completely soluble	Yellow to red-brown
Turpentine	Soluble (slight residue)	Yellow
Linseed oil	Slightly soluble	....
	SOFT COUMARONE RESIN (BOTTLER)	
Ether	Soluble	Yellow
Carbon tetrachloride	Completely soluble	Brownish yellow
Trichlorethylene	Completely soluble	Brown color
Benzine	Easily soluble	Brownish color
Turpentine	Almost completely sol.	Yellowish brown color
Ether and 90% alcohol	The resin is precipitated	....
		COLOR OF FILM ON TIN PLATE (BOTTLER)
Ether		Lustrous and yellow
Carbon tetrachloride and trichlorethylene		Light yellow or yellow
Benzine		Brownish red
Turpentine		Yellow and lustrous
Ether and trichlorethylene		Yellow

Kraemer and Spilker state that para coumarone is easily soluble in ether, benzol and chloroform but difficultly soluble in benzol.[1] The films obtained from different varieties of resin in either carbon tetrachloride, trichlorethylene, benzine and turpentine possessed a certain degree of elasticity. It is stated that the resin possesses drying properties when exposed to air in thin layers.[2]

PREPARATION OF PURE INDENE

Kraemer and Spilker[3] describe a process for the purification of indene by means of picric acid. According to this method the fractions of crude naphtha boiling between 176–182° C. are treated with as much picric acid as is necessary to combine with all the unsaturated bodies present. The crystalline precipitate formed contained the picrates of coumarone and naphthalene as well as that of indene. On steam distillation the indene picrate is decomposed and indene distills over. Ten kg. of crude naphtha boiling between 176–182° gave 3 kg. of crude indene. The process is not without danger as these picrates are highly explosive.

Weisberger[4] describes several methods of a more practical nature, for the preparation of pure indene. Sodium amide is treated with the crude indene fraction boiling between 175–185° C. Ammonia is evolved and amide is converted into a dark heavy oil. The mixture is heated for 2 hrs. under agitation at 110–175° C. It is then distilled at 20–30 mm. pressure

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[1] German Patent 277,605; *Z. angew. Chem.*, **27**, II (1914), 583.

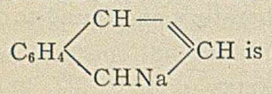
[2] *Kunststoffe*, **1915**, 277.

[1] *Ber.*, **23** (1890), 81.

[2] *Seifen.-Ztg.*, **1913**, 289, 344, 694.

[3] *Ber.*, **23** (1890), 3276.

[4] *Ibid.*, **42** (1909), 569, and German Patent 205,465 (1908), and 209,694 (1909).

to remove the unchanged hydrocarbons which come over at 110–130° C. The solid amorphous mass left behind and to which Weisberger assigned the formula  $C_6H_4{<}\genfrac{}{}{0pt}{}{CH-}{CHNa}{>}CH$ is decomposed by water into indene and sodium hydroxide. The indene is recovered by steam distillation. A rough fractionation of this product yields pure indene.

A still purer product may be prepared by treating the crude indene with the theoretical quantity of metallic sodium and passing a slow stream of ammonia into the mixture at 120–130° C. for 5 or 6 hrs. The indene sodium compound obtained by this process resembles rosin in appearance, is very sensitive to the action of air and is easily decomposed by water yielding a very pure indene.

By heating the indene and sodium above 130° C. in the presence of small amounts (2 per cent) of basic bodies such as aniline, toluidine or pyridine, pure indene may be obtained without the use of ammonia gas. Weisberger states that by this method the yields of indene obtained from the fraction of heavy benzol boiling between 175–185° C. amounted to 35 per cent.

The methods for preparing pure coumarone are more involved and are of scientific rather than of practical interest.

THE PROPERTIES OF INDENE AND COUMARONE

Spilker and Dombrowsky[1] describe indene prepared from the sodium compound as melting at 92° C., and boiling at 182° C., having a specific gravity of 1.0002. Pure indene absorbs oxygen and becomes acid. The oxidized indene is insoluble in alcohol and cannot be distilled by steam.[2] It combines with mercuric sulfate, giving an indene mercuric oxide compound.[3]

Bizzarri[4] describes coumarone as a colorless liquid boiling at 169° C. and very resistive towards chemical agents or heat. Aniline or alcoholic ammonia has no action on it. Aluminum chloride was found by Heusler[5] to act violently on coumarone and indene with the production of a resin soluble in hydrocarbons. He states that it is impossible by a single treatment with sulfuric acid to remove completely the indene and coumarone from coal-tar naphtha, but that by the action of aluminum chloride these two bodies may be completely resinified. Two and one-half per cent of aluminum chloride is sufficient for this purpose. The indene and coumarone resins remain dissolved in the naphtha.

EXPERIMENTAL WORK

In some experimental work carried out by us, the fraction of varnish makers' solvent naphtha which boiled between 160–180° C. was treated with 1 per cent of 66° Bé. sulfuric acid and was stirred for several hours at room temperature. The temperature of the mixture did not rise above 35° C. The product was then washed free from acid and steam-distilled with superheated steam. There was left in the vessel a pasty material which gave on drying on the steam bath a transparent brown substance of the consistency of molasses. Six hours of steam distillation with superheated steam did not materially affect the hardness of this product. Some of this soft resin was heated for 15 to 20 min. to 220° C. with about 10 per cent of sulfuric acid (66° Bé.). The resin darkened considerably and carbonized without undergoing any change in hardness. Another portion was subjected to the action of anhydrous zinc chloride and also to stannic chloride at 200° C. without undergoing any change. Chlorine combined readily with the coumarone resin giving a fairly hard, dark product. Darkening was the only visible effect that a powerful ultraviolet light had on coumarone resin after a 3-hr. exposure.

The effect of other polymerizing agents on solvent naphtha containing coumarone and indene was investigated in this laboratory. In one case, the naphtha was heated to boiling with reflux condenser for one hour with silver oxide. A part of the silver oxide was reduced to metallic silver with the formation of a bright mirror on the walls of the vessel. The liquid was filtered and steam-distilled. A dark brown material was left in the vessel which was considerably harder than the resin obtained with sulfuric acid. Phosphorus trichloride, phosphoric acid, chromic acid, hydrochloric acid, ammonium dichromate, formaldehyde and potassium hydroxide did not polymerize coumarone or indene in solvent naphtha, under the conditions tried. Zinc chloride at the boiling point of solvent naphtha gave rise to a small amount of resin. The action of anhydrous stannic chloride was similar to that of zinc chloride, while iodine was without effect.

Soft coumarone resin was distilled at 29 in. vacuum. When the temperature rose to 160° C. the distillation was stopped. The resin left in the flask was rather dark and melted completely at 60–65° C. It softened in the hands to a flexible mass which was not tacky.

Twenty grams of the soft coumarone resin were distilled at 29 in. vacuum.

Weight of Distillate	Weight of Residue	Temperature
9.0 g.	10.5 g.	to 168° C.
2.5 g.	8.5 g.	168–180° C.

From this data it can be seen that 57.5 per cent of the soft resin went over into the distillate. The hardness and melting point of the residue of resin increased with the amount of material distilled. The distillate was a highly viscous liquid which was somewhat brown in color. This coloration was due to the small amounts of resin that were carried over mechanically during the distillation. The distillate is probably an intermediate polymerization product. Its iodine number was found to be 28.5.

The resin obtained in this way became plastic at 38° C. and melted completely at 71° C. Its saponification number did not exceed 0.2. The iodine number of the hard resin was 38 to 43.5, which, it will be noted, is higher than the iodine number of the distillate.

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[1] *Ber.*, **42** (1909), 573.

[2] Weger and Billmann, *Ibid.*, **36** (1903), 640.

[3] *Pharm.-Ztg.*, **1915**, 46.

[4] *J. Chem. Soc.* [*Abs.*], **1891**, 566.

[5] *Z. angew. Chem.*, **1896**, 319.

In another case a sample of crude solvent naphtha, 25 per cent of which boiled above 160° C., was treated with 1 per cent of sulfuric acid of 98 per cent strength and the mixture was agitated for 2 hrs. It was then freed from acid and distilled under ordinary atmospheric pressure at 190° C. The residue from this distillation was distilled to 165° C. under a vacuum of 29 in. and the residue from this second distillation was a thick, very viscous substance, dark in color and possessing a strong unpleasant odor which was quite different from the harder resin obtained from the solvent naphtha fraction (b. p. 160–180° C.) used above. The yield of this viscous material amounted to 1.9 per cent of the solvent naphtha taken.

An interesting observation on the unsaponifiable nature of the coumarone resin was made with one of the harder samples obtained in this investigation. Solutions of the resin in benzol, etc., were applied to glass to form a thin film of the resin and when dry the plates were immersed in a liquid made by agitating Portland cement with water during the setting period. A thin paste of the cement and water was obtained in this way which was alkaline in reaction. The effect of this alkaline extract on the coumarone resin film was compared with the results obtained by similar treatment of films of drying oils and acid resins. In the case of the saponifiable bodies, the destructive effect of the alkali was quickly observed, but with the films of coumarone resin no disintegrating action was noticed even after exposure to the alkaline liquid for a period of several days. The films clouded and in some cases turned white, but the hardness and integrity of the coating did not appear to be affected. This property of the resin is of interest in connection with the production of a coating for concrete and stucco which is entirely resistant to the action of concrete alkali.[1]

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ON CALAMARY OIL

By Mitsumaru Tsujimoto

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This oil (Japanese: "Ika-abura") is obtained from the internal organs, especially the livers, of various species of cuttle-fish, among others the calamaries (the genera *Ommastrephus* and *Loligo*), and is a by-product of the manufacture of the so-called "dried cuttle-fish" (Japanese: "Surumé"). Although the annual production of the latter in Japan amounts to about 9,375,000 kg., the oil has been brought into market rather lately. According to a report of the Yokohama Fish Oil Company, the production of the oil in Hokkaido and other districts of Japan has annually increased, and it is stated that the Iwaté district (the northeastern coast of Honshiu) alone produced about 50,000 kg. of the oil in 1913. If all the fish used for the drying purpose were utilized, the production of the oil would be increased very considerably.

The oil is prepared by boiling the organs of the fish with water. The process appears to be rather primitive and rough, judging from the quality of the commercial oil. The oil-content is recorded as about 2 to 3 per cent of the wet raw material.

J. Lewkowitsch, in his well-known work on oils, fats and waxes, has described the livers of decapods to be very rich in oil, but hitherto any further information on such oils seems to have been lacking.

The sample of calamary oil examined by the author was obtained from the Yokohama Fish Oil Company; it was produced in Miyako-chô in the Iwaté prefecture. The oil is a brownish red liquid of a very unpleasant odor; when spread on skin, a fishy smell peculiar to fish oils was observed. The taste is also very disagreeable. Cooled by ice, it solidified in a few hours. With concentrated sulfuric acid, a dark brown coloration with a slight purple tinge was formed. The chief properties of the oil were determined with the following results:

Specific gravity (15°/4° C.)	0.9316	Unsaponifiable matter	1.14%
Acid value	3.88	Glycerine (extraction method)	10.24%
Saponification value	189.64	Oxidized acids	0.69%
Iodine value (Wijs)	177.02	Melting point of the mixed fatty acids	35–36°C.
Refractive index (20° C.)	1.4806	Polybromide of the mixed fatty acids	57.45%
Butyro refractometer (20° C.)	84.0		

The polybromide was obtained by dissolving the mixed fatty acids in ether, and dropping bromine into the ice-cooled solution. It is a white powder, turning brown at 200° C. and decomposing at 240–250° C. without previous melting. Its bromine content was determined to be 70.91 per cent by the Carius method.

Calamary oil dries in the air when exposed in a thin layer, the drying property nearly corresponding to that of sardine oil.

The oil is not refined by Kambara earth with good results. It is best refined by alkali in the following way:

To 100 g. of the oil, 5 cc. of 20 per cent aqueous solution of caustic soda is added and stirred well. On gentle warming to about 60–70° C. the brown emulsion "breaks," with the separation of a dark viscous precipitate of coloring matters and impurities (the brown coloration is probably due to the soaps of oxidized acids). A little further heating suffices, and the oil is then filtered from the precipitate. The refined calamary oil is pale yellow; its smell somewhat recalls that of cod liver oil, the unpleasant odor being nearly removed.

The Yokohama Fish Oil Company values the calamary oil as about equal to herring oil. The refined calamary oil may be used as a substitute for cod liver oil, although its medicinal effects require some investigation. The oil may also be used for tanning, burning and soap-making purposes.

The oil, especially the refined, is easily hydrogenated by nickel catalyzer, giving, according to the author's experiment, a white tallow-like fat of m. p. 43–44° C. and iodine value 49.25.

The chief use of the oil will, therefore, probably be as a raw material for hardened oils, as its price is below that of other fish oils.

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[1] See U. S. Patents to Ellis, Nos. 999,439, 999,708 and 1,005,818.

ON HARDENED CHRYSALIS OIL

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Raw chrysalis oil is unsuitable for the purpose of hydrogenation, as its nitrogenous and other impurities largely affect the activity of the catalyzer, even if we neglect the dark color and bad odor of the oil. However, the refining of chrysalis oil is by no means an easy one; but the process proposed by the author, which essentially consists in heating the oil with 5 to 10 per cent by vol. of dilute sulfuric acid (sp. gr. 1.39) and then treating it with Kambara earth, gives an excellent result.[1] The refined oil hardened by nickel catalyzer is a white fat which may be used as a useful raw material for soap-making.

The composition of chrysalis oil has been as yet little investigated. The results of experiments published by the author some years ago appear to be the only report on this subject.[2] According to this report, the fatty acids of chrysalis oil consist of about 25 per cent saturated and 75 per cent unsaturated acids (iodine value 178.73). Among the saturated acids, palmitic acid was identified; stearic acid is probably not present. The unsaturated acids consist of oleic, linolenic and isolinolenic acids; besides them, some isomers of linolic acid are present in a somewhat large quantity.

If the conclusion of the above-mentioned investigation be really the case, the final product of the hydrogenation of these unsaturated acids must be stearic acid. A study of the product is important from the point of view of utilizing the hardened chrysalis oil for technical purposes. The author made a few experiments which are described below.

I—HYDROGENATION OF THE UNSATURATED (LIQUID) FATTY ACIDS OF CHRYSALIS OIL

Fifty grams of chrysalis oil[3] were saponified in a flask with 38 cc. of 50 per cent aqueous solution of KOH and 113 cc. of 96 per cent alcohol, by warming on a water bath; the excess of alkali was neutralized with acetic acid and 500 cc. of 7 per cent aqueous lead acetate solution was stirred into. The resulting lead soap was twice washed with 500 cc. of hot water and treated with 500 cc. of ether at 10° C. and then filtered (Tortelli and Ruggeri's method). The filtrate was then treated with dilute HCl, in order to decompose the lead soap, and was well washed with water: 250 cc. of the ethereal solution of the free unsaturated acids thus obtained, which contains about 20 g. of the acids of iodine value 176.17, were transferred into a strong glass bottle; 0.5 g. of Loew's platinum black was added.

The bottle was then connected to a hydrogen holder.[4] On expelling the air from the bottle by hydrogen, it was strongly shaken by means of a mechanical contrivance. After $3^1/_2$ hrs. shaking, a loss of about 2900 cc. of hydrogen was observed on the holder. Here the hydrogenation was stopped for a time. On evaporating off the ether, a residue amounting to 17.52 g. was obtained. It was a brown-yellow crystalline mass which when melted formed a brown-red liquid; it melted at 56.2° C., having the neutralization value 188.92 and iodine value 45.91. The hydrogenation was apparently incomplete; but before continuing the operation, it was found better to remove the unsaponifiable and coloring matters from the product.

Eleven grams of the above product were saponified with 50 cc. of 8 per cent alcoholic solution of NaOH; then 5 g. of $NaHCO_3$ and about 50 g. of pure sand were thoroughly mixed with it. The mass was dried, powdered and exhausted in a Soxhlet extractor with petroleum ether.

The crude unsaponifiable matter thus extracted was 2.22 per cent. The soap in the extractor was dissolved in hot water and decomposed with dilute HCl and then taken up with ether. The ethereal solution of the fatty acids which appeared brownish yellow, was decolorized with animal charcoal, and made up to 250 cc. by adding ether; then adding 0.3 g. of the platinum black, it was hydrogenized for 2 hrs. in the same way as before (the reading of the volume of hydrogen was omitted).

On evaporating off the ether, 8.3 g. of the hydrogenated acids were obtained. The white crystalline mass had a melting point of 68 to 68.5° C., neutralization value 195.19 and iodine value 0. This product is therefore a saturated compound, which in its m. p. and neutralization value nearly coincides with stearic acid (m. p. 69.3° C., neutralization value 197.5, molecular wt. 284). A mixture of the product with about an equal quantity of pure stearic acid melted at 68 to 68.3° C.

In order to perform the fractional crystallization of the acids, 5 g. of the hydrogenated product were dissolved in 100 cc. of 90 per cent alcohol and separated into three portions successively as follows:

(1) 4.27 g.; white laminae with pearly luster; m. p. 69.5 to 70° C.; neutralization value 197.82; mean mol. wt. 283.59. A mixture with pure stearic acid melted at 69.5 to 69.7° C.

(2) 0.21 g.; m. p. 68° C.; neutralization value 197.20.

(3) Residue left on evaporating the mother liquor, 0.41 g.; a little colored solid; m. p. 50° C.; neutralization value 177.42.

The low m. p. and neutralization value are probably due to the accumulation of the impurities in this part and also to the esterification of the acids on evaporating off alcohol.

The result of the elementary analysis of (1) was as follows:

0.1245 gave 0.3487 CO_2 and 0.1439 H_2O; C = 76.39; H = 12.84.
$C_{18}H_{36}O_2$ requires C = 76.06; H = 12.68.

Therefore, the substance was confirmed to be stearic acid.

From the above experiment, it was concluded that the hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.

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[1] *J. Chem. Ind., Tokyo,* **17**, No. 191; *Chem. Rev.,* **1914**, 58.

[2] *J. Coll. Eng., Tokyo,* **4** (1908), No. 3; *J. Soc. Chem. Ind.,* **1908**, 455.

[3] This sample of the oil was procured from an oil factory in Ibaraki prefecture. It had the following properties: acid value 104.84, saponification value 187.03, and iodine value (Wijs) 140.33.

[4] Hydrogen was prepared by pure zinc and dilute H_2SO_4, and passed through the wash bottles containing concentrated potassium permanganate solution and concentrated H_2SO_4.

II—ON THE SATURATED (SOLID) FATTY ACIDS OF CHRYSALIS OIL

Although the saturated acids have no direct relation to hydrogenation, an experiment supplementary to the former investigation[1] was performed as follows: The impure lead soap of the solid fatty acids obtained in the previous experiment on the liquid acids, was carefully detached from the filter paper and heated in a beaker with dilute HCl. The acids were then dissolved in ether and decolorized with animal charcoal. The crude solid acid which was left on evaporating off the ether, formed a yellow colored crystalline mass. The yield amounted to 11.5 g.

By dissolving in 100 cc. of 96 per cent alcohol, it was fractionally crystallized into five parts.

(1) 3.78 g.; granular crystals; on melting, solidifies to a grayish white mass; m. p. 55–55.5° C.; neutralization value 205.09.

(2) 1.40 g.; m. p. 55.5–56° C.; neutralization value 209.30.

(3) 0.77 g.; somewhat granular crystals, faintly yellow; m. p. 56.5° C.; neutralization value 210.70.

(4) 0.21 g.; pale yellow laminae; m. p. 57° C.

(5) 3.61 g.; residue from the mother liquor; an orange-yellow soft mass.

A mixture of 3 g. consisting of 2.2 g. of (1) and 0.8 g. of (2) was dissolved in 100 cc. of 96 per cent alcohol and fractionally precipitated with magnesium acetate into the following fractions:

(1) 0.9895 g.; m. p. 55.5° C.; neutralization value 203.22; mean mol. wt. 276.05.

(2) 0.4920 g.; m. p. 56° C.; neutralization value 205.43; mean mol. wt. 273.09.

(3) 0.4305 g.; m. p. 59° C.; neutralization value 207.98; mean mol. wt. 269.74.

(4) 0.4785 g.; m. p. 60.5–61° C.; neutralization value 215.25; mean mol. wt. 260.16.

(5) No precipitate was obtained by adding an excess of the precipitant. Therefore, it was abandoned. (The acid contained in this part corresponds to 0.6095 g.)

The result is not decisive, but it is certain that an acid or acids higher than palmitic are present. The mean molecular weight of about 270 seems to point to the presence of daturic acid, $C_{17}H_{34}O_2$. But as by repeated precipitations, the m. p. and neutralization values are regularly changed a little, it is more probable that the substance under examination consists of an eutectic mixture of stearic and palmitic acids.

III—DETECTION OF HIGHER SATURATED FATTY ACIDS IN HARDENED CHRYSALIS OIL

To decide whether the hardened chrysalis oil contains saturated acids higher than stearic, the author applied the method proposed by H. Kreis and E. Roth[2] which had been modified and applied to the analysis of the hardened oil by W. Normann and E. Hugel.[3]

Ten grams of the mixed fatty acid obtained from a hardened chrysalis oil[4] (an oil from Nagano prefecture hardened by means of nickel catalyzer) were dissolved in 100 cc. of 96 per cent alcohol in a flask. By heating it on a water bath, 0.75 g. of lead acetate dissolved in 50 cc. of alcohol was added. On cooling the solution to the room temperature (20° C.), it was soon filtered through a filter paper; the precipitated lead salt was washed well with alcohol and decomposed by dilute hydrochloric acid. The free acid was taken up with ether, and washed free from the mineral acid; the ether was then evaporated and a white solid acid was left.

It was dissolved in 25 cc. of 90 per cent alcohol and cooled to room temperature for 30 min. The mother liquor was filtered off; the deposited crystals were dried by pressing between dry filter papers. It was then twice dissolved in 12.5 cc. and 6 cc., respectively, of 90 per cent alcohol by repeating the same treatment as above.

The final deposit weighed 0.35 g. and consisted of nacreous laminae; m. p. 69.5–70° C.; neutralization value 194.76. This substance was, therefore, identified as stearic acid. No saturated acid higher than stearic was found in the hardened chrysalis oil. This result is in a good accordance with that obtained in the previous experiment.

IV—INNER IODINE VALUE OF HARDENED CHRYSALIS OIL

It has been shown by J. Marcusson and G. Meyerheim,[1] that the inner iodine values of hardened fish oils are higher than 100, whereas lower values are found in the cases of hardened terrestrial animal oils. With a sample of "Talgol" which is of fish oil origin, they found a value of 107.

While belonging to a class of terrestrial animal oils, as chrysalis oil has a high iodine value, it appears not unlikely that the inner value of the hardened product still exceeds 100, and so in this respect it may resemble fish oils. To determine this, the author used the following two oils for examination:

(A) The same sample used in the previous experiment III.

(B) A hardened oil having the following properties: m. p. 56–56.5° C.; acid value 57.46; saponification value 191.08; iodine value 45.53. [The *original* chrysalis oil was the same as (A), the time of hydrogenation only being different.]

Three grams of the sample were treated in a manner equivalent to Tortelli and Ruggeri's method. After keeping at 6 to 10° C. for $2^{1}/_{2}$ hrs., the ether solution of the lead soap was filtered off and decomposed with hydrochloric acid.

The iodine values were determined by Wijs' method. The inner iodine value of Sample A[2] was 87.60; of Sample B, 103.22, nearly approaching that of "Talgol."

In spite of the low iodine value (45.53) of Sample B, the inner value was comparatively very high. So, for a sample of the hardened chrysalis oil which has an iodine value near to that of "Talgol" (iodine value 65 to 70), a still higher inner value may be expected.

Of course, the process of hydrogenation, *i. e.*, the catalyzer, temperature, time, and method of stirring, etc., will essentially influence the inner iodine value

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[1] *Loc. cit.*

[2] *Chem.-Ztg.*, **1913**, 58.

[3] *Ibid.*, **1913**, 815.

[4] *Chem. Rev.*, **1914**, 58. This sample is the No. B hardened oil. Its properties are as follows: m. p. 56° C.; acid value 57.16; saponification value 190.71; iodine value 35.81.

[1] *Z. angew. Chem.*, **1914**, 201.

[2] The liquid fatty acids of this sample obtained as above, solidified at the room temperature. It seems, therefore, to have contained more or less solid fatty acids.

of the product. That hydrogenation takes place by degree according to the unsaturation of the fatty acids, will not always be anticipated. It will be, therefore, unsafe to attach too much importance to the inner iodine value of a hardened oil without taking into account the iodine value of the oil itself. For hardened chrysalis oil of an iodine value above 50, an inner iodine value exceeding 100 may probably be expected.

V—SUMMARY

The results of the present investigations may be summarized as follows:

I—The hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.

II—Besides palmitic acid, some higher saturated acid or acids are present in chrysalis oil. This substance is probably an eutectic mixture of stearic and palmitic acids.

III—By the Kreis and Roth method, no saturated acid higher than stearic was found in the hardened chrysalis oil.

IV—An inner iodine value exceeding 100 may probably be expected in the case of a hardened chrysalis oil having the iodine value above 50.

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THE USE OF DIPHENYL GLYOXIME AS AN INDICATOR IN THE VOLUMETRIC DETERMINATION OF NICKEL BY FREVERT'S METHOD

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A volumetric method for determining nickel in iron and steel as devised by H. L. Frevert was published in Blair's "Chemical Analysis of Iron," 7th edition, 1912. Since that time the method has been constantly in use in this laboratory, but inasmuch as some small changes have been made from time to time it seems best to republish the method with these modifications. Accordingly we give below Frevert's method as originally proposed, except for the modifications mentioned above, and follow it with a discussion of the use of diphenyl glyoxime as an indicator.

FREVERT'S METHOD FOR THE DETERMINATION OF NICKEL IN STEEL

(A) SOLUTION OF THE SAMPLE—For ordinary nickel steels, a 1-g. sample is taken, but with less than 0.10 or more than 5 per cent of nickel, larger or smaller samples may be taken. In the absence of more than small amounts of chromium, solution is most rapid in 50 cc. of hot dilute nitric acid (sp. gr. 1.13), but with chromium present in amounts greater than 0.5 per cent, or under circumstances where chromium carbides are present, more satisfactory results are obtained by dissolving the sample in 60 cc. of dilute hydrochloric acid (1 : 1) with the aid of heat. When solution is complete, the iron and the carbides are oxidized by adding nitric acid, drop by drop, until effervescence ceases. Boiling removes the products resulting from the decomposition of the nitric acid after which the solution is cooled. The quantities of acid given here are those which are convenient for use with samples of 1 g. or less.

(B) PRECIPITATION OF NICKEL DIMETHYL GLYOXIME—The solution obtained, as described above, is rapidly cooled by the addition of a lump of ice, after which are added in succession, 12 g. of citric acid or equivalent solution, 20 cc. ammonia water (sp. gr. 0.90), sufficient solution of dimethyl glyoxime to precipitate all nickel present and enough more ammonia to make the solution distinctly ammoniacal. The mixture is thoroughly stirred after each of these additions. The solution of dimethyl glyoxime is prepared by dissolving 20 g. of the reagent in 1300 cc. of ammonia water (sp. gr. 0.90), after which enough water is added to bring the volume up to 2000 cc. Ten cc. of this solution allow sufficient excess to completely precipitate 1.5 per cent of nickel in a 1-g. sample, *i. e.*, about 0.0150 g. of nickel.

(C) TREATMENT OF NICKEL DIMETHYL GLYOXIME PRECIPITATE—When the amount of nickel is small (0.10 per cent or less), time must be allowed for complete precipitation—an hour is usually ample. With amounts larger than this, no danger of low results attends immediate filtration. For this purpose an asbestos mat on a 2-in. perforated porcelain plate or a Buchner funnel may be used. The solution containing the suspended precipitate will usually have a volume of 200 to 250 cc. It should be stirred thoroughly and poured on to the asbestos mat in such a way that the funnel always remains partly filled with liquid. Strong suction should be avoided. Quantities of precipitate corresponding to less than 5 per cent of nickel in a 1-g. sample rarely cause trouble in filtering, but the difficulty rapidly increases with larger amounts. When all of the precipitate has been transferred to the asbestos, it is thoroughly washed with water. Both wash water and filtrate are discarded, although the latter may be tested with dimethyl glyoxime if it is believed that all of the nickel may not have been precipitated.

(D) SOLUTION AND DECOMPOSITION OF THE PRECIPITATE—The receiving flask and tip of the funnel are next well rinsed with water. With the mat still in place, but with suction off, enough nitric acid is added to cover the asbestos to a depth of $^1/_8$ in. After a minute, suction is applied, the acid drawn through the filter and about as much more added, taking care to cover the entire surface. At this point there should remain no visible trace of the red precipitate. The mat is now to be thoroughly washed with water, the washings being collected in the flask with the acid. The solution so obtained is then transferred to a 400 cc. beaker in which it is heated to boiling. Here the solution is allowed to cool slightly to facilitate the addition of 1 g. of either potassium chlorate or ammonium persulfate. The solution is boiled until clear; this usually involves a considerable reduction in bulk, often as much as 50 per cent. Insufficient boiling may cause trouble (1) through failure to decompose the dimethyl glyoxime, which would reprecipitate when the solution is subsequently made ammoniacal, or (2) because if the solution is not freed from oxidizing products of the chlorate or persulfate decomposition the indicator which is used to determine the presence of an excess of ammonia may be destroyed.

A cheaper and somewhat simpler device for dissolving and decomposing the dimethyl precipitate consists in treating it with 50 cc. of a mixture made up of 40 cc. of hydrochloric acid and 10 cc. of nitric acid. This acid filtrate and the wash waters when evaporated to a bulk of 50 cc. will be found to be free from dimethyl glyoxime and ready for the next step, the neutralization with ammonia.

(E) THE NEUTRALIZATION OF THE ACID NICKEL SOLUTION WITH AMMONIA—The cooling of the acid solution may be hastened by adding ice. Neutralization need not be made with great care, but it is well not to have the excess of ammonia indefinitely large: 5 cc. of strong ammonia water in excess of that necessary to neutralize 300 cc. of solution causes no harm, but quantities larger than this interfere. Out of several indicators tried, rosolic acid showed more stability in this solution than any other. Strong ammonia is usually added rapidly in excess. Dilute nitric acid and dilute ammonia are then used to complete neutralization, leaving a slight excess of ammonia. The red color of the indicator seems to have a beneficial effect upon the subsequent titration of the nickel. The volume should be 250 cc.

(F) TITRATION OF THE AMMONIACAL NICKEL SOLUTION—Titration is made with potassium cyanide, using silver iodide as indicator. In this connection solutions containing 8.0 g. potassium iodide, 0.5 g. silver nitrate, and 4.6 g. potassium cyanide per liter are used. The strength of the potassium cyanide solution is so adjusted that 1 cc. of the solution is equal to 0.0010 g. of nickel. This is accomplished by comparison with a nickel solution of known nickel content, or with a standard steel.

To make the titration, exactly 10 cc. each of the potassium iodide and silver nitrate solutions are added (with stirring), followed by the potassium cyanide. The first additions of potassium cyanide increase the turbidity of the solution, and up to this point the addition of the cyanide may be rapid. From then on, it is added in rapid drops (with stirring) until the turbidity is about the same as before adding any cyanide. The last 15 to 20 drops are added slowly, the end-point being taken as the disappearance of the last trace of turbidity. The cyanide added of course titrates the silver iodide as well as the nickel, and the result therefore must be corrected by the subtraction of a blank. To determine the blank, add 10 cc. each of the potassium iodide and silver nitrate solutions to a nickel solution which has been titrated and which has the volume at which titrations are usually made, and titrate with KCN. By repeating this several times with the same solution an average blank will be obtained which may be regularly used where these conditions apply. In this laboratory the blank has been found as 1.00 cc. of potassium cyanide solution, and this blank is accordingly subtracted from all titrations before calculating the result. The formula for calculating percentage of nickel in the sample is

$$\frac{\text{Number of cc. of KCN} - \text{blank}}{\text{Number of grams in sample} \times 10} = \text{per cent of nickel.}$$

(G) SOME DETERMINATIONS OF NICKEL IN STEEL—Sample A is a sample of steel prepared as a private standard which has been analyzed in this laboratory by a number of methods and found to have 3.03 per cent nickel. This sample is analyzed by this method twice daily as a check on the determination. The last fifty determinations made average 3.03(06) with the highest value 3.08 and the lowest 3.01.

Samples 32 and 33 are samples prepared at the Bureau of Standards. Our analyses with the official figures are given below:

Bureau of Standards Sample		Official Value	Per cent Ni Found			
No.	Name		Four determinations			
32	Chrome Nickel Steel	1.62% Ni	1.63	1.64	1.62	1.64
33	Nickel Steel	3.33% Ni	3.34	3.32	3.34	3.32

THE USE OF DIPHENYL GLYOXIME[1] AS AN INDICATOR

In outline, the method consists in adding a measured excess amount of standard potassium cyanide solution to an ammoniacal solution of the nickel salt. A quantity of the indicator is then added and the excess of potassium cyanide titrated with standard nickel sulfate solution. In the early work on the method, the more widely used dimethyl glyoxime was employed as an indicator. This was suggested by Lundell[2] in an article in which he uses this method in the analysis of cyanide solutions. Our experience with this reagent demonstrated that it was unsuited to use as an indicator in the determination of nickel because the results were found to vary with the concentration of the indicator in the solution and with the excess of cyanide used. Theoretically diphenyl glyoxime is open to the same objections as the above reagent except in one respect, *viz.*, that owing to the lower solubility of its nickel complex it is not necessary to use the indicator in as high concentrations as was found to be necessary with dimethyl glyoxime.

A solution of the diphenyl glyoxime was obtained by dissolving 1 g. in a solution of 5 g. NaOH in 100 cc. of water. This was diluted to 1000 cc. Wetting the diphenyl glyoxime with alcohol before treating it with the sodium hydroxide often helps in obtaining more rapid solution. A solution of nickel sulfate was prepared which contained about 0.001 g. of nickel per cc. This was a convenient strength, for in working with a 1 g. sample of steel 0.1 cc. corresponded to 0.01 per cent of nickel. It was standardized by titration against potassium cyanide solution of known strength, using silver iodide as indicator. The titration by the method described here was made by making the nickel solution alkaline with ammonia, adding a measured excess of potassium cyanide solution, followed by a quantity of the indicator, and titrating with standard nickel sulfate solution. All titrations were carried on in a volume of 250 cc., and with every change in the amount of indicator solution used a new blank was determined, using the same volume of water and 5 cc. of ammonia (sp. gr. 0.90).

FACTORS UNFAVORABLE TO THE METHOD—Early in

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[1] This reagent was recommended as a quantitative precipitant for Ni by Atack, *J. Chem. Soc.*, **103**, 1317.

[2] *Trans. Am. Electrochem. Soc.*, **25** (1914), 369.

the work on this method it was noted that it is unfavorably affected by (1) the presence of salts of strong acids or bases in more than small amounts (2 to 4 per cent), (2) by strong bases, (3) by weak bases to a less extent, and, of course, (4) by acids. Salts such as the chlorides, nitrates and sulfates of sodium, potassium or ammonium, in quantities of more than 4 per cent in the solution to be titrated, caused precipitation of the indicator and prevented its reaction with the nickel salt when this was present in excess. Strong alkalies, such as sodium hydroxide, in amounts greater than traces, entirely prevented the reaction between the nickel salt and the indicator. Quantities of ammonia corresponding to a concentration greater than two parts of strong ammonia in 100 parts of solution, made the end-point unsatisfactory. The fact that the titration depended upon the formation of the double cyanide of course made the absence of free acid necessary.

THE CONCENTRATION OF THE INDICATOR—In the results showing the variation in values obtained upon the nickel sulfate solution itself with a constant concentration of ammonia and differing concentration of indicator and nickel, the cyanide solution was of such strength that each cc. was equivalent to 0.001 g. of nickel; the nickel sulfate solutions contained 0.00106 g. of nickel per cc.; all titrations were made at room temperature in a volume of 250 cc. The results clearly indicated that 1 cc. of the indicator was too little to use. As we increased the concentrations of the indicator a point was reached where the end-point tended to appear too soon by larger and larger amounts. Titrating in a volume of 250 cc. with nickel solution of the concentration used here, 5 cc. of the indicator solution appeared to us to be the best amount. It is probable, however, that in titrating in smaller volume or with more concentrated nickel solution, it would be desirable to use less indicator; and on the other hand a larger amount of indicator would probably prove convenient if the titration were carried on in larger volume, or if a more dilute nickel solution were employed. The conditions which determine the amount of indicator and the concentration of nickel solution are that the amount of indicator shall be such as to give a definite color indication, yet avoid such concentrations in either nickel solution or indicator as will cause the precipitation of the nickel diphenyl glyoxime complex as a consequence of the momentary appearance of a local excess of nickel during the titration.

THE CONCENTRATION OF AMMONIA—Below are given results showing the effect of moderately high concentrations of ammonia upon the titration. In these experiments the indicated quantities of ammonia (sp. gr. 0.90) were added to 10 cc. portions of a solution of nickel salt which had previously been made barely alkaline with ammonia. The volume at titration was 250 cc., containing 5 cc. of indicator, 11 cc. of KCN solution and 0.106 g. nickel.

Ammonia used	5 cc.	5 cc.	10 cc.	10 cc.	15 cc.	15 cc.
Nickel found (g.)	0.0107	0.0108	0.0092	0.0104	0.0100	0.0089

It is evident from these results that there is a maximum above which the concentration of ammonia should not go. A large number of determinations not shown here lead the authors to believe that equally good results may be obtained from any concentration from the minimum necessary to maintain the alkalinity of the solution during the addition of the nickel solution, up to 5 cc. of ammonium hydroxide (sp. gr. 0.90) in 250 cc. of solution. This wide margin makes neutralization comparatively easy, for in working with dilute ammonia several cc. in excess may be added without harm and the sense of smell is a sufficiently good indicator.

THE PREPARATION OF THE NICKEL SOLUTION FOR TITRATION—The nickel in the samples is separated from the iron and other constituents of the steel as described above under Frevert's method, Sections A, B and C. The solution of the precipitate is different from that given under Section D, however, with the object of avoiding a high concentration of salts in the resulting solution. Concentrated hydrochloric acid containing 10 per cent nitric acid is poured over the precipitate to dissolve it. Solution proceeds less rapidly than when nitric acid is used, but if the suction is not strong, no difficulty will be encountered in dissolving the precipitate in about 50 cc. of acid. Care must be taken that every visible trace of the red precipitate has disappeared before proceeding to the next step which consists in washing the asbestos with about 100 cc. of water. The total filtrate, having a volume of 150 cc., is now evaporated to small bulk. The combination of nitric acid and hydrochloric acid serves to oxidize the dimethyl glyoxime which would otherwise precipitate as the nickel complex upon subsequent addition of ammonia. The evaporation is carried almost to dryness in order to keep the concentration of ammonium salt, which will be formed when ammonia is added, down to the lowest possible value. If some separation of salt has occurred, a drop of either nitric or hydrochloric acid may be added, along with water enough to take it up. The volume of the solution is raised to 150 to 200 cc. by the addition of water and about 5 cc. of dilute hydroxide solution (1 to 3) added. (If this amount of ammonia water is not enough to render the solution alkaline, evaporation has not been carried far enough and trouble may be met later through precipitation of the indicator.) The solution is now ready to titrate and accordingly standard potassium cyanide solution is added with stirring until the opalescence (or bluish tinge) disappears, after which a further quantity of about 15 cc. is added. The next addition is of 5 cc. of the indicator solution which is followed by titration with standard nickel solution.

THE ANALYSIS OF SAMPLES OF STEEL—In Table I are given results obtained in the analysis of steels with and without added nickel solution.

TABLE I—ANALYSIS OF STEELS

Sample	Gram Nickel Added	Per cent Ni Found Duplicates		Per cent Ni Theoretical
A	None	3.03	3.03	3.03
A	0.0053	3.58	3.57	3.56
A	0.0106	4.08	4.07	4.09
A	0.0212	5.18	5.18	5.15
B. of S. No. 32	None	1.63	1.64	1.62
B. of S. No. 33	None	3.30	3.31	3.33

SUMMARY

I—In the foregoing paper, Frevert's excellent method for the determination of nickel has been restated in amplified form and methods for avoiding all of the ordinary difficulties have been indicated.

II—A new indicator has been suggested for use in the titration which may find favor with some who prefer the appearance of a color as an end-point to the disappearance of an opalescence.

III—Both methods are more accurate than any volumetric method for determining nickel in steel which does not involve the separation of the iron, and more rapid and less laborious than those which do. By Frevert's method a single determination of the nickel in a sample of steel may be made in 25 min. even in the presence of chromium. A trained operator can make 50 or more determinations in a day of 8 hrs. The method employing diphenyl glyoxime as indicator requires 35 to 40 min.

IV—While the methods are perhaps slightly less accurate than the method which involves weighing the precipitate of Ni-dimethyl glyoxime, the greater speed which is possible in routine determinations more than compensates for so small a loss in accuracy.

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THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOL AND WATER IN ETHER FOR ANAESTHESIA

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A recent study of the methods for the detection of the common impurities in ethyl ether by one of the writers made it seem desirable, on the grounds of completeness, to have a method for determining quantitatively the amounts of alcohol and water in anaesthetic ether. No claims for originality are made for the method given in the following pages since it is a development of one already used. Pure ether dissolves only about 1 per cent of water. Anaesthetic ethers in this country never contain more than 3 or 4 per cent of alcohol. Obviously, therefore, we are dealing with small quantities and extreme accuracy cannot be claimed. The results obtained by applying the method to five well-known brands of anaesthetic ether are given.

Of the numerous methods proposed for the detection of water in ether, only the colorimetric procedure with rosaniline acetate,[1] the bluing of anhydrous copper sulfate when brought into contact with moist ether,[2] the evolution of gas by amalgamated aluminum,[3] and the determination of the density before and after dehydration by potassium carbonate,[4] appeared to be applicable to the quantitative estimation of water in fairly pure ethers.[5]

A set of standard ethers containing respectively 0.1, 0.25, 0.5, 0.75 and 1.0 per cent water by weight was prepared. Five milligrams of dried rosaniline acetate were placed in a dry test tube and 10 cc. of ether added. The colors varied but the differences were not sufficiently marked to allow placing some seven ethers containing varying amounts of alcohol and water in between known members of the series using the eye to judge the tints.

Anhydrous ether containing 0.1 per cent of absolute alcohol gives a wine-yellow color different from the above colors. It would require considerable study to perfect the method even if the tint produced by alcohol could be shown not to interfere.

Ten milligrams of copper sulfate finely powdered and well dried at 220° C. were shaken with 10 cc. of each of the above standard ethers. After 15 min. the copper sulfate showed no change from its original light gray color in ether containing 0.1 per cent water, but in ether containing 0.5 per cent water, the salt became bluish and the difference between the ethers containing 0.5 per cent, 0.75 per cent and 1 per cent could be detected. After about half an hour the sample containing 0.25 per cent could be placed in its proper position below the 0.5 per cent sample. The seven unknown ethers could be placed in this series more satisfactorily than in the previous method, but the procedure is at best only an approximation.

Contrary to the experience of Baskerville,[1] we had no success with amalgamated aluminum although considerable effort was spent upon this reagent because it is stated to have the advantage of being uninfluenced by alcohol. We have observed the evolution or disengagement of small bubbles even when the amalgam is placed in pure ether rendered anhydrous by metallic sodium and ether containing 0.1 per cent of water showed no evident increase in the amount of gas liberated. It is not easy, therefore, to distinguish what degree of bubbling indicates the presence of water. Bein,[2] working with a dilatometer filled with pure ether at 25°, experienced great difficulty due to the disengagement of small gas bubbles from the slightest jarring of the instrument. The amalgam offering many sharp points might be expected to have a greater effect.

In passing, mention may be made of the fact that the test for the detection of water in ether by shaking with carbon bisulfide is valueless, for, where alcohol is present, little or no turbidity is produced.[3]

We also tried subjecting ether to a temperature of about —70° C. produced by carbon-dioxide-snow and acetone, in order to freeze out the water as a hydrate of ether.[4] The presence of about 0.1 per cent of added water may be detected in alcohol-free anhydrous

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[1] *Squibb's Ephemeris*, **2** (1884), 594.

[2] Adrian, *Mon. Sci.*, **44**, ii, 835.

[3] Wislicenus and Kaufmann, *Ber.*, **28**, 1325.

[4] Regnauld and Adrian, *J. Pharm. et Chem.*, [3] **45** (1864), 193.

[5] Prof. Frankforter's valuable test (*J. Am. Chem. Soc.*, **37**, 2566) for the detection of water in ether was not published until after the experimental work in this paper had been completed. A few trials indicate that it is far more delicate than the known tests. It would be desirable to make the procedure quantitative if possible.

[1] This Journal, **3** (1911), 312.

[2] W. Bein, "Zur Ausdehung des Aethylaethers und einiger mischungen des Aethers mit Aethylalkohol" Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs-Kommission. Metronomischen Beitrage, Heft. VIII, p. 11.

[3] Squibb (*Squibb's Ephemeris*, **2** (1884), 594) states that absolute ether after the addition of 0.1 per cent of "watery alcohol" does not show the faintest cloudiness upon admixture of equal volumes of oil of copaiba or carbon disulfide.

[4] Berthelot, *Compt. rend.*, **86**, 765; also Franchimont, *Ber.*, **10**, 830.

ether by the appearance of a slight cloudiness, but the presence of a few per cent of alcohol destroys the sensitiveness of the reaction.

Tyrer[1] found that the amount of water present in alcohol-free "wet" ether could be accurately determined by measuring the solubility of cadmium iodide in the ether since the solubility is greatly influenced by small additions of water. The method is not applicable, however, when alcohol is present because alcohol increases the solubility of cadmium iodide considerably and after preliminary trials we abandoned it altogether.

REGNAULD AND ADRIAN'S RESULTS

Obviously the density of ether is influenced both by the presence of alcohol and of water, and affords no insight into the proportion in which they exist in any given sample. This proportion is dependent upon laws of distillation. At 25° C. according to our experiments, the addition of 0.1 per cent of water to pure ether increases the specific gravity about 0.0004, or four times as much as the same amount of pure alcohol. Regnauld and Adrian[2] determined the water from the change in density produced after absorbing the water by means of a dehydrating agent. The density of the resulting mixture which then consisted only of ether and alcohol indicated the quantity of alcohol present. They found that while potassium carbonate, which proved to be the best dehydrating agent for the purpose, removed the water completely from ether in the absence of alcohol, it was unable in the presence of alcohol to dehydrate the alcohol beyond 98 per cent by volume. This conclusion rested upon the fact that the densities of mixtures containing respectively 5 cc. of alcohol (98 per cent by volume) + 95 cc. of pure ether and 35 cc. of (98 per cent by volume) alcohol + 65 cc. of pure ether showed no change after treatment with anhydrous potassium carbonate. Since their densities were expressed only to the third place, having been taken by means of a hydrometer, it seemed desirable to test the point more accurately, especially since it can be shown that the effect of 2 per cent of water in the 5 cc. of alcohol of the first mixture is of sufficient magnitude to increase the density only about three in the fourth place.

Having convinced ourselves by some preliminary trials that potassium carbonate is insoluble in ether containing 4 per cent of absolute alcohol and that it removes water, if present, more completely than Regnauld and Adrian believed, we proceeded to test this point quantitatively. To 100 cc. of pure ether containing 2 per cent absolute alcohol, 0.5 per cent of water was added and shaken. This mixture, before the addition of the water, as will be seen from the density curve, had a specific gravity of 0.71205, ether and water both at 25° C. Forty-five grams of potassium carbonate dried for 5 hrs. at 240 to 280° were added and the mixture allowed to stand for 20 hrs. with occasional shaking, after which the specific gravity was found to be 0.71201. The experiment was repeated with ether, containing 4 per cent absolute alcohol, which had a specific gravity of 0.71424.[1] One-half per cent of water was added and the mixture dried by potassium carbonate after which the specific gravity was 0.71425. It is evident that water is removed quantitatively from ether containing as much alcohol as is likely to occur in anaesthetic ethers, but Regnauld and Adrian's contention that potassium carbonate does not act quantitatively when 35 per cent of alcohol is present is true as the following experiments show.

The specific gravity of a mixture of 300 cc. of pure ether and 162 cc. of absolute alcohol (99.8 per cent) was found to be 0.7435, pycnometer full of water and ether weighed in air[2] at 25°. No change in the density was produced by treatment with potassium carbonate. To reduce the strength of the alcohol to about 98 per cent 2.743 g. of water were added. Carbonate of potassium in the usual proportion of 45 g. per 100 cc. of mixture was added and the mixture allowed to stand with occasional shaking for 44 hrs. The pycnometer now showed a specific gravity of 0.7447 and further treatment with potassium carbonate did not lower it. These results, however, do not agree with the statement of the above authors that potassium carbonate is unable to dehydrate the alcohol in such a mixture beyond 98 per cent by volume since the specific gravity is within 0.0012 of the original figure before the addition of water. Since 0.1 per cent of water raises the gravity in anaesthetic ether 0.0004, 100 g. of the mixture should still contain about 0.3 g. water; in other words, approximately two-thirds of the water has been removed.

THE DETERMINATION OF WATER

We determined the water directly by weighing the potassium carbonate although the method of Regnauld and Adrian appears to be fully as satisfactory. The procedure for determining the water is best illustrated by the following experiment:

To 94 g. of pure ether, dried over sodium, 0.7588 g. of distilled water was added by sealing the water in a glass bulb and breaking under the surface of the ether. Solution therefore contained 0.80 per cent water. Potassium carbonate was dried for 5 hrs. at 250° C. and cooled in a desiccator. About 24 g. of this were put into a glass-stoppered Erlenmeyer flask and then weighed. Seventy grams of the ether-water mixture were introduced and the flask violently shaken on a shaking machine for 8 hrs. It was then removed and allowed to stand for 28 hrs. A calcium chloride tube bent downward having been fitted by means of a cork to avoid the entrance of moisture from without, the flask was partially submerged in water at 50° C. and the ether distilled off through the calcium chloride tube. Without removing the calcium chloride tube, the apparatus was then put

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[1] *Chem. Soc. Proc.*, **27** (1911), 142–143.

[2] *Loc. cit.*

[1] The density of this mixture does not coincide with the other points on the curve. An error was evidently made in the amount of alcohol added in making up the mixture rather than in the density determination since the density after treatment with potassium carbonate agrees with that before treatment. Such an error, however, does not invalidate the experiment since the point here involved is the removal of water.

[2] These determinations were not reduced to the vacuum basis, all others were so reduced.

in an electric oven at 60° C. and dried for about 12 hrs. The calcium chloride tube was removed and a gentle stream of air was drawn through the flask for 30 sec. in order to sweep out the ether vapor. The flask was now stoppered and weighed after cooling in a desiccator.

The calcium chloride tube was replaced and the apparatus again heated for 3 hrs. at 60° C. Air was drawn through as before. The weight was constant to within 1 mg. The increase, due to the absorption of the water, was 0.5717 g., corresponding to 0.82 per cent found as against 0.80 per cent added.

An attempt was made to apply the same method to a similar mixture but containing in addition 3 per cent of alcohol, but no constant weight could be obtained on drying the potassium carbonate, due to the retention of some alcohol. When the temperature of the oven was raised sufficiently to drive out the alcohol, some water was lost. This difficulty was overcome by washing the alcohol from the potassium carbonate with pure anhydrous ether as the following experiment shows: To 243 g. of pure ether, dried over sodium, 2.536 g. of distilled water and 13 cc. of absolute alcohol were added corresponding to 0.99 per cent and 4 per cent, respectively.

About 20 g. of freshly dried potassium carbonate were introduced into a small flask having a long, narrow neck and a ground glass stopper. A glass wool plug was fitted into the neck and the apparatus weighed. Fifty grams of the above mixture were then run in and the flask shaken for 5 hrs. and allowed to stand over night. The ether was filtered out through the glass wool plug but did not come clear, so it was evaporated and the weight of the suspended potassium carbonate added to the calculation. The potassium carbonate was washed successively with three portions of 10 cc. each of absolute ether, introduced and expelled by alternately cooling and warming the flask. The flask was then dried at 60° C. to constant weight, air being drawn through for 30 sec. to remove ether vapor as in the previous experiments. In duplicate determinations the water found was 0.5263 g. and 0.4887 g., corresponding to 1.05 per cent and 0.98 per cent, respectively.

DETERMINATION OF THE DENSITIES OF ETHER-ALCOHOL MIXTURES

Having shown that the water may be determined directly by weighing the potassium carbonate, it remained to construct a curve for alcohol-ether mixtures from which, having given the specific gravity of any mixture after dehydration, the percentage of alcohol may be read off. Mixtures containing by weight 1, 2, 3 and 4 per cent were made by breaking glass bulbs containing the absolute alcohol of 99.9 per cent[1] under pure ether. The latter was prepared by shaking 10 liters of anaesthetic ether five times with 1/2 its volume of distilled water. The ether was then shaken with 3000 cc. of 0.5 per cent NaOH solution in which was dissolved 2 g. of permanganate of potassium.[2] This was done three times, letting the permanganate stand in contact with the ether until reduced to a brown color. After separating, the ether was dried twice over $CaCl_2$ and then over sodium-potassium alloy until no reaction was observable on the alloy. It was now distilled from the alloy through a three-section Young column, discarding the first and last 10 per cent. Before using, the pure ether was tested for peroxide with cadmium potassium iodide and for aldehyde with ammoniacal silver nitrate solution. The ether, just after preparation, was without effect upon both reagents but later it was found to contain a trace of ethyl peroxide, not more than 0.002 per cent as estimated by producing the same tint with aqueous hydrogen peroxide. Such traces are without sensible influence on the specific gravity.

The determinations of the specific gravity were made with a 50 cc. "Squibb" pycnometer having a capillary neck integral with the body. The upper end of the neck terminated in the usual enlargement provided with a ground glass stopper. The body of the pycnometer was cylindrical and about 1 in. in diameter.

Owing to the high coefficient of expansion of ether, we thought it desirable to define the temperature at which we worked quite accurately. Obviously the curve of gravities for different percentages of alcohol in ether would be of most general use if the temperature were defined by the international hydrogen scale. For some, however, it may be easier to construct their own density curve than to reproduce in their thermostat the temperature of 25° C. on the hydrogen scale.

Since the density determinations were made in summer, it was necessary to provide a room having a constant temperature in which to place the thermostat and balance for weighing. An insulated room which was designed for cold storage purposes was provided with an iron tank filled with ice and two large electric heater lamps controlled by a four-bulb glass thermostat filled with ether electrically controlling the heating current by means of a telegraph relay. The air was circulated by an electric desk fan on a shelf in one corner and directed against the wall near the corner diagonally opposite and also toward the ceiling. The two heating lamps were placed under the fan and slightly forward so that the ascending warm air was at once distributed by the fan. The temperature of the room could be held at 25° easily within 0.5°.

An enamelled iron pot 15 in. in diameter and 12 in. deep served as the constant temperature bath or thermostat proper. It was surrounded by another vessel of galvanized iron 3 in. larger in diameter and 1 1/2 in. deeper, thus leaving a space all around of 1 1/2 in. which was packed with ground asbestos-magnesia steam pipe covering. Molten tar was poured on top of this covering to prevent the absorption of moisture. Circulation was maintained in the water by a propeller wheel revolving at high speed, driven by an electric

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[1] Assuming that in the operation the alcohol had absorbed moisture sufficient to lower its percentage to 99.8, the effect on the percentage of alcohol in the mixture is negligible, being less than 0.5 per cent of the absolute amount of alcohol present.

[2] Wade and Finnemore, *J. Chem. Soc.* (*London*), **95**, 1846. For extreme purity further washing with water would be advisable. The ether prepared as above, however, compares favorably as to density with pure ether prepared by other experimenters. See W. Bein, *Loc. cit.*, p. 20.

Table I—Full Data for Curve of Specific Gravities of Alcohol-Ether Mixtures

	June 1914						December 1915		April 1916	
	Temperature when weighed (Hydrogen Scale): 24.99°						25°(a)		24.93°	24.94°
Per cent ether:		100	99	98	97	96	0.100	97	100	96
Per cent alcohol:	(Water)(b)	0	1	2	3	4	...	3	0	4(e)
Weight of full pycnometer	... 78.6572 78.6571	... 64.1966 64.1954	... 64.2492 64.2484	64.2996 64.3028 64.3035	... 64.3505 64.3515	... 64.4412 64.4115	... ... 64.1928	... 64.3487 64.3488	... 64.1961(a) 64.1954(b)	64.3994 64.4006 64.4026
Average	78.6572	64.1960	64.2488	64.3019	64.3510	64.4113	...	64.3488	....	64.4009
Correct on for weights	+0.0007	+0.0007	+0.0007	+0.0007	+0.0007	+0.0007	+0.0008	+0.0007	+0.0007	+0.0007
	....	....	....	....	...	...	...	...	0.0007(a)	...
Correction for evaporation loss	...	0.0005	0.0005	0.0013	0.0009	0.0009	0.0001	0.0003	0.0005(b)	0.0002
	78.6579	64.1972	64.2500	64.3039	64.3526	64.4129	64.1937	64.3498	64.1970	64.4018
Weight empty pycnometer(c)	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665
	49.7914	35.3307	35.3835	35.4374	35.4861	35.5464	35.3272	35.4833	35.3305	35.5353
Correction for reducing to vacuum	0.0530	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550
Wt. in vac. pycnometer contents	49.8444	35.3857	35.4385	35.4924	35.5411	35.6014	35.3822	35.5383	35.3855	35.5903
Volume of pycnometer = 49.9904 cc.(d) Sp. gr. $^{25°}/_{25°}$ = $\frac{\text{Wt. ether} + 1.040533 + 0.9970795}{49.8444 + 1.040550 + 0.9970770}$ =		0.70991	0.71097	0.71205	0.71303	0.71424	0.70985	0.71299	0.70984	0.71396

(a) These determinations were made a year and a half later in another thermostat. The thermometer, which was graduated in tenths of a degree and read by a telescope, had been compared with the standard thermometer a month previous, and this correction used to bring the thermostat to exactly 25°. This temperature is probably accurate to 0.01°.

(b) Freshly boiled distilled water.

(c) After the determinations of April, 1916, the pycnometer was found to weigh within 0.2 mg. of the original weight which has therefore been used throughout for the sake of uniformity. The volume of the pycnometer was not redetermined.

(d) The volume as determined a year previous by three weighings at 25.04° hydrogen scale was 49.9914 cc. Densities of water taken from *Circular* 19, Bureau of Standards, Table I.

(e) The three figures recorded in this column represent successive weighings of the full pycnometer after complete emptying and refilling with fresh portions of the mixture.

motor, and forcing a current downward against the bottom of the bath, thus spreading it in all directions. The cooling due to surface evaporation was found sufficient. The heating coil was made of nichrome wire wound on mica and covered with a jacket of copper foil. The heating coil was controlled by a two-bulb regulator, filled with ether and having a side tube connected by a glass stopcock so that the approximate adjustment of the mercury level could be made by this means. The stopcock was in the portion filled with mercury and no difficulty was encountered on account of leakage. The final adjustment was made by a platinum wire contact controlled by a finely threaded screw. The surface of the mercury making the electrical contact was protected by a layer of glycerin. By means of the resistance of various sizes of incandescent lamps in the circuit, the temperature of the heating element was adjusted so that the heat was just insufficient to maintain the desired temperature in the bath. The regulator controlled, by means of a relay, an additional heating current sufficient to warm the bath slowly, slightly above the desired temperature. In this way the temperature fluctuation was small and the lag due to heat transference was reduced to a minimum.

The thermometer used was a Baudin Standard No. 17730, graduated in 0.1°, and calibrated by the International Bureau of Weights and Measures at Sevres. It was carefully adjusted to vertical position by means of a small plumb bob, and was read by a leveled cathetometer. The thermometer could be easily read to 0.002° and the variation of the bath during any determination never exceeded 0.005°.[1] The coefficient of expansion of ether is such[2] that a change of 0.01° C. in the temperature changes the density a little more than 0.00001. Since it may be questioned whether the fifth decimal figure is entirely significant in the determination of the density of such a volatile liquid as ether, it is evident that the temperature of the bath was defined with sufficient accuracy. The mercury column projected out of the water 12°. A thermometer placed close to the standard thermometer was observed not to vary more than 0.5° during the actual determination, which gives a stem correction of 0.001° C.

The details of the temperature calculation are as follows:

Thermometer reads in bath	25.150°	in ice(a) + 0.100°
Correction for calibration	+0.020	—0.001
Correction, external pressure (b) (barom. = 751 mm. + 159 mm. H_2O)	—0.0003	(barom. + 64 mm. H_2O) +0.0004
Correction, internal pressure	+0.029	+0.008
Correction, zero point	—0.107	+0.107
	25.092	
Correction, fundamental interval	—0.006	
True temp. on mercury scale	25.086	
Converting to hydrogen scale	—0.095	
Final temperature of the bath on hydrogen scale	24.991°	
Uncertainty for exposed stem	±0.001	

(a) The ice point was made after completing the series of weighings at the end of the second day.

(b) The barometer on the second day read 753 mm. but since a difference of 10 mm. affects the temperature reading only 0.001°, the temperature of the bath in the second decimal would not be affected. All corrections were applied as indicated in the pamphlet and tables accompanying thermometers standardized by the International Bureau.

The corrected temperature of the bath while the adjustment of the pycnometer was being made was therefore 24.99° on the international hydrogen scale for the first six columns of Table I. The check determinations in the seventh and eighth columns were made a year and a half later in another thermostat provided with a thermometer which had been compared a month previous with the Baudin standard thermometer. The thermostat was then adjusted to exactly 25°, using this correction. The thermometer could be read to 0.01 by a small telescope and the tem-

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[1] For this degree of accuracy it was thought sufficient to read the mercury column from the front instead of taking the average of both front and back readings in order to eliminate irregularities in the thermometer stem.

[2] Bein, *Loc. cit.*

perature may be assumed to be defined to this degree of accuracy. For the check determination in the last two columns, the same thermostat was used without, however, adjusting to exactly 25° since the standard thermometer was employed, hence the temperatures 24.93 and 24.94 are entitled to the same confidence as 24.99 in the original series; the corrections, being similar to the above, are omitted.

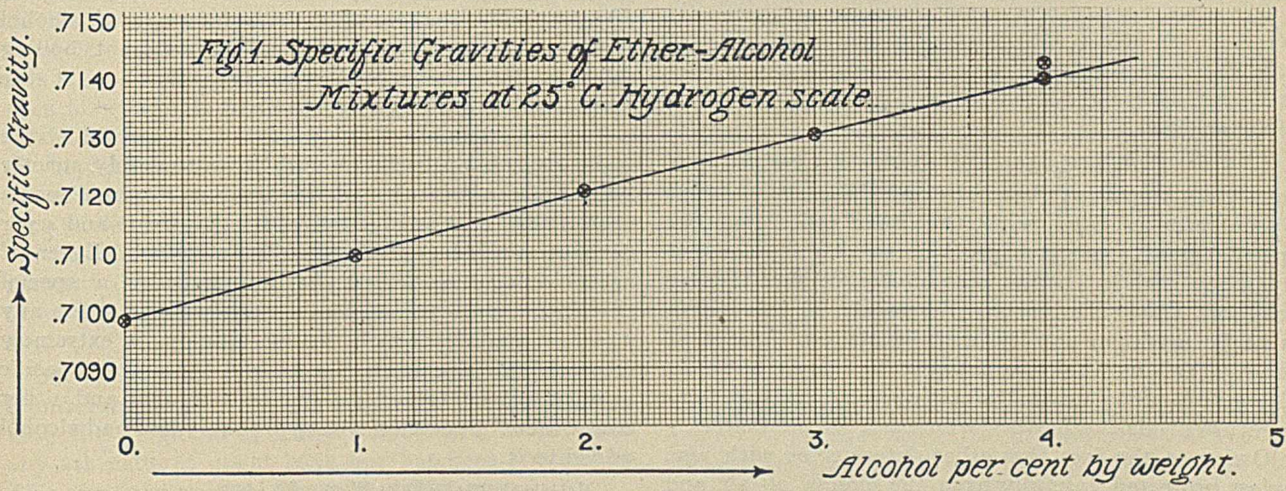

Fig. 1. Specific Gravities of Ether-Alcohol Mixtures at 25° C. Hydrogen scale.

The pycnometer was filled with the ether mixture and suspended in the thermostat for 45 min.[1] The temperature was observed three times during this interval and if there was any variation the determination was started over. The adjustment of the pycnometer was made while it was in the bath. It was then removed, dried and weighed, taking care that the final adjustment of the rider was made exactly 10 min. after removing from the bath. After standing an additional 10 min. in the balance case, the pycnometer was again weighed. The difference between the first and second weighings represents loss by evaporation in 10 min. and was added to the first weighing. The balance, being in a constant temperature room, was never more than 0.5° different for the bath. In order to ascertain if the moisture adhering to the pycnometer was different at the end of 10 min. and 20 min., respectively, two series of weighings were made on the empty pycnometer, after wetting and drying at 10, 20, and 30 min.; all weighings checked to 0.0001 g.

Table I gives the full data. As will be seen, at least two weighings were made on each mixture, in some cases three. When the amount of the sample permitted, the pycnometer was emptied, and refilled, otherwise it was simply replaced in the bath and readjusted to the mark. Since the weighings were made at temperatures slightly below 25°, it was necessary to correct for the slightly lower densities which ether and water would have had if weighed at exactly 25°, the expansion of the pycnometer itself being negligible. The expression given makes use of the coefficient of expansion of ether[1] to calculate the volumes 1.040533 cc. and 1.040550 cc. which 1 cc. of ether at 0° would have at 24.99° and 25°, respectively, the remainder of the expression giving the densities of water at these temperatures. It applies to the first six columns. For the remaining columns the calculation is similar: these columns show determinations made at a later date to check the density of the 3 and 4 per cent mixtures since the density as first found for the 4 per cent mixture did not lie on the curve.

The original of the plot (Fig. 1) was made sufficiently large to show variations of one in the fifth place, and it was seen that the densities fell evenly upon the curve with the exception of the first determination on the 4 per cent mixture which we believe must have received more than 4 per cent of alcohol through some error in preparation. The curve is very nearly a straight line. Since a variation of 0.0001 in density, or one of the small divisions on the coördinate paper, corresponds to 0.1 per cent of alcohol in the mixture, it is evident that the curve is of ample accuracy for the purpose of the analysis.

DIRECTIONS FOR THE COMPLETE ANALYSIS

The flask used (Fig. 2) was a 100 cc. Regnault pycnometer for taking the density of solids. It is best to have two and make the analysis in duplicate.

Fifteen grams of potassium carbonate dried at 200 to 250° are placed in the bulb *A* and accurately weighed after replacing the stem *B*. Remove the stem and introduce quickly 50 cc. of the ether for analysis. Replace stem and allow the flask to stand 14 hrs. with frequent shaking. By removing the stopper and holding the inverted flask in the warm hand, the ether can be filtered out through the cotton plug *X*. Care must be used to insure a clear filtrate, otherwise there will be a loss of potassium carbonate. Examine the filtrate after standing to see that no finely divided carbonate has separated out. Fill the upper enlargement *B* with absolute ether and cause it to be drawn in by pouring some of the ether over the bulb. Shake well

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[1] A pycnometer which had a thermometer attached for taking the temperature of the liquid within, but similar in other respects when filled with ether at 15° C. and immersed in the thermostat, was found to have acquired the bath temperature in 15 min.

[1] The coefficient of expansion of pure ether has been used in the case of the mixtures containing alcohol since owing to the close proximity of the temperatures to 25° the error so introduced is negligible. See Bein, *Loc. cit.*, p. 15.

and expel the ether as before. Wash four times in this manner, which removes the alcohol from the salt. Now dry the flask, with cap *C* removed, at 50° until the carbonate can be shaken down into the flask. Remove the stem and replace it with a drying tube filled with carbonate of potassium to prevent access of external moisture and dry for 1 hr. at 50°. Remove the drying tube and after sweeping out the remaining ether vapor with gentle suction for 15 sec., replace the stem and cool in a desiccator and weigh. Since it does not require much ether vapor to affect the weight, care is required to secure its complete removal without introducing moisture from an excess of air. A second weighing should be made after drying again for half an hour. The weights should be constant within about 4 mg. The difference between the weights of the potassium carbonate before and after treatment with ether is the weight of water in the sample taken.

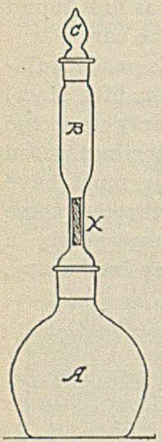

Fig. 2

For the alcohol analysis, treat 100 g. of the sample with 40 g. of freshly dried potassium carbonate for 14 hrs. in a glass-stoppered flask, shaking frequently. The pycnometer is filled with the clear ether and the specific gravity is determined at exactly 25° on the hydrogen scale. The per cent of alcohol may then be read off from the curve. Obviously if this curve is to be used, the gravity must be made in a bath at exactly 25° on the international hydrogen scale or else a new curve made by the operator at the temperature of his thermostat, which is a simple matter.

Owing to the fact that ether deteriorates with age, unless protected carefully from the effects of air and light, only fresh samples should be used for analysis. As the accuracy of this method depends to a considerable extent on the manipulation, strict adherence to the procedure, as given, cannot be too strongly recommended.

TABLE II—ANALYSES OF KNOWN MIXTURES (1 TO 13, AND 18) AND MARKET ANAESTHESIA ETHERS (14 TO 17, AND 19) BY DIFFERENT ANALYSTS

DETERMINATIONS	Analyst	No.	PER CENT ALCOHOL Added	PER CENT ALCOHOL Found	PER CENT WATER Added	PER CENT WATER Found
Made in same Thermostat as used for the Density Curve	Mr. A.	1	0.82	0.85	0.22	0.258 0.234
		2	3.17	3.28	0.75	0.756 0.751
		3	2.85	2.90	0.27	0.269 0.277
		4	3.32	3.38	1.10	1.07 1.08
	Mr. C.	5	3.40	3.67	0.75	0.834
		6	3.63	3.57	0.60	0.545
		7	2.51	2.47	0.30	0.327
		8	2.01	2.00	0.21	0.229
Made in Ordinary Laboratory Thermostat	Mr. P.	9	2.94	2.93	0.46	0.39
		10	3.11	3.00	0.63	Lost
		11	2.86	2.70	0.41	0.39
		12	3.85	3.83	0.79	Lost
		13	4.02	3.93	0.53	0.53
	Mr. A.	14	..	1.42	..	1.08 1.08
		15	..	0.85	..	1.21 1.22
		16	..	0.12	..	0.12 0.11
		17	..	4.25	..	0.36 0.36
		18	1.70	1.62	1.10	1.12 1.19
		19	..	0.32	..	0.26 0.25

Table II gives the results obtained by three different experimenters in our laboratory on known mixtures and five well-known market brands of anaesthetic ethers. The compositions of these mixtures were unknown to the experimenters. Mr. C. and Mr. P. had never used the method before and worked entirely from the directions as given above. Nevertheless, the agreement between the amounts found and actually added demonstrates that the method is reliable and sufficiently accurate for the analysis of anaesthetic ether.

CONCLUSION

In his classic articles on ether, Squibb[1] estimated that the 4 per cent of aqueous alcohol remaining in his ether contained about 90.75 per cent of pure alcohol. It is interesting to note from the table that the water and alcohol exist in proportions which are more nearly equal than Squibb believed. This is in accordance with the experiments of Wade and Finnemore[2] who have shown that ether and water form a constant boiling mixture containing 1.3 per cent of water which boils 0.35° lower than pure ether. They also showed that alcohol and ether form no such mixtures, neither is this the case if all three components occur together. Consequently, the mixture rich in water is the one which distills most readily. The amount of alcohol which persistently accompanies the constant boiling mixture depends largely upon the efficiency of the fractionation process employed.

It is questionable whether ether can be made by the usual process of distillation which will comply strictly with the requirements of the present Pharmacopoeia that it shall consist of 96 per cent ethyl oxide and 4 per cent of alcohol containing a little water. Ether of such composition might be prepared by a special distillation process if it could be shown to possess any superior qualities which, in our opinion, is extremely improbable. Specimen No. 14 had the proper specific gravity but contained 1.4 per cent alcohol and 1 per cent water. Specimen No. 17 probably had had alcohol added to it.

MALLINCKRODT CHEMICAL WORKS, ST. LOUIS

THE ANALYSIS AND COMPOSITION OF SOME CIGARETTE PAPERS

By STROUD JORDAN

Received February 4, 1916

Recent reports on cigarette papers[3] contain some very valuable information as to the process of manufacture, ash values and alkaloidal tests. Only a very general description is given and some of the necessary details are omitted in the foregoing papers, so that it has been thought expedient to publish some analytical results on two of the more common papers used by the manufacturers of cigarettes.

The samples reported in this article were taken from reels actually running on cigarette machines and Numbers 1, 2 and 3 represent Austrian papers of the type known as "Sunshine," made by Stefan Robitsek of Vienna. These papers come in lengths of 3900 meters to the reel, have an average width of 31 mm. and weigh from 19.4 to 22.1 g. to the square meter, corresponding to a thickness of 0.0014 to 0.0016 in. Numbers 4 and 5 were both of the French type, known

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[1] *Loc. cit.*, p. 596.

[2] *Ibid.*, p. 1850.

[3] *Paper*, No. 24, **15** (1915), 19–31; *Woch. Papierfabr.*, **45**, 2296–2302, *Zentr. oesterr-ungar. Papierind.*, **32** (1914), 623–4; and in *Bull.* **2**, Agr. Comm. of Ohio, Dairy and Food Div., Bureau of Drugs.

as "Vierge Egyptien" (combustible), and measure about 1560 meters to the reel. The average width of these papers is 30 mm., having an average weight of 18.75 g. to the square meter and a corresponding thickness of about 0.0014 in.

METHODS OF ANALYSIS

MOISTURE determinations should be made according to Bureau of Chemistry, *Bull.* **107**, 14.

ASH—The sample used for moisture determination was incinerated over a Tirrill or Bunsen lamp, using a very low flame, then the ash removed to a blast flame and incinerated until no further loss in weight was observed. [This ash should show only a slight effervescence or none at all, when it is suspended in water and treated with a few drops of concentrated hydrochloric acid (absence of carbonates).]

FIBER (PULP)—10.000 g. of finely cut paper were weighed into a liter Erlenmeyer flask and 500 cc. of distilled water and 10.0 cc. of hydrochloric acid (sp. gr. 1.20) were added. The mass was boiled over a free flame for 1 hr. or until the whole was well pulped, then filtered on a Buchner funnel, using a tared, acid-washed filter, and washed with water until a drop of the filtrate showed only a slight opalescence when tested in the usual manner for chlorides. The filtrate was preserved for determination of the constituents of the ash. The pulp was washed three times with 95 per cent alcohol, packed well with a glass rod, removed to a drying oven and dried to constant weight at 105° C.

The pulp was then reduced to ash and the ash found subtracted from the weight of the pulp, along with the weight of the filter paper used, from which any ash value it might have had has been subtracted. This gives the weight of pulp by difference.

MINERAL FILLER is calculated by difference, by subtracting the combined weights of moisture, fiber and size from 100 per cent.

As a check on the determination of mineral filler, the constituents of the ash were calculated to the compounds occurring in the paper and this total weight compared with the filler as found by difference.

SIZING, COATING, KINDS OF FIBER, ETC.—These constituents were determined according to the methods laid down in Allen's "Commercial Organic Analysis," **1**, 473–479 (4th Ed.).

ANALYTICAL RESULTS (PERCENTAGES)

SAMPLE:	1	2	3	4	5
Moisture	4.05	4.14	3.99	4.30	4.62
Ash (as oxides)	12.25	12.07	12.95	4.95	5.12
Fiber (pulp)	71.07	71.35	72.57	87.08	85.74
Filler	24.88	24.10	23.19	8.62	9.64
Size (less than)	1.00	1.00	1.00	0.10	0.10

CONSTITUENTS OF THE ASH—The compounds which occurred in the ash were calculated in the usual manner by the official methods as laid down in Bureau of Chemistry, *Bull.* **107**, *e. g.*, CaO (p. 15), MgO (p. 16) and $(Fe + Al)_2O_3$ (p. 15).

As a check on the above ash determination, the filtrate from the fiber determination was evaporated to dryness and the acid expelled. This residue was taken up in a convenient volume of water and the compounds present determined as above.

COMPOSITION OF THE ASH (PERCENTAGES)

SAMPLE:	1	2	3	4	5
Calcium oxide	12.06	11.74	11.01	4.39	4.30
Magnesium oxide	0.17	0.26	1.29	0.20	0.24
Aluminum oxide	Trace	Trace	0.24	0.30	0.11
Iron oxide	Trace	Trace	Trace	Trace	Trace
Silica	Trace	Trace	Trace	Trace	Trace
H_2S precipitate	None	None	None	None	None
Sulfates	None	None	None	None	None
Nitrates	None	None	None	None	None
Chlorides	Trace	Trace	Trace	Trace	Trace

As a check on the above results, Samples 1 and 2 were compared with the compounds found in the filtrate from the pulp determination. The following gives a comparison:

SAMPLE:	1(*a*)	1(*b*)	2(*a*)	2(*b*)
Calcium oxide	12.06	11.76	11.74	11.69
Calcium carbonate	21.52	21.00	20.95	20.87
Magnesium oxide	0.17	0.15	0.26	0.33
Magnesium carbonate(*c*)	0.36	0.31	0.54	0.67

(*a*) Result from ash. (*b*) Result from filtrate from pulp. The other traces showed up the same in both samples. (*c*) $3MgCO_3.Mg(OH)_2.4H_2O$.

FIBER AND SIZING—All fibers were found to be linen. Sizing in the first three were found to be dextrine and the last two carried traces of starch but no dextrine.

COMPOSITION OF THE PAPER

The composition of the papers appears to be: linen fiber slightly sized with starch or dextrine and filled with the carbonates of magnesium and calcium. The filler in the first three averaged 24.05 per cent, while the last two showed an average of 9.13 per cent.

The fillers were calculated to the carbonates, while it is possible that a portion of the magnesium was added as the peroxide or oxide for accelerating the burning of the paper. This change would not affect the resulting weights appreciably.

SUMMARY

Nothing injurious was found in the ash, filler or pulp. The paper burns to a clean white ash which shows good combustion and the absence of compounds formed by destructive distillation. The filler is not materially changed when the paper is burned, so has no effect except to promote combustion and to make the papers "tight." No tests were found for alkaloids or alkaloidal salts. No poisonous metals were found (absence of hydrogen sulfide precipitate). No bad effect was had from the small amount of sizing, as is evidenced by the good burning qualities and the absence of compounds formed by destructive distillation.

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TIN IN CANNED FOODS

By W. D. BIGELOW

Received July 17, 1916

It has long been known that the acids of canned fruits dissolve more or less tin from the container, the amount depending partly on the age of the product and the temperature of storage. It is also well known that some foods having but a slightly acid reaction, such as pumpkin, string beans, and shrimp, attack tin to a considerable extent. This has been shown[1] to be due in some cases at least to the presence of amino bodies in the food. The tin in canned foods has usually been assumed to be in solution. Articles on this subject and reports of analytical work frequently refer

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[1] Bigelow and Bacon, Bureau of Chemistry, *Circ.* **79**.

to the tin contained in the food as "soluble tin salts." It was pointed out by the writer[1] some time ago that the tin in canned food was largely, sometimes chiefly, in some insoluble form.

It is a common experience in the laboratory that compounds of tin separate out from reagent solutions of tin chloride. This is ordinarily prevented by the use of strong hydrochloric acid. The same separation occurs with solutions of compounds of tin with organic acids. It appears, therefore, that the acid acts as a carrier dissolving the tin from the coating of the container and carrying it into the food where the tin separates in an insoluble form, leaving the acid free.

With nonacid or slightly acid foods of the types mentioned above, this deposition of tin in insoluble form probably occurs to a greater extent than with the acid fruits. In both cases it appears that a considerable proportion of the soluble tin salts is carried within the solid particles of food before being hydrolyzed.

It is conceivable that the higher tin content of the drained solids than of the liquor might be due to metathesis, the tin replacing calcium or magnesium, for instance, in its insoluble compounds within the solid particles of food. The property of solutions of tin salts, however, to deposit insoluble tin compounds, and especially the property of stannous solutions to yield insoluble basic stannic compounds, appears to afford a more probable explanation of the presence of insoluble in place of soluble tin compounds in canned foods. In either case the drained solids of canned foods contain a materially higher amount of tin than the liquor, and this difference increases with the age of the sample. Thus the high tin content of old canned foods is largely due to insoluble compounds of tin which are presumably less likely than soluble compounds to be absorbed from the intestinal tract.

The figures given in Table I were obtained by determining the amount of tin in drained solids and liquor, respectively, and calculating the amount of tin in the original sample from the figures thus obtained and from the weight of drained solids and liquor, respectively.

TABLE I

VARIETY OF FOOD	MILLIGRAMS TIN PER KILOGRAM IN Liquor	Total sample	Drained solids
Cranberries	33	170	254
Raspberries	39	194.	294
Cherries	52	107	163
Peaches	86	193	251
Pears	99	130	151
Plums	43	125	180
Shrimps	67	224	381
Spinach	35	86	131

The relation of the tin content of the drained solids to that of the liquor of certain canned foods is brought out more definitely in Table II. The samples shown in this table were taken from an experimental pack in which the various cans were as uniform as they could be made. At intervals after the food was packed, sample cans were examined to determine the tin content of the food. At least two cans were taken for each sample. The drained solids and liquor were weighed separately, the tin determined in each and expressed in terms of milligrams per kilogram of drained solids and liquor, respectively. From these figures, the tin content of the original sample was calculated.

By a study of this data we are able to form a rough approximation of the amount of tin which is in soluble form. For this purpose it is necessary to assume that the tin of the liquor is all soluble. This is probably not the case. It is extremely unlikely that the soluble tin compounds all find their way into the solid particles of the food before the separation of the tin in insoluble form. It is much more likely that a considerable portion of the tin in the liquor is a finely divided insoluble oxide, hydrated oxide, or basic salt of tin. It is altogether probable that the amount of soluble tin in these samples did not increase after the first analyses were made, and that the subsequent increase of tin in the liquor was due to the separation of finely divided insoluble compounds of tin. The thought also suggests itself that a considerable portion of the tin that appears to be in solution is probably in colloidal form. If we assume all the tin of the liquor to be soluble, therefore, the amount of tin calculated as insoluble will be less than the amount actually present in that form and the results will at least be conservative.

TABLE II

VARIETY OF FOOD	Age of sample Yr.	Age of sample Mo.	MILLIGRAMS TIN PER KILOGRAM IN: Total sample	Drained solids	Liquor	Soluble tin in drained solids(a)	Insoluble tin in drained solids(b)	Soluble tin in total sample(a)
Asparagus	.	8	280	322	200	193	129	196
	1	5	433	489	252	248	241	249
	2	7	470	554	238	229	325	233
Lima beans	.	9	80	99	46	38	61	41
	2	9	173	254	40	33	221	35
String beans	.	2	124	169	63	60	109	62
	.	7	130	174	64	61	113	63
	1	3	299	442	97	93	349	95
	1	8	250	382	102	98	284	100
	2	6	434	658	132	127	531	130
Wax beans	.	3	93	143	39	38	105	39
	.	7	116	176	52	50	126	51
	.	10	139	251	55	53	198	54
	1	3	230	391	72	69	322	71
	1	8	217	359	87	84	275	86
	2	4	347	616	88	85	531	86

(a) The figures in these columns are doubtless higher than they should be as they are based on the assumption that the tin of the unfiltered liquor is all in solution.

(b) For the reason given in footnote (a), the figures in this column are doubtless lower than they should be.

The figures given in Table II in the column headed "Insoluble tin in drained solids" were obtained in the following manner, taking, as an example, the sample of asparagus which was examined 2 yrs. and 7 mos. after packing. The liquor in this sample contained 5.2 per cent of solids or 94.8 per cent of water. One kilogram of the liquor, therefore, contained 948 g. of water. Since a kilogram of liquor contained 238 mg. of tin and 948 g. of water there was in the liquor $238 \div 948 = 0.25$ mg. of tin for each gram of water. The drained solids were found to contain 8.3 per cent of solid matter or 91.7 per cent of water. One kilogram of the drained solids, therefore, contained 917 g. of water.

Now it is fair to assume that the relative amount of water and dissolved tin in the drained solids is substantially the same as in the liquor. Figuring on that basis, the amount of soluble tin in the drained solids is $914 \times 0.25 = 229$ mg. per kg. Since the total tin content of the drained solids was found to be 554 mg.

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[1] Research Laboratories, National Canners' Association, *Bull.* **2**, August, 1914.

per kg., it follows that 554 — 229 = 325 mg. per kg. must be in an insoluble form.

As stated above, this amount must be well within the truth. If any considerable amount of the tin of the liquor is insoluble, the insoluble tin of the drained solids must be considerably more than 325 mg. per kg. The remaining figures in the column marked "Insoluble tin in drained solids" were all calculated in the same manner, using average figures for the weight and water content of drained solids and liquor as the individual determinations were not made.

The column headed "Insoluble tin in drained solids" is of particular interest although, as stated above, it is believed that the figures in this column are somewhat less than the truth; the relative amount reported as insoluble tin in samples of different ages shows that the process of hydrolyzation is a continuous one.

The figures given in the last column headed "Soluble tin in total sample" were obtained by adding together the figures in the columns headed "Milligrams tin per kilogram liquor" and "Soluble tin in drained solids," after calculating these respective figures to milligrams of tin per kilogram of tin of original sample. It is interesting to note that the figures in this column are almost identical with the figures in the column headed "Milligrams tin per kilogram liquor." It is probable, therefore, that an approximate idea of the amount of soluble tin in a sample of canned food can be obtained by determining the amount of tin in the liquor of the food, although the figure so obtained will obviously include any insoluble tin which may be present in the liquor in a finely divided state and also any tin that may be present in colloidal form.

Recent workers agree that the ideas of the earlier writers on the toxicity of tin were erroneous. It is now known that the toxicity of soluble tin compounds is at least very much less than it was formerly supposed to be. It is evident, however, that the results obtained in the study of soluble tin salts cannot be used as a criterion on which to judge the toxicity of tin in canned foods. Whatever the insoluble combination in which tin occurs in canned foods it is in all probability less likely to be absorbed from the intestinal tract than soluble tin compounds. The same is true, perhaps to a less extent, of tin in colloidal form. At any rate, the need of experimental work on the toxicity of tin as it occurs in canned foods is obvious.

National Canners' Association, Washington

THE EFFECT OF CURING ON THE AROMATIC CONSTITUENTS OF VANILLA BEANS[1]

By Frank Rabak

Received March 13, 1916

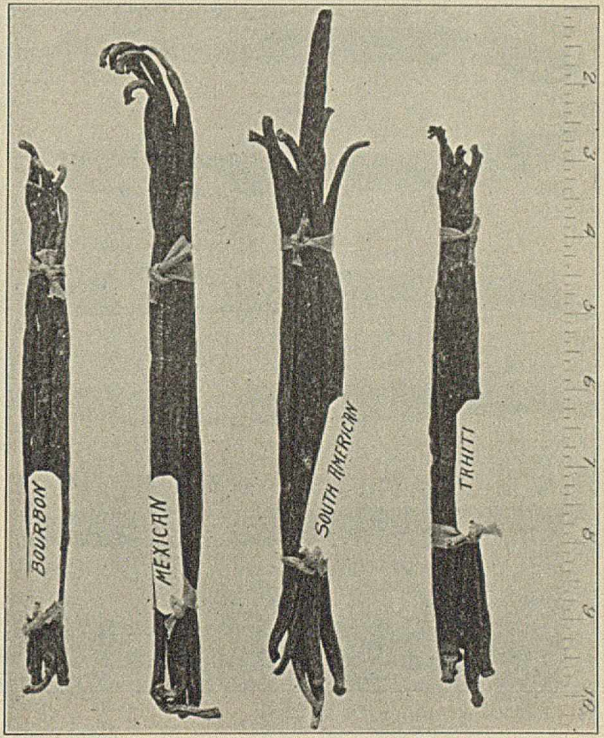
The fruit of vanilla has long been used as a flavoring agent. The plant is native to Mexico, where it is at present extensively cultivated for the production of the vanilla beans of commerce. It has been introduced into a number of other tropical and subtropical countries where it is also profitably cultivated. Among the other sources are South America (Guadaloupe), Tahiti, Reunion, Madagascar, Comores, Seychelles, and Mauritius.

Vanilla beans as found on the market are described by the United States Pharmacopoeia[1] as the "cured, full grown, but immature, fruit of *Vanilla planifolia*, Andrews. (Family *orchidaceae*.)"

Vanilla is used for flavoring purposes in the form of the so-called extract or tincture of vanilla, which is prepared by extracting the coarsely comminuted beans with a hydroalcoholic menstruum varying in strength from 45 to 65 per cent.

The aroma of vanilla, to which the flavor is attributed, does not preëxist in the beans but is formed by a chemical reaction induced during the drying or curing process to which the beans are subjected after harvesting.

Behrens[2] states that ripe vanilla beans have little or no odor but become strong in odor by curing, due to the splitting up of an existing glucoside with the formation of the compound vanillin. The above statement regarding the odor of vanilla was confirmed by Busse,[3] who states that vanillin is formed from a nonodorous body partaking of the nature of a glucoside.



Commercial Vanilla Beans

In an extensive research with vanilla, Lecomte[4] found that the fruit of vanilla contained, besides the glucoside coniferin, two ferments, one an oxidase and the other a hydrolyzing agent. The latter con-

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[1] Published by permission of the Secretary of Agriculture.

[1] United States Pharmacopoeia, Eighth Decennial Revision, **1900**, 497.

[2] J. Behrens, "Ueber das Vorkommen des Vanillins in der Vanille," *Der Tropenpflanzer*, **3** (1899), 299.

[3] W. Busse, "Vanille—Chemie der vanille Frucht. Arbeiten aus dem Kaiserlichen Gesundheitsamte," Berlin, XV, 1898 bis 1899, p. 101.

[4] H. Lecomte, "Sur la formation du parfum de la vanille," *Compt. rend.*, **133** (1901), 745.

verts the glucoside coniferin into coniferyl alcohol and glucose, the former oxidizing this alcohol into vanillin.

Later investigations have shown that the agreeable aroma of vanilla is not due alone to the compound vanillin but is strongly influenced by other substances of entirely different character.

Walbaum[1] states that the value of vanilla beans does not depend solely on the vanillin content. The oleoresinous constituents of the beans were examined and found to contain anisaldehyde and anisic alcohol besides other compounds which could not be identified, but which possessed a characteristic agreeable odor.

The presence of other odorous constituents in vanilla beans is also mentioned by Iserman,[2] who states that the special aroma and taste is probably due to vanilla resins. Busse[3] states that vanillin is present in the living fruits only in insignificant quantities and is mainly produced in the process of curing. Vanillin is not the sole criterion of quality and does not represent the natural aroma of the fruit. Besides vanillin there is present in the beans vanillic acid, resin, oil, sugar, mucilage, and tannin.

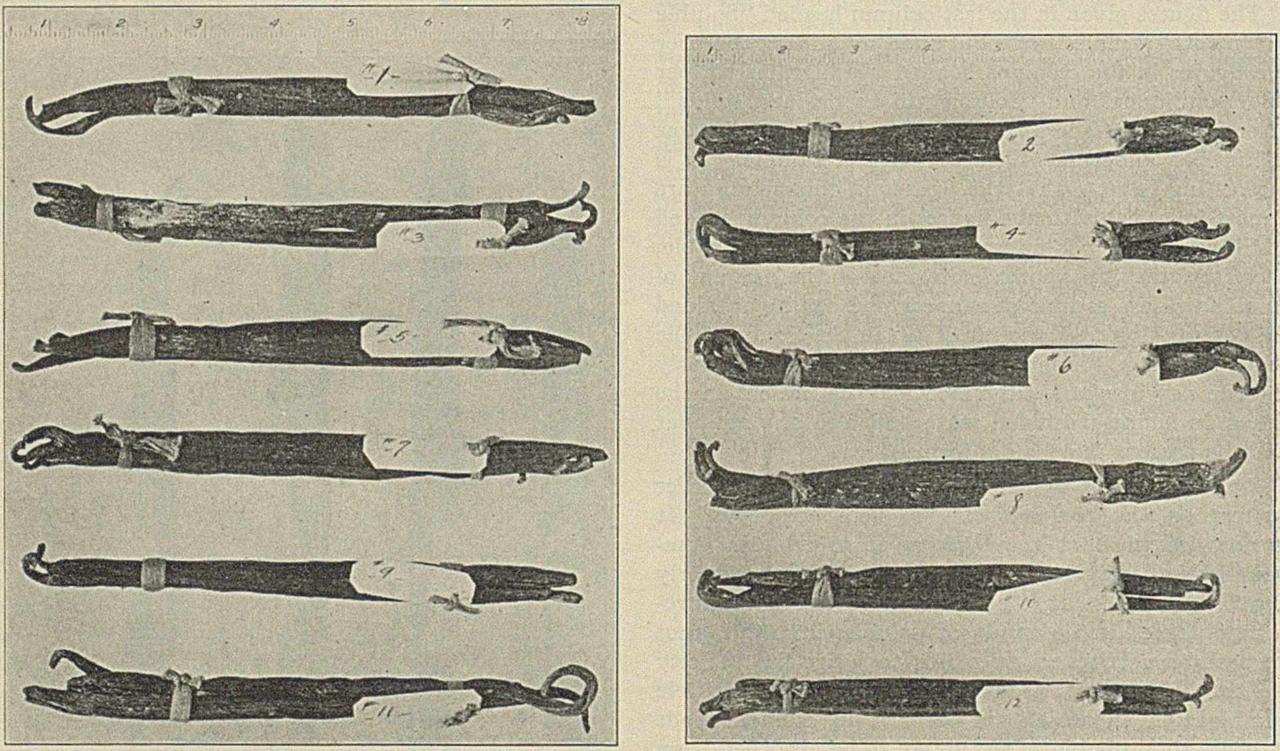
Up to the present time attention has been largely directed towards the vanillin content of the beans, only bare mention being made of the resinous constituents which are known to impart much of the pleasant flavor to the cured beans.

CURING OF BEANS

As has been previously stated, the flavor of vanilla beans is brought about by a curing process with a consequent development of the true flavor upon which the efficacy of the beans as a flavoring material depends.

The curing process varies somewhat according to the source of the beans, the prime object, namely, the evaporation of the moisture and the formation of the flavoring constituents, being attained in every case. This is accomplished in a general way by a process of heating and subsequent sweating, the details of which vary in the different producing countries.

Two general methods are in vogue for the curing of vanilla beans, the dry and the hot water methods.



Laboratory Cured Vanilla Beans

The dry method, in use in Mexico, consists essentially of placing the freshly gathered beans in the sun for several hours, after which they are wrapped in woolen cloths to promote sweating, and the process of heating and sweating is continued for several days until most of the moisture has evaporated. The final drying is usually completed in the shade. In unfavorable weather a drying oven is employed, in which the beans are sweated at a temperature of 60° C. The curing process is continued until the beans are soft and supple and have acquired a chocolate-brown color, the complete length of time required being frequently as long as 5 mos.

The hot water method, used in Reunion, consists in placing the beans in hot water (90 to 100° C.)

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[1] H. Walbaum, "Das Vorkommen von Anisalkohol und Anisaldehyde in der Früchten der Tahiti-vanille. Festschrift, Otto Wallach. Zur Erinnerung an seine Forschungen auf dem Gebiete der Terpene in den Jahren 1884–1909," p. 649.

[2] S. Iserman, "Vanilla Beans: Chemistry and Character of Constituents," *Western Druggist*, July, **1910**, 358–362.

[3] H. Busse, "Studien ueber die Vanille," *Apoth. Zeit.*, **13** (1898), 894.

for 10 to 30 secs., after which they are wrapped in woolen blankets or placed in a box lined with blankets, where the sweating process takes place. Subsequently the beans are exposed to the sun and later the curing is completed in a drying room until the finished beans have the proper color and texture. This process requires from 1 to 2 mos. for completion.

The curing process is difficult and precarious, calling for a high degree of skill and experience. Weather conditions also have much to do with the rapidity and success of the process. The exact details of the two methods differ greatly according to locality. The general method of procedure for both processes is considerably modified in the minor details, the one object being to produce finished beans which will have the maximum amount of flavor of superior quality and at the same time will have had removed from them sufficient moisture to prevent molding when the beans are finally packed for the market. As a general rule from 5 to 7 lbs. of the fresh beans are required to produce 1 lb. of cured beans.

TABLE I—TREATMENT, LOSS IN WEIGHT AND CURING OF VANILLA BEANS AT ROOM TEMPERATURE AND IN THE WATER OVEN

Immersion in water three successive times at temperature given, for periods indicated, at intervals noted

	BEANS CURED AT ROOM TEMPERATURE				BEANS CURED IN WATER OVEN (40–60° C.)			
TREATMENT	No.	Per cent Loss in Weight	Curing Period Days	REMARKS	No.	Per cent Loss in Weight	Curing Period Days	REMARKS
None	1	53.0 66.4	14 24	Curing progressed slowly for 7 days after which color developed rapidly to uniform brown; beans well cured in 14 days. At end of this time, however, beans were wrapped in wax paper and allowed to dry. Cured beans were dark brown in color, soft, pliable and possessed fine aroma.	2	32.5 67.0	8 33	Beans became uniformly brown in 6 days, sweating continuous until 8th day when beans were wrapped in waxed paper and allowed to dry until soft and pliable. Beans possessed characteristic but mild aroma.
Temp., 40° C. Period, 30 sec. Interval, 1 min.	7	39.3 68.5	14 46	Curing proceeded about same as No. 1. After subjecting to sweating process for 14 days beans were uniformly brown in color. Beans wrapped in waxed paper and allowed to dry until they presented a wrinkled appearance and proper pliability. Beans possessed very fine aroma.	8	49.6 66.6	8 28	Beans all brownish color in 5 days with good odor developing. After 8 days' sweating in water oven beans were wrapped in waxed paper and allowed to dry slowly until proper texture was attained. Odor was fine vanilla-like characteristic but not especially strong.
Temp., 60° C. Period, 20 sec. Interval, 1 min.	5	36.5 66.0	11 33	Beans became yellowish green after third day. After 11 days all were uniformly brown in color and had characteristic wrinkled appearance. Beans wrapped in waxed paper and allowed to dry to proper flexibility. Beans characterized by strong and exceptionally fine odor.	6	41.4 66.2	8 33	After 5 days beans were uniformly brown in color with pronounced odor and apparently curing rapidly. After 8 days' sweating beans were treated as above and dried to proper pliability. Odor was strong, vanilla-like.
Temp., 80° C. Period, 10 sec. Interval, 1/2 min.	3	40.7 66.2	12 24	Beans assumed brown color and developed odor more rapidly than any of above. After 12 days' sweating beans wrapped in waxed paper and set aside to dry. After 12 days of drying beans possessed a most exquisite aroma, deep brown color and fine texture.	4	31.2 64.0	8 29	Uniformly brown after 4 days' sweating, curing more rapidly than any of above and becoming soft and pliable. After sweating 8 days beans treated as above. Final appearance excellent both as regards color and pliability. Odor strong.
Temp., 90° C. Period, 10 sec. Interval, 1/2 min.	9	23.3 66.1	10 28	Beans were all pliable, wrinkled and brown in 10 days with odor fairly strongly developed. Allowed to dry in air for 18 days. Beans pliable and wrinkled with only faint odor and pale brown color.	10	30.0 66.3	3 25	Beans possessed a uniform dark brown color in 2 days with prominent odor developing. After 3 days' sweating beans were exposed to air and dried until proper degree of pliability was reached. Strong but unpleasant odor noted.
Temp., 100° C. Period, 10 sec. Interval, 1/2 min.	11	35.2 64.0	10 18	Beans became light brown and soft on third day. Taken from towel on 10th day and allowed to dry in air for 8 days. Odor prominent but not strong. Color pale brown.	12	44.0 69.0	3 17	Beans uniformly brown but pale after 1 day's sweating. Odor only fair and color pale brown after 3 days. Beans allowed to dry sufficiently, the cured beans being very light in color with faint odor.

It is stated by Ellis[1] that the temperature of the water into which the pods are dipped before curing has much to do with the successful curing of vanilla.

Treatment with hot water supposedly kills the pods and prevents dehiscence. It is, however, essential that the temperature be not sufficiently high to destroy the action of the oxidase which is present in the pericarp. A destruction of the oxidase would seriously interfere with the formation of the odorous constituents of the cured beans.

The object of this investigation was twofold. A number of modifications of the process now used in curing vanilla beans were made. It was also desired to ascertain whether the long-continued curing as now practiced is absolutely necessary for the production of beans of commerce and whether shorter time of curing noticeably affects the percentage of vanillin in the cured beans.

A comparison of the efficacy of the two general methods of curing, namely, the dry method and the hot water method, and the effect of temperature upon the curing was sought. Furthermore, it was desired to study the effect of the various curing methods upon the formation of the oleoresins of vanilla which are present in all cured beans and which agreeably modify the flavor of the beans.

LABORATORY CURING EXPERIMENTS

A small quantity of green beans was obtained from Mexico through a prominent manufacturer of vanilla extract. The small ends of the beans were very slightly yellow but were practically devoid of odor.

The curing experiments were conducted with twelve lots of beans, one-half of which were cured at room temperature and the other half in a water oven at somewhat higher temperature. Each of the six lots cured at room temperature were given different treatment prior to the sweating and drying. The treatment consisted in dipping the green beans into water at various temperatures up to the boiling point. Each lot was kept wrapped in a soft towel and placed on the laboratory shelf to undergo the sweating and drying process.

The duplicate lots of beans cured in the water oven at a temperature of 40–55° C. received exactly the same treatment as those cured at room temperature.

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[1] F. R. Ellis, "Vanilla," *The Chemist and Druggist*, **67** (1905), 593.

A description of the treatment, loss in weight, and time of curing of the green beans at room temperature and in the water oven is given in Table I.

The general treatment in the curing at room temperature and in the water oven was similar to that employed in the commercial curing of the beans. The processes of sweating and drying were applied, however, under very different conditions than those obtaining at localities where the beans are cured commercially. During the sweating process the beans were wrapped in soft towels and later in waxed paper to complete the drying.

The treatment of the two sets of samples was identical in that one sample in each set was cured without previous treatment, while the remaining five samples were subjected to the action of hot water at increasing temperatures up to the boiling point. The subsequent treatment of each sample was identical in every case.

It will be noted that the time of sweating or the length of time required to produce the brown color and the characteristic odor of the cured beans decreases with the increase in temperature of the water in which the green beans were immersed. Indications, therefore, point to increased activity of the oxidases which supposedly bring about the changes. Whether this increased activity is favorable or detrimental to the production of color and odor will be apparent later.

TABLE II—GENERAL COMPARISON OF LABORATORY CURED AND COMMERCIALLY CURED VANILLA BEANS

Sample	Cured Beans Av. Wt. G.	Cured Beans Av. Length Mm.	Brown Color	Odor	Description of Whole Beans	Description of Cut Beans (Cross Section)
1	4.1	19	Chocolate	Fragrant, vanilla-like	Uniformly colored, soft, pliable. A few small vanillin crystals on surface	Uniformly red-brown, inner portion redder than surface
7	5.1	19.5	Pale	Fine, fragrant	Soft and pliable, wrinkled. No crystals	Reddish brown, inner portion redder than surface
5	4.9	18	Chocolate	Fine, mild	Pliable and wrinkled. A few crystals on surface	Reddish brown, inner portion redder than surface
3	5.1	19.5	Dark	Especially fine	Nearly covered with vanillin crystals	Dark brown, somewhat lighter than surface
9	4.4	19	Light chocolate	Very mild	No crystals	Uniformly brown
11	5.2	19.5	Reddish	Lacking fineness	Not uniformly colored. A few crystals at ends	Lighter but uniformly brown
2	5.2	19.5	Dark	Good, strong	A few crystals at one end	Inner portion lighter brown than surface. Charred odor
8	5.1	20	Chocolate	Mild, fragrant	Uniformly colored. No crystals	Uniformly chocolate-brown
6	5.6	20	Pale	Prune-like	No crystals	Uniformly pale brown
4	4.7	19	Chocolate	Good, but lacking bouquet	No crystals	Inner portion paler than surface
10	4.8	18.5	Chocolate	Very mild	Not uniformly colored. No crystals	Lighter in cross section
12	4.8	18	Pale	Prune-like	Not uniformly colored. No crystals	Uniformly brown
Mex. A	5.1	23	Dark	Strong, not agreeable	Pliable, sticky. No crystals	Much lighter brown than surface. Odor somewhat tobacco-like
Tahiti	3.2	18	Dark	Strong	Conspicuous pale, longitudinal stripes	Uniformly brown. Odor somewhat tobacco-like
S. Amer.	3.9	20	Very pale	Mild, sweet	Not pliable. A few crystals	Inner portion reddish brown
Bourbon	2.7	17	Almost black	Pleasant	Very pliable. No crystals	Inner portion lighter brown than surface
Old (*a*)	2.5	16	Pale	Very faint	Nearly dry. No crystals	Uniformly pale brown

(*a*) Beans several years old.

After the sweating process, the time required for drying to the proper appearance and texture varied somewhat according to the previous treatment with hot water. The beans were dried until the proper pliableness was obtained, or until the loss of moisture was from 64 to 69 per cent. In a general way the drying increased in rapidity as the temperature to which the beans were originally subjected was increased.

The formation of the brown color as well as the vanilla odor was seemingly most rapid in the samples subjected to the hottest water. These changes were also most marked and rapid in the samples sweated in the water oven at a temperature ranging from 40 to 60° C.

The various lots of cured beans were wrapped in waxed paper, placed in tight containers, and allowed to stand for a period of 2 mos. After this time the samples were carefully examined and compared with regard to average weight and length, also color, odor, and general appearance, with several commercial samples of cured beans, and the results tabulated, as shown in Table II.

The average weight and length of the laboratory cured beans compare very favorably with the commercially cured samples. In color and odor several of the laboratory samples were superior to the commercial samples. The presence of crystals of vanillin on the surface of the beans usually occurs when beans with high content of this constituent are kept in a confined space for a period of time. Crystals of vanillin were observed to be most prevalent in the samples cured at room temperature, an entire absence of crystals being noted in the samples cured in the water oven with one exception, that of Sample 2, on which a few crystals were observed.

A decided red-brown color was apparent in the cross section of the beans cured at room temperature, with a decreasing tendency as the temperature of the water increased into which the beans were immersed.

Physical tests being insufficient and inadequate to determine accurately the quality of beans cured by the various modifications of the methods, a chemical examination was necessary. Not only was it desired to ascertain the respective qualities of the beans with regard to vanillin content, but also the oleoresin content, which is considered an important adjunct to the flavor of the beans.

PREPARATION AND PROPERTIES OF EXTRACTS

In order more advantageously to judge the quality of the cured beans and to make a thorough comparison of the various samples with the commercial beans, extracts were made from the samples according to the directions in the United States Pharmacopoeia[1] for the preparation of tincture of vanilla. The resulting extracts afforded an excellent means for com-

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[1] United States Pharmacopoeia, Eighth Decennial Revision, **1900**, 484.

paring the general physical and chemical properties of the individual samples with those prepared from commercial vanilla beans. These comparisons are shown in Table III.

The general physical properties of the extracts from the samples cured at room temperature were superior to those cured in the water oven at somewhat higher temperature. The colors of the former were distinctly more red and brownish red than the latter. All the laboratory extracts were more attractive in color than the extracts from the commercial beans. The deeper color of the extracts from the laboratory cured beans was perhaps due to the presence of vanilla resins which possess a color of deep red to brown.

The odor and taste of the extracts from the beans cured at room temperature were superior to those from the oven cured beans. The presence of a distinct flowery or fruity odor and taste was apparent. Extracts from the commercial beans seemed lacking in this respect.

In vanillin content less difference is noted between the extracts from the commercial beans and the laboratory cured beans. The extracts from the beans cured at room temperature assayed considerably higher in general average than from the beans cured at higher temperatures.

TABLE III—PHYSICAL AND CHEMICAL COMPARISON OF VANILLA EXTRACTS FROM LABORATORY CURED AND COMMERCIAL BEANS

	PHYSICAL PROPERTIES OF EXTRACTS			PER CENT
SAMPLE	COLOR	ODOR	TASTE	VANILLIN
1	Wine-red	Pleasant, fruity, very fragrant	Very agreeable, fruity, lasting	0.255
7	Deep wine-red	Pleasant, fruity	Agreeable, vanilla-like	0.253
5	Very deep wine-red	Pleasant, less fruity	Mild, characteristic, pleasant	0.210
3	Wine-red	Very pleasant, flowery	Very pleasant, fruity	0.317
9	Wine-red, slight brownish tint	Pleasant, vanilla-like	Agreeable, not fruity	0.212
11	Wine-red, slight brownish tint	Mild, pleasant	Agreeable, slight	0.212
2	Wine-red	Pleasant, agreeable	Mild and pleasant	0.215
8	Brown with reddish tint	Strong, pleasant	Strong, lasting	0.252
6	Light wine-red, brownish tint	Mild, lacking fragrance	Characteristic, pleasant	0.228
4	Brown with only trace of red	Pleasant, fragrance lacking	Pleasant, lasting	0.201
10	Wine-red, distinct brownish tint	Mild, characteristic	Characteristic, less agreeable	0.239
12	Wine-red, distinct brownish tint	Mild, agreeable	Pleasant, slightly prune-like	0.225
Mex. A	Light brown	Pleasant, characteristic	Agreeable, not fruity	0.259
Mex. B	Wine-red. with brownish tint	Strong, vanilla-like, lacking fragrance	Strong, harsh, not fruity	0.291
Tahiti	Very pale brown	Strong, extract-like, lacking fragrance	Strong, unpleasant, licorice-like	0.200
S. Amer.	Wine-red	Pleasant, agreeable, vanilla-like	Strong, agreeable, vanilla-like	0.268
Bourbon	Wine-red, with brownish tint	Pleasant, agreeable, vanilla-like	Characteristic, not fruity	0.248
Old	Brown	Mild, vanilla-like	Mild, not agreeable	0.196

Considerable variation in vanillin content exists, however, in samples prepared from the beans which had received the hot water treatment before curing. It is very probable that the effect of this treatment as regards composition of the beans will be more pronounced in other constituents than in the vanillin.

To the writer the laboratory cured beans and also the extracts appeared to possess a better odor and taste than any of the commercial beans or extracts. The color of the extracts in every case also distinctly excelled in color those from the beans cured at higher temperatures.

Judging from a purely physical standpoint of color, odor, and taste, the extracts from Samples 1 and 3 were considered the finest, followed by Samples 5, 7, 9 and 11. Samples 2, 8, 6, 4, 10 and 12 were all lower in color estimation and slightly inferior in odor and taste. Of the extracts from the commercial beans, the South American sample was distinctly superior to the others in every respect and more nearly corresponded to Samples 1 and 3 of the laboratory cured beans. The Bourbon and Mexican samples were next in order, followed by the Tahiti and the old sample.

In order partly to obtain more expert judgment and partly to verify the writer's judgment of the samples, a sample of each extract was submitted to a prominent manufacturer of flavoring extracts, who, without having any knowledge of the identity of any of the 18 samples submitted, made the following report on the color, odor, and taste:

> COLOR—South American, the best.
>
> ODOR—Nos. 3, 5, 1 and 7 ranked highest; Tahiti, No. 11, and South American, next; Mexican A, Nos. 9, 8, and 2, Bourbon, 4, 6, 10, and 12, Mexican B and old sample follow in order.
>
> TASTE—Nos. 1, 2 and 3 ranked first; South American, Nos. 11, 7, 9, and 8, were next in rank, followed by Tahiti, Mexican A, No. 2, Bourbon, Nos. 4, 6 and 10; No. 12, Mexican B, and old sample were stated to contain a foreign taste.

According to the report the color of the extract from the South American beans was considered best. This is in close accordance with the colors as described in Table III. Extracts 1 and 3 possessed about the same color as the South American, namely, a bright wine-red, while Nos. 5 and 7 were slightly darker. The remainder of the laboratory extracts possessed an admixture of brown, this color being more prominent in some than in others.

Not only was the rating of the various samples by the manufacturer with respect to odor and taste in close accordance with the writer's selections, but it is a singular fact that three of the laboratory cured samples were stated to excel in point of odor and taste the extracts from the commercial beans and in nearly all cases the beans cured at room temperature were superior to those cured in the water oven.

In order to ascertain whether the various modifications of the curing process produced any effect upon the composition of the beans, an analysis of the residues remaining from the preparation of the extracts was examined.

EXTRACTION OF THE RESINS

Since it is generally conceded that resins or oleoresins tend strongly to modify the agreeable odor of vanilla beans, it is very probable that the superior aroma and flavor of several of the cured samples of beans were due to the presence of these odorous resinous substances. These substances are for the most part soluble in alcohol, to a less extent, however, in hydroalcoholic solutions. In preparing the extracts described 65 per cent alcohol was used. Not all of the resinous constituents of the beans were dissolved by alcohol of this strength but it is assumed that approximately the same percentage of these constituents was extracted from each sample. Provided that more resinous constituents were present in some samples than in others, and granting that the 65 per cent alcohol extracted only a small portion of these constituents, the residues from the preparation of the extracts still contained much of the unextracted resinous substances.

These residues were therefore subjected to extraction with 94 per cent alcohol in order to obtain the residual resins. The residues remaining from the alcohol extraction were further extracted with ether. The percentages of alcohol and ether extracts, and descriptions of each, are given in Table IV.

The quantity of alcohol-soluble constituents remaining in the beans after the preparation of the extracts is considerable. While a number of constituents are no doubt present in these extracts, a large portion probably consists of vanilla resins, together with some vanillin.

The percentage of alcohol extracts from the samples of beans cured in the laboratory at room temperature is uniformly higher than from those cured in the water oven. Likewise those extracts were considerably deeper and richer in color. It would seem, therefore, that curing at room temperature is more conducive to the formation of vanilla resins and coloring matter.

TABLE IV—ALCOHOL AND ETHER EXTRACTS FROM VANILLA RESIDUES

	ALCOHOL EXTRACT OF VANILLA RESIDUES				CHEMICAL CONSTANTS OF ALCOHOL EXTRACT OF RESIDUES			ETHER EXTRACT OF VANILLA RESIDUES			
		DESCRIPTION							DESCRIPTION		
SAMPLE	Per cent	COLOR	STATE	VANILLA ODOR	Acid Value	Ester Value	Sapon. Value	Per cent	COLOR	STATE	ODOR
1	19.23	Dark red	Semi-solid	Fine	13.4	170.5	183.9	4.14	Red-brown	Oily	Fatty
7	27.25	Brownish red	Nearly solid	Fine	27.0	182.3	209.3	4.50	Brownish red	Oily	Balsamic
5	18.22	Brownish red	Nearly solid	Fine	14.3	169.0	183.3	5.34	Pale brown	Oily	Fatty(*a*)
3	20.80	Reddish brown	Semi-solid	Mild	14.6	180.0	194.6	3.73	Pale brown	Oily	Fatty(*a*)
9	21.41	Reddish brown	Semi-solid	Pronounced	39.0	161.4	200.4	3.71	Pale yellow	Oily	Slight fatty
11	16.07	Brownish red	Nearly solid	Fine	36.0	167.5	203.5	3.88	Pale brownish red	Oily	Mild, pleasant
2	23.19	Pale brownish red	Partly liquid	Yes	34.3	124.6	158.9	4.86	Pale brown	Oily	Slight balsamic
8	13.30	Reddish brown	Nearly solid	Pronounced	34.0	132.0	166.0	3.33	Brownish red	Oily	Slight vanilla
6	17.18	Brownish	Semi-solid	Faint, agreeable	60.1	126.1	186.2	4.99	Pale brown	Oily	Nearly odorless
4	21.28	Pale brown	Nearly solid	Mild	48.3	134.5	182.8	4.33	Pale yellow	Oily	Faint vanilla
10	13.11	Brownish	Semi-solid	Faint	53.2	127.3	180.5	4.38	Pale brown	Oily	Faint
12	15.50	Brown	Partly liquid	Faint	40.0	142.2	182.2	3.70	Pale brown	Oily	Faint
Mex. A	19.60	Brown	Liquid	Faint, fatty	25.8	145.6	171.4	4.01	Red-brown	Oily	Fatty(*a*)
Mex. B	12.76	Brown	Semi-solid	Yes	12.9	155.3	168.2	4.11	Dark brown	Oily	Fatty
Tahiti	6.43	Pale brown	Solid	Faint	39.7	.....	.....	6.03	Dark red-brown	Oily	Faint balsamic
S. Amer.	27.20	Dark red-brown	Semi-solid	Pleasant	8.4	85.0	93.4	2.81	Dark brown	Oily	Slight vanilla
Bourbon	19.75	Dark brown	Nearly solid	Good	38.2	155.0	193.2	4.46	Yellow	Oily	Faint
Old	13.35	....	....	....	28.2	134.2	162.4	4.22	Pale brownish	Oily	Faint

(*a*) Fatty taste as well as odor.

The highest percentage of alcohol extract (vanilla resins) in the commercial beans was in the South American sample. This sample also produced a vanilla extract with the deepest color. The residues from the Mexican and Bourbon beans also contained a high percentage of alcohol-soluble substances, and likewise a highly colored extract. These facts are significant of the effect of curing upon the color of prepared extracts and also of the comparatively large quantity of flavoring resins which remain in the residues.

The ether extracts were found to consist largely of fatty oil and were nearly devoid of odor. Some of the less soluble resinous constituents are doubtless present in these extracts. The percentages of ether extract seem to bear no direct relationship as regards treatment during curing. Some variation is apparent, however, among the samples from different sources.

EXAMINATION OF RESINS EXTRACTED WITH ALCOHOL

In order to obtain further knowledge of the alcohol extracts obtained from the residues, the chemical constants, acid, ester, and saponification numbers were determined. The results are shown in Table IV.

Considerable variation exists in the acid, ester, and saponification values of the alcohol extracts obtained from the residues of the laboratory cured beans. The general average of these constants is higher than that of the commercial beans, as was also the percentage of extract. The content of free acid constituents of the resinous extracts is high in nearly all instances, signifying the presence of considerable resin acids. The ester values are likewise high, showing the presence of saponifiable resinous compounds. The resin acids and the combined saponifiable resins seem to have been formed to a greater extent in the beans cured in the laboratory than in the commercially cured samples. Provided these substances tend to add fragrance to the odor of the vanilla bean and therefore also to the extract made from the beans, it would seem that methods which would insure a high percentage of these resinous substances should be preferred. Doubtless a certain percentage of these substances are extracted by the hydroalcoholic menstruum used in preparing the extracts of commerce, the quantity in solution depending largely upon the strength of the alcohol employed.

CONCLUSIONS

From the results reported herein it may be said in general that the curing process as at present commercially applied to vanilla beans is unnecessarily long and extended, requiring on an average several months for the transformation of the green to the cured beans.

In the laboratory experiment conducted it has been shown that the beans can be cured in a much shorter time by means of a much less tedious process. It has further been demonstrated that the process is simplified to the advantage rather than to the detriment of the aromatic constituents. In order to produce uniformity in the composition of the beans, and thereby insure more uniform extracts, the importation and curing of the green beans are suggested.

While the amount of vanillin in the beans was not increased appreciably, as compared with commercial beans, it may be stated with assurance that the beans cured in the laboratory were in most cases superior in vanilla resins and coloring matter. This is significant since vanilla resins and coloring matter are considered important adjuncts to the quality of vanilla beans. The superior flavor of the extracts prepared from the laboratory cured beans may therefore be ascribed to the resinous constituents. A considerable proportion of the vanilla resins are left unextracted when the menstruum is less than 65 per cent alcoholic strength.

Curing the green beans at room temperature either without previous treatment or after treatment with water up to 90° C. for a short period of time apparently produces beans of the best quality, as judged by the flavoring extracts prepared from the samples.

BUREAU OF PLANT INDUSTRY, WASHINGTON

A STUDY OF THE STEREO-ISOMERISM OF A FERMENTATION LACTIC ACID

By STANLEY JUDSON THOMAS

Received December 21, 1915

Investigations of the isomerism of lactic acid soon followed Pasteur's famous work with tartaric acid. In 1890, Lewkowitsch[1] showed that ammonium lactate when exposed to the action of *Penicillium glaucum* for several weeks became optically active. In 1892, Professor T. Purdie proved, by direct analytical evidence, that commercial lactic acid can be resolved into two oppositely active isomeric acids.[2] The results of experiments of various writers on the kind of lactic acid formed in naturally soured milk do not agree. Some found inactive acid, some dextro-, and some laevo-rotatory acid. Dr. P. G. Heinemann cleared up most of this conflicting testimony by showing that different bacteria produce different kinds of acid. As a summary to an excellent paper on the subject, he says: "Racemic lactic acid is the result of the formation of pure dextro acid and pure laevo acid by at least two different species of microörganisms. Racemic (inactive) lactic acid is not known to be the product of one species only."[3]

The object of this paper is to discuss the kind of lactic acid present in Matzoon, an Armenian artificially soured milk, and to give the results of an investigation of its optical powers.

Matzoon is a beverage prepared from cows' milk with the aid of an appropriate ferment. From this ferment, or "starter," the author isolated a bacillus, a streptococcus, and a yeast. The bacillus was determined as a member of the *B. bulgaricus* group, corresponding more closely to *B. caucasicus* (Flugge) than to any other member. The streptococcus isolated was *Str. kefir* (Kuntze), a member of the *Str. lebenis*[4] group. The yeast was determined as *Saccharomyces kefir*: this organism is unable to ferment milk or lactose, excepting a slight production of alcohol.

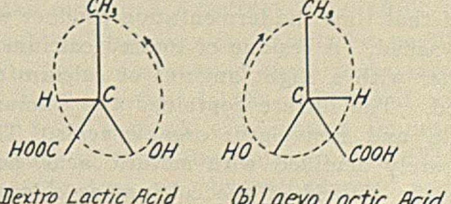
Lactic acid was discovered by Scheele. It exists in sour milk, human gastric juice and in muscle. It has been found in the vegetable kingdom in the peduncles of *Solanum dulcamara*.[1] There are four lactic acids, three having the formula $CH_3.CHOH.COOH$, and one the formula $CH_2OH.CH_2COOH$. Inactive or ethylidene lactic acid (α-hydroxy propionic acid) may be prepared by treating α-chlorpropionic acid with potassium hydroxide: it forms a zinc lactate that crystallizes with three molecules of water of crystallization. Sarco- or dextro-lactic acid ($CH_3CHOH.COOH$) is found in meat: the zinc lactate made from this acid crystallizes with two molecules of water of crystallization.

Laevo-lactic acid ($CH_3CHOH.COOH$) differs from the dextro acid only in its optical powers: its zinc lactate crystallizes with two molecules of water of crystallization.

Beta hydroxy propionic acid (hydracrylic or ethylene lactic acid) has the formula CH_2OHCH_2COOH. When heated it liberates water and forms an unsaturated acid, acrylic acid, $CH_2CHCOOH$.

Thus we have three lactic acids having the same structural formula but different properties. This is known as stereo-isomerism, physical isomerism, or optical isomerism. Ethylene lactic acid, CH_2OHCH_2COOH, is inactive under all circumstances. Ethylidene lactic acid, $CH_3CHOHCOOH$, on the other hand, may exhibit optical activity. On close examination the latter is found to contain a carbon atom in its molecule which holds four other atoms or groups of atoms, all different from each other. Optically active substances, without exception, contain one or more such carbon atoms in their molecules, and the property of turning the plane of polarization bears a close relation to the structure of a substance. Optical activity is, therefore, due to the presence of a carbon atom in a molecule which holds four dissimilar groups with its four bonds. Such a carbon atom is known as an asymmetric carbon atom. Furthermore, an optically active substance may show dextro-rotation, that is, turn the plane of polarization to the right; or laevo-rotation, that is, turn the plane of polarization to the left. A closer examination of the lactic acid molecule may show why the acid exhibits both dextro-rotation and laevo-rotation.

Let us now examine the lactic acid molecule. If we attempt to draw a picture of the molecule in space we may have:



(a) Dextro Lactic Acid (b) Laevo Lactic Acid

The difference between these formulae is only that of an object and its image in a mirror. If *b* be superimposed upon *a*, we will find that the OH group

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[1] *Ber.*, **16**, 2720.

[2] *J. Chem. Soc.*, **1892**, 754.

[3] *J. Biol. Chem.*, **2**, 612.

[4] Freudenreich, *Landw. Jahrb. d. Schweiz.*, **10** (1896), 1.

[1] Standard Dispensatory.

of *b* will lie on the COOH group of *a*. If we take the groups in order, CH_3, H, OH, we find that in the first (*a*) they travel counter-clockwise, while in the second (*b*) they travel clockwise.

As we may see, if these two active lactic acids are mixed in equal proportions, inactive lactic acid will result. If we make lactic acid synthetically from symmetrical substances we always get the inactive lactic acid. Thus propionic acid evidently yields an intimate mixture of dextro- and laevo-rotatory acids and the product is therefore inactive.

Among the earliest methods of obtaining lactic acid on a commercial scale was that proposed by Beusch:[1] 6 lbs. of cane sugar and $^1/_2$ oz. of tartaric acid (which serves to convert the cane sugar into dextrose) are dissolved in 26 lbs. of boiling water. After 2 days, 2 lbs. of chalk are added, together with 4 oz. of putrid cheese suspended in 8 lbs. of sour milk. The mixture is then set aside at a temperature between 30 and 35° C. and well stirred every day until, in the course of 6 or 8 days, it is converted into a thick paste of calcium lactate. This paste is boiled for $^1/_2$ hr. with $^1/_2$ oz. of quicklime and 20 lbs. of water, the solution strained through cheesecloth and evaporated to a syrup. The crystalline mass which first forms is pressed by itself, then three or four times after having been each time stirred up with $^1/_{10}$ part of cold water, and the lactate of calcium thus purified is dissolved in twice its weight of boiling water. To 32 parts of the solution of the calcium salt is added a mixture of 7 parts of sulfuric acid and 7 parts of water. The lactic acid thus formed is strained through linen while still hot to separate it from the sulfate of lime, and boiled with $1^3/_8$ parts of zinc carbonate for 15 min. Lastly, one part of the zinc salt is dissolved in $7^1/_2$ parts of boiling water and treated with sulfuretted hydrogen until zinc sulfide ceases to precipitate. The filtrate, containing the pure lactic acid, is evaporated on the water bath.

The method used in this experiment was as follows: A synthetical culture medium was prepared consisting of asparagin 10 g., magnesium sulfate 0.2 g., dipotassium phosphate 1 g., sodium chloride 0.5 g., potassium nitrate 0.2 g., dextrose 20 g. to each liter of distilled water: to this solution were added 15 g. of pure calcium carbonate per liter. To the medium thus prepared, was added a small amount of previously prepared Matzoon as a starter, and the mixture allowed to incubate at 37.5° C. for 2 wks. At the end of that time the fermentation product was filtered and washed. A residue of unused calcium carbonate together with a slight amount of calcium oxalate remained. The filtrate contained the calcium salts of volatile and nonvolatile organic acids. This filtrate was barely acidified with sulfuric acid, heated, and filtered to get rid of the calcium as calcium sulfate. The filtrate was then distilled to one-half volume, and steam passed through the residue in the flask so as to separate the volatile acids from the nonvolatile acids.

TESTS FOR VOLATILE ACIDS—The distillate was treated with sodium hydroxide (care being taken to avoid an excess) and heated gently. The solution was evaporated on the water bath and the crystals of the sodium salts of the volatile acids were obtained.

FORMIC ACID was tested for in four ways: (1) To a small portion of the dry residue in a test tube was added a little sulfuric acid. The mixture was heated gently while the mouth of the tube was covered. Carbon monoxide would be liberated during the heating if formic acid were present. Carbon monoxide burns with a characteristic blue flame. The reaction which takes place is: $HCOONa + H_2SO_4 = NaHSO_4 + H_2O + CO$. (This test should be tried in a dark room.) Where a large amount of formic acid is present it is not necessary to heat the mixture.

(2) To a small portion of the salt were added a little alcohol and a drop of sulfuric acid. If formic acid were present ethyl formate would be formed which has a characteristic odor. The following reactions show what takes place:

$$HCOONa + H_2SO_4 = NaHSO_4 + HCOOH,$$
$$HCOOH + C_2H_5OH = HCOOC_2H_5 + H_2O$$

(3) To a solution of the salt was added a little silver nitrate. On heating, a formate, if present, would reduce the silver nitrate to free silver.

(4) A little of the dry formate was mixed with soda lime ($CaO + NaOH$) and the mixture heated. Hydrogen would be liberated were a formate present, as

$$CaO + HCOOH = CaCO_3 + H_2.$$

By none of these tests could the author show the presence of formic acid.

ACETIC ACID—Since no formic acid was present, acetic acid was tested for by the following methods:

(1) A small portion of the solid was just acidified with sulfuric acid and a drop of alcohol was added to the mixture. Acetic acid was shown to be present by the odor of ethyl acetate which was given off. The odor is similar to that of bananas. The reactions which take place are:

$$CH_3COONa + H_2SO_4 = CH_3COOH + NaHSO_4$$

and

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

(2) The cocodyl test. A little of the dry salt was mixed with arsenious oxide (As_2O_3) in a hard glass tube and heated to a high temperature. A strong garlic-like odor of cocodyl oxide shows the presence of acetic acid:

$$4CH_3COONa + As_2O_3 = (CH_3)_4As_2O + 2CO_2 + 2Na_2CO_3$$

(3) A small amount of the solution of the sodium salt was treated with a drop of ferric chloride and the mixture boiled. A red-brown precipitate of basic ferric acetate formed which showed the presence of acetic acid:

$$CH_3COONa + FeCl_3 + H_2O = CH_3COO(OH)_2Fe + NaCl + 2HCl$$

Propionic and *butyric acids* were found to be present by the following method: A rather large amount

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[1] *Ann. Chemie Pharm.*, **61**, 174.

of the distillate after the first treatment with the sulfuric acid was neutralized with baryta water and evaporated to dryness. The residue was heated to boiling with 80 per cent alcohol, by which process the barium propionate and butyrate were dissolved, leaving the barium salts of the lower acids which are insoluble. The alcoholic solution was evaporated, the residue dissolved in water and decomposed by silver sulfate by boiling. After filtering, the silver salts were dissolved in concentrated sulfuric acid which liberated the pure propionic and butyric acids. They appeared as minute oily drops on the sulfuric acid. No attempt was made to separate the propionic and butyric acids.[1]

After testing for the volatile acids the author continued the purification of the lactic acid. After the volatile organic acids were removed the residue contained lactic acid, succinic acid and some calcium sulfate which continued to separate out on concentration. This latter substance was very hard to remove: repeated filtrations, washing regularly to keep the succinic acid in solution, and concentrating on the water bath, were necessary. After all the calcium sulfate was removed, the residue was a very dark syrupy liquid (lactic acid and charred organic impurities) containing a white, crystalline solid (succinic acid). The succinic acid was removed by filtration with suction, and its melting point determined as 183° C. (very sharp): a large amount of succinic acid was formed due to the use of a derivative of this acid—asparagin—in the original culture medium.

The lactic acid, which still contained a large amount of charred organic matter, was diluted to about four times its volume with distilled water and purified by boiling, under a return condenser, with animal charcoal. The charcoal and its occluded organic compounds were filtered off under suction and a clear solution of lactic acid remained. The colorless liquid obtained was diluted with distilled water and neutralized with zinc carbonate, thus:

$$CH_3CHOHCOOH + ZnCO_3 = (CH_3CHOHCOO)_2Zn + CO_2 + H_2O$$

The zinc lactate obtained was crystallized, washed and recrystallized several times to obtain as pure a salt as possible. The zinc was removed by hydrogen sulfide, filtered off, and the optical properties of the lactic acid determined by means of the polariscope.

The lactic acid obtained from Matzoon proved to be of the usual inactive variety. The problem now presented itself to resolve this acid into its active components. The method proposed by Purdie and Walker[2] was the one used:

150 cc. of the lactic acid solution were neutralized with strychnine. This required slightly over 28 g. of strychnine. Since strychnine unites with lactic acid in molecular proportions,[3] there must have been about 8.5 g. of pure lactic acid present in the 150 cc. of the diluted acid. The liquid was then subjected to systematic fractional crystallization, the crystalline solid in each case being separated as far as possible by the aid of suction and recrystallization being carried out in a vacuum desiccator.

After several successive crystallizations the less soluble crystals were dissolved in water and the strychnine was precipitated by the addition of ammonium hydroxide. The filtrate was evaporated and a slight excess of ammonium hydroxide added to completely precipitate the strychnine. After again filtering the solution, it was tested in the polariscope in a 220 mm. tube. It gave a rotation of +0.9°. The mother liquor was then treated in the same way with ammonium hydroxide, filtered and tested. It gave a rotation of —0.9°. In this way it was proved that lactic acid obtained from Matzoon was capable of being resolved into its active components.

CONCLUSIONS

I—Matzoon, an Armenian lactic acid food, owes its peculiar properties to the Bulgarian bacillus together with *Streptococcus lebenis* and *Saccharomyces kefir*.

II—Fermentation lactic acid may be separated and purified by the method described in this paper.

III—The acid produced by Matzoon in a synthetic culture medium is optically inactive, but this inactive acid is capable of being resolved into active components.

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PLANT FOOD DEFICIENCIES OF COASTAL PLAIN AND PIEDMONT SOILS[1]

By C. B. WILLIAMS

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In approaching the solution of this kind of a problem for any section, it is necessary to conduct experimental field work on the soils of known types which occur in the area and which are important ones agriculturally in the sections. These facts may be determined by a soil survey which had best precede, if possible, the taking up of field studies to determine the plant food deficiencies of soils of the section. After the mapping has been finished in the soil survey, a trained and experienced man is sent over the area to draw representative samples of soil and subsoil for analyses from each type occurring in the area. These are sent to the chemical laboratory for a determination of the total amount of nitrogen, phosphoric acid, and potash present.

WHAT CHEMICAL ANALYSES WILL SHOW

From such an examination it will be possible to calculate the total amounts of these plant food constituents actually present in the soil, but it will not be possible from such an examination to determine the availability of these for plant growth. This can be satisfactorily done only by well planned and carefully conducted fertilizer experiments with different crops on each type of soil, and carried on a sufficient length of time to eliminate seasonal and other factors that might occur to interfere with a fair deduc-

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[1] See Fresenius, "Qualitative Analysis," p. 419.

[2] *J. Chem. Soc.*, **61**, 754.

[3] *Ibid.*

[1] Presented at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, Ill., April 17 to 21, 1916.

tion from one or two years' results. Below are tabulated the average amounts of nitrogen, phosphoric acid and potash contained in the leading types of soil occurring in the Coastal Plain and Piedmont regions in which field work has been conducted. In the Coastal Plain, the Norfolk series embraces decidedly the most important soils of the whole South Atlantic States, while in the Piedmont section the Cecil series occupies the greatest area and are the soils of the greatest importance agriculturally. The data show very strikingly that the total amounts of phosphoric acid and nitrogen present in all the different types of soil on which the experimental fields are located are each much smaller than is the amount of potash. From these facts alone, with reference to the different types under consideration, the only inferences that could safely be made would be that potentially most of the soils are fairly well supplied with potash, but that the amounts of phosphoric acid and nitrogen, one or the other, or both, are at present, or soon will be, limiting factors in the production of large crops.

AVERAGE LBS. PLANT FOOD IN SURFACE $6^2/_3$ IN. OF SOIL PER ACRE OF SOME OF THE LEADING SOILS IN THE COASTAL PLAIN AND PIEDMONT REGIONS

Type and Location of Soil	N	P_2O_5	K_2O	Experimental Field
COASTAL PLAIN				
Portsmouth Fine Sandy Loam.	1660	590	7051	Pantego
Portsmouth Silt Loam........	1131	555	28884	Edenton
Norfolk Sand.................	1275	298	1978	Greenville
Norfolk Fine Sandy Loam....	912	546	8873	Edgecombe
Norfolk Sandy Loam.........	639	1439	4552	Goldsboro
PIEDMONT				
Cecil Clay....................	1285	1430	17743	Charlotte No. 1
Cecil Sandy Loam............	801	571	49260	Gastonia
Cecil Loam....................	865	1512	27702	Charlotte No. 2
Iredell Loam..................	909	2238	4247	Iredell

The economical increase of the nitrogen supply of all these soils for the production of general crops like corn, cotton, or oats will have to be brought about largely by the growing of leguminous crops in rotation with these and possibly other general field crops and turning a part of these into the soil for soil improvement. By this means, not only can the nitrogen supply of the soil be kept up, wholly or largely, but the soils will be kept in good physical condition by the organic matter turned into them. It will probably be necessary, with many of our soils, where this practice is followed, to add lime in fairly liberal amounts at intervals of 4 to 6 years. On the other hand, in the case of phosphoric acid, its supply for plant growth will have to be kept up in most cases by additions of some material carrying the plant food constituent in more or less readily available form (*e. g.*, acid phosphate, basic slag, phosphate rock or ground bone) if large crops are expected to be produced. In some of the leading types of soil occurring in the South the total amount of phosphoric acid is very low. Potentially soils of the Iredell and Houston series are some of our richest in phosphoric acid supply. This has been brought out both by chemical examination and by field experiments.

WHAT FERTILIZER EXPERIMENTS IN FIELD SHOW

For the Coastal Plain section and the Piedmont section the following general deductions which will have wide application throughout the Southern States, may be made from data obtained in field experiments:

COASTAL PLAIN SOILS—With *Portsmouth fine sandy loam* the chief deficiency is generally for nitrogen in available form. Next in importance to be supplied are lime and phosphoric acid.

For the *Portsmouth silt loam type*, plant food constituents producing the greatest returns when added to the soil are phosphoric acid, nitrogen and lime in the order given.

For the *Norfolk sand type of soil*, the chief deficiencies are shown by our results to be *first*, nitrogen; *second*, lime; and *third*, potash. For the *Norfolk fine sandy loam* the main deficiencies of the soil have shown up to be *first*, nitrogen; *second*, potash; and *third*, phosphoric acid and lime. This type of soil is one of the largest in extent and importance of all the Coastal Plain soils. Field observation on the *Norfolk sandy loam* soil has shown that the chief plant food requirements are for nitrogen, lime and potash in the order given. Phosphoric acid, when used, seems to have on an average caused a decrease in yield of all the crops except in the case of cotton. Ordinarily with all the Norfolk series of soils of the Coastal Plain Region, phosphoric acid and potash give little or no increase in crop yields until nitrogen has been added to the soil.

PIEDMONT SOILS—The chief deficiencies of the *Cecil Clay* type of soil have been shown by the field results to be nitrogen, lime and phosphoric acid. The chief plant food requirements of the *Iredell Loam* type of soil have been shown to be *first*, nitrogen decidedly; and *second*, potash. On an average, phosphoric acid has seemed to decrease rather than prove beneficial when applied to this type of soil. Nitrogen, phosphoric acid and lime have been shown to be the chief requirements of the *Cecil Sandy Loam* of this field.

In the production of grain and seed cotton on average *Cecil Loam* soil, phosphoric acid was found to be the chief deficiency while applications of nitrogen gave the greatest response when hays were grown. Practically no grains on an average were secured from the use of lime and potash, except in the case of lime, in the growing of oats for hay, and in the case of potash in growing red clover for hay.

Taking the results as a whole for the leading soils of both the Coastal Plain and Piedmont sections, which no doubt have wide application to soils throughout the South Atlantic States, it will be seen that the chief needs for plant growth in the Coastal Plain Region are generally, *first*, for nitrogen, and *second*, for potash and lime. Those soils of chief importance and extent in the Piedmont Region show a lack *first*, for phosphoric acid and *second*, for nitrogen. Without the addition of these deficient plant food constituents, it will be impossible to grow large crops for any great length of time, for, with most of the types of soil of these two regions of the South, the growth of 2500- to 3100-bu. crops of corn would require an amount of phosphoric acid and nitrogen equal to the total amount of these two constituents contained in most of the Coastal Plain and Piedmont soils.

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LABORATORY AND PLANT

THE PRINCIPLES OF COUNTER-CURRENT EXTRACTION

By W. K. Lewis

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A large number of processes in chemical engineering practice involve the transfer of some substance from one to the other of two bodies. This process is in general spoken of as extraction. For the sake of clearness we shall designate the body bringing into the system or process the matter which it is desired to transfer to some other body as the "*carrier*." The matter which the carrier brings into the system and which is to be transferred to some other body shall be called the "*solutum*."[1] The body which is to absorb the solutum from the carrier and thus take it out of the system, shall be called the "*extractor*." It is therefore the function of the extractor to absorb from the carrier, in general as completely as possible, the solutum, either for the purpose of recovering the solutum in the extractor or for removing the solutum from the carrier, or in certain cases for both. To secure efficiency of extraction the principle of the counter-current must be employed, *i. e.*, fresh carrier entering the system must be treated first not with fresh extractor, but with extractor which is already nearly saturated with solutum from contact with previous batches of carrier, while toward the end of the system fresh extractor as free as possible from solutum must be used for final removal of solutum from the carrier.

The calculation and design of systems for counter-current extraction is at present a matter of empiricism. Several years ago this laboratory undertook the study of the problem and a large amount of work has been done upon it. The problem is by no manner of means an easy one and especially from the experimental side the verification of the methods of calculation developed has been a difficult matter, but our results, while even yet incomplete, are sufficiently definite to justify us in presenting our methods of calculation and our data, especially in view of the fact that these things are greatly needed by the profession.

We first present the formulas which we have developed and later the experimental evidence which we have accumulated indicating the validity of our methods of calculation. The derivation of the formulas we shall add separately.

GENERAL CONSIDERATIONS

If a carrier and extractor be brought into contact any solutum present will distribute itself between the two and ultimately an equilibrium will be attained. The concentrations of solutum in carrier and extractor will at equilibrium bear a certain relation to each other and this distribution of solutum between the two phases will usually follow, at least approximately, one or the other of two laws. If we call the concentration of solutum on the carrier x and in the extractor y, we shall have either $x = \alpha y$ or $x = \alpha y^{1/n}$. In the first case the solutum is said to be linearly distributed between carrier and extractor, while in the second case the solutum is spoken of as adsorbed upon the carrier. The nature of the extraction process is decidedly different in the two cases.

When carrier and extractor are brought together this equilibrium is not immediately set up, but, on the other hand, solutum passes from one phase to the other at a rate depending upon the specific case and conditions involved. It is exclusively this rate of interchange of solutum between carrier and extractor which determines the capacity of any industrial system.

Both the equilibrium conditions and the rate of transfer of solutum from one phase to the other are subject to the influence of a number of variables such as the nature of both carrier and extractor, the temperature, the pressure, the concentration of solutum in both phases, the viscosity of the phases, etc. On the other hand, most of these variables are fixed by the nature of the case. For example, if we are extracting tannic acid from hemlock bark the extraction must be carried out with water as an extractor. The distribution of tannic acid between hemlock bark and water is itself influenced by both temperature and concentration, but inasmuch as extraction is always more rapid the higher the temperature, we shall employ in extraction the highest temperature possible. The temperature may be limited by the boiling point of the solution obtained, by deterioration of the tannin extract, or by the extraction at too high temperatures of excessive amounts of non-tannin material. In any case, however, the temperature of extraction is dictated by considerations which are not under control of the designer of the extraction system. While it is also true that the concentration influences the distribution and the extraction, the initial concentration of the tannin on the bark is determined absolutely by the tannin content of the bark available for extraction, and furthermore, even the concentration of tannin left on the bark is dictated by the necessity of securing as high a tannin recovery as possible, so that the initial, and to at least a degree, the final concentration are not subject to variation. On the other hand, the concentration of the tannin in the extract obtained can be varied by the designer within wide limits by the use of larger or smaller quantities of water for the extraction. The rate of extraction will be greater the greater the concentration difference between carrier and extractor, and it is therefore primarily this which can be varied in a given system. If this concentration difference becomes small so that the two phases are nearly in equilibrium, the rate of transfer of solutum will become negligible and to secure an appreciable transfer will require an excessive time. The two variables

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[1] This term, the word formerly used for solute, is employed because the thing transferred, especially when a material substance, can usually be conceived as in solution; the use of the word *solutum* rather than *solute* will indicate that a transfer from one phase to another is under consideration, that the separate phases need not be solutions in the ordinary sense, and that the thing transferred may be either energy or matter.

which the designer of a counter-current system can control are in general the ratio of extractor to carrier and the size of the extraction system, or what is equivalent to the same thing, the time of contact between carrier and extractor. In the following discussion we shall assume that all other variables such as the nature of extractor, carrier and solutum, the temperature and pressure of extraction, the distribution law between the phases, etc., are beyond the control of the designer and are therefore fixed for the given case. The following treatment is a study of the influence of the time of contact and ratio of extractor to carrier upon any extraction system.

In all extraction systems either carrier or extractor is a fluid: *i. e.*, either a liquid or a gas. Furthermore, either one or the other of these phases is finely divided, the separate particles being more or less completely separated from each other and offering a large surface of contact, while the other phase, which is always a fluid phase, fills the voids between the particles of the first. For example, in the extraction of solids such as tan bark, pyrites cinder, black ash, and the like, with liquids, the solids are always divided and completely immersed in a continuous liquid medium. In the washing of gases, *e. g.*, benzol and ammonia from coal gas, the washing liquid is separated in the form of either a spray or exposed in a large surface for contact with the gas. In any case it is probable that the extraction process consists primarily in the diffusion of the solutum through a stationary layer of fluid which envelops separate particles of the finely subdivided phase. The fluid in immediate contact with the separate particles is probably nearly in equilibrium with them and the diffusion process is determined by the difference in concentration between the saturated solution on the very surface of the separate particles of the dispersed phase and the main body of the solution around those particles but outside of the stationary surface film. Our formulas are derived upon the assumption of this mechanism.

Assuming the nomenclature given in the list below, our formulas are as follows: For the case of the extraction of solids by liquids,

$$\log\left[1 + \frac{c_1}{x_0}(\rho - \alpha)\right] = \frac{\beta u V}{\alpha A^2}(\rho - \alpha).$$

For the case of transfer of solutum from a gas to a liquid or *vice versa* they become,

$$\log\frac{x_0 - \alpha c_0}{x} = \frac{KV}{u}(\rho - \alpha),$$

for apparatus in which the velocity of gas past the liquid is constant (spray washers), or

$$\log\frac{x_0 - \alpha c_0}{x} = \frac{\beta U l}{\rho A}(\rho - \alpha),$$

for apparatus in which the absorbing liquid forms a film over a stationary surface.

DERIVATION OF FORMULAS

The mechanism by which the solutum is removed from the carrier by the extractor is assumed to be as follows: The more fluid medium (either liquid or gaseous) forms a film on the surface of the other phase, which is practically stationary. Let us consider first the extraction of a solid carrier by a liquid extractor. In immediate contact with the carrier, on the interior of this film, the extractor is saturated with solutum, the equilibrium between the carrier and the extractor being practically perfect at this particular point. The concentration of the solutum in the body of the extractor is, however, considerably lower than this, and the solutum diffuses through this stationary film according to ordinary diffusion laws. A more complete discussion of the factors governing diffusion will be given later.

In considering the extraction we may look at the matter from either one of two points of view. Either we may consider the decrease in concentration of solutum on the carrier or the increase in concentration in the extractor. The total amount of solutum given up by the one must of course be equal to that taken up by the other. If we designate, by t, the time of contact of extractor with carrier, leaving the exact formulation of this quantity, t, for later discussion, we may write the equations

$$(1)\quad \frac{dc}{dt} = k(c' - c), \text{ and } (2)\quad \frac{dx}{dt} = K(c' - c),$$

c being the concentration of the solutum in the liquid extractor at any particular point in the apparatus, x the concentration of the solutum on the carrier at the same point, and c' the concentration of solutum in the extractor in immediate contact with the surface of the carrier, and therefore, from what has been said above, in equilibrium with the solutum on the carrier. The two constants k and K will not necessarily be identical, but there will exist between them a proportionality which will be developed later.

The value of c' is a function of x, two cases requiring consideration. In the first of these the quantities in the two phases are proportional and we may write

$$(3)\quad x = \alpha c'.$$

In the case we are considering, namely, the extraction of a solid by a liquid, this relationship probably never rigidly holds. On the other hand, in many cases of this type this equation is a very close approximation of the facts and enables us very satisfactorily to calculate the behavior of extraction systems. The two most important cases are, first, those in which the solid carrier is a porous material and holds the solutum in it merely as a solution contained in its pores. Such is the case in the extraction of copper sulfate from pyrites cinder, of grease from wool, and of various substances from organic fibers by the use of organic solvents, etc. The second case is that of a solutum held in a gel, as for example salt in skins. In both these cases diffusion out of the carrier is experimentally found to be nearly proportional to the difference in concentration of the solutum in the extractor held within the pores of the material in the one case, or within the gel in the other, and the concentration in the main body of the extractor. In the second case we have adsorption of the solutum from the liquid upon the carrier, and in that case it is experimentally found that the relationship existing between c' and x is

$$(4)\quad x = \alpha c'^{1/n},$$

$\alpha c'$ and n being constants, the latter greater than unity, usually having a value between 2 and 20.

In either case we may substitute in (1) the values given for c' and obtain, when $x = \alpha c'$,

$$(5)\quad \frac{dc}{dt} = k\left(\frac{x}{\alpha} - c\right), \quad \text{and} \quad (5a)\quad \frac{dx}{dt} = \mathrm{K}\left(\frac{x}{\alpha} - c\right);$$

when $x = \alpha c'^{1/n}$

$$(6)\quad \frac{dc}{dt} = k\left(\frac{x^n}{\alpha^n} - c\right), \text{ and } (6a)\quad \frac{dx}{dt} = \mathrm{K}\left(\frac{x^n}{\alpha^n} - c\right).$$

The integration of these differential equations gives us the solution of the problem in hand.

Let us now apply the principle of the equality of input and output in any continuously operating process. Let us call the weight of carrier passing any section per unit time equal to U, and likewise the weight of extractor per unit time equal to u. Call the concentration of solutum on the carrier and in the extractor, at one end or the other of the system, in general, at that end where the fresh extractor enters the system, equal to x_0 and c_0, respectively. Usually c_0 will be equal to zero. The equality of input and output requires that

$$(x - x_0)\mathrm{U} = (c - c_0)u.$$

For the usual case where $c_0 = 0$,

$$(7)\quad x = x_0 + uc/\mathrm{U}.$$

Inserting this value in the above equation we obtain

$$(8)\quad \frac{dc}{dt} = k\left(\frac{x_0}{\alpha} + \frac{uc}{\alpha\mathrm{U}} - c\right)$$

or

$$\frac{dc\left(\frac{u}{\alpha\mathrm{U}} - 1\right)}{\frac{x_0}{\alpha} + \frac{uc}{\alpha\mathrm{U}} - c} = kdt\left(\frac{u}{\alpha\mathrm{U}} - 1\right).$$

Integrating,

$$\log\left[\frac{x_0}{\alpha} + \left(\frac{u}{\mathrm{U}\alpha} - 1\right)c\right] = kt\left(\frac{u}{\alpha u} - 1\right) + \text{const.}$$

The limits are as follows:

$$\left.\begin{array}{llll} l = 0 & t = 0 & c = 0 & x = x_0 \\ l = l & t = t & c = c_1 & x = x_1 \end{array} \quad \begin{array}{c} \text{constant of inte-} \\ \text{gration} \end{array}\right\} = \log\frac{x_0}{\alpha}$$

$$(9)\quad \left[\frac{x_0}{\alpha} + \left(\frac{u}{\mathrm{U}\alpha} - 1\right)c_1\right] = kt\left(\frac{u}{\alpha\mathrm{U}} - 1\right) + \log\frac{x_0}{\alpha}$$

ADSORPTION

If $x_0 + \frac{uc}{\mathrm{U}}$ be substituted for x and $\rho = \frac{u}{\mathrm{U}}$ in Equation (6) we obtain

$$(10)\quad \frac{dc}{dt} = k\left[\left(\frac{x_0 + \rho c}{\alpha}\right)^n - c\right]$$

or

$$(11)\quad \int_{c=0}^{c=c} \frac{dc}{\left(\frac{x_0 + \rho c}{\alpha}\right)^n - c} = kt.$$

This equation may be integrated graphically but will not be further discussed here. In consequence of its importance we shall treat this case at some future time.

NATURE OF DIFFUSION PROCESS

The constants k and K are in reality diffusion constants, representing the rate at which diffusion will take place under conditions of unit difference of concentration and unit distance of flow. These constants will depend upon the solutum involved, upon the fluid medium through which the flow takes place (*i. e.*, upon the extractor), upon the temperature, and perhaps also upon still other variables. On the other hand, in general all these variables will be fixed by the conditions necessarily imposed upon the engineer; *e. g.*, in the extraction of grease from wool, petroleum naphtha is the only solvent available on account of the greater expense of other materials. Furthermore, the temperature to be employed for the extraction will be limited rigidly by the boiling point of this material unless the system be kept under pressure, and in that case by the allowable pressure in the system. In the same way in all cases the extractor which must be employed, the highest temperature which it is possible to utilize, and other such variables will not be at the discretion of the engineer, but beyond his control. If in any case these things are capable of modification, each new possible modification must really be considered as a separate problem, to be solved by the methods outlined in this discussion.

This being the case, the only factors which the engineer can control are, in the first place, the time of contact of the carrier with the extractor and, in the second place, the amount of extractor used per unit amount of carrier treated. It will be developed later that the velocity with which the extractor flows past the carrier is also an important factor, which is to a greater or less extent under the control of the engineer.

The discussion of the matter of time of contact now becomes necessary. If we consider a single particle of the carrier passing through any given system, that particle will remain in the system a certain length of time, and that time is the time of contact of that particle of solid carrier with the extractor, and such we might define it to be. On the other hand, if we consider a drop of the liquid extractor flowing through the system, this drop of extractor will also be in the system a certain length of time, depending upon its linear velocity and the length of the system. This drop will not, however, be in contact with the carrier throughout the whole of its path. Indeed, it is practically impossible in this case to define contact at all, but if we agree to consider the drop as in contact with the carrier during any time when it is within a certain maximum distance of the carrier surface, the drop will be in contact with the carrier a certain definite fraction of the total time the drop remained in the system, that fraction depending in general upon the amount of carrier in the system and being proportional to that amount. Thus, if in extracting wool, in one case we pack into an extraction tank twice as much wool as in another case, a drop of solvent passing through this tank will have twice the chance to come in contact with the fiber, and its time of contact will thus in a very real sense be twice as great as under the second assumption. The actual value of the time of contact of the drop of extractor with the carrier will depend upon our arbitrary assumption as to the limiting distance between carrier and drop beyond which contact is neglected. Inasmuch as this assumption would be an entirely arbitrary one, it is allowable and advisable to omit this particular factor altogether and to define arbitrarily the time of contact of the liquid with the carrier as the average time which any particular drop of liquid remains in the system. This time must be multiplied by the amount of carrier per unit volume of the system unless this quantity, as is usually true, is constant.

Another factor influencing the time of contact is the surface which the carrier exposes to the action of the extractor. Thus the more finely divided the carrier, the greater its surface per unit amount, and in case the influence of surface, or what is the same thing fineness of subdivision of the carrier, is to be taken into consideration, the time of contact must be defined as proportional to the surface per unit weight of the carrier. On the other hand, this quantity is usually fixed, owing to the fact that the carrier is either not subdivided at all to avoid the expense of grinding, or else is subdivided as far as possible without causing packing of the material in the extraction tanks, resulting in interference with the extraction process. This matter of surface exposure of the carrier is therefore generally not one which is varied in a given extraction system.

It must be realized that these definitions of time of contact are arbitrary ones, the time of contact being really proportional to the factors which we have mentioned, but inasmuch as the proportionality constant cannot possibly be determined except by making arbitrary assumptions, the simplest thing to do—and a thing entirely admissible—is to make the proportionality factor equal to unity. Time of contact may therefore be defined as the time the extractor or carrier, as the case may be, is in the system, times the weight of carrier per unit volume of the system, and also times the surface of the carrier per unit weight. Usually these last two terms are omitted provided they are not subject to variation.

If the carrier per unit volume of the system be constant, the voids between the particles of carrier will also remain unchanged, and the time of contact will therefore be proportional to the total volume of the extraction system, divided by the amount of carrier or extractor per unit time. We shall therefore limit ourselves throughout to this definition of time of contact, *i. e.*,

Time of contact of carrier = *total volume of system/ amount of carrier per unit time.*

Time of contact of extractor = *total volume of system/ amount of extractor per unit time.*

Returning again to the diffusion constants k and K, and indicating the time of contact of the carrier by t_x and of the extractor by t_c, Equations (5) and (5a) become,

$$\frac{dc}{dt_c} = k\left(\frac{x}{\alpha} - c\right), \text{ and } \frac{dx}{dt_x} = \mathrm{K}\left(\frac{x}{\alpha} - c\right).$$

Dividing,

$$\frac{dc}{dx} = \frac{k}{\mathrm{K}}\frac{dt_c}{dt_x}.$$

However, from the equation

$$(x - x_0)\mathrm{U} = (c - c_0)u,$$

$$\frac{dc}{dx} = \frac{\mathrm{U}}{u} = \frac{k}{\mathrm{K}}\frac{dt_c}{dt_x}.$$

Integrating, remembering that zero contact for carrier must also be zero contact for extractor, $\frac{\mathrm{U}}{u} = \frac{k}{\mathrm{K}}\frac{t_c}{t_x}$.

This equation represents the relationship which must exist between the constants k and K, the ratio of carrier to extractor, and the times of contact, t_x and t_c. The constants k and K are in reality diffusion constants, as previously pointed out, and it is desirable to have them numerically identical. They will be numerically the same provided $ut_c = \mathrm{U}t_x$. By definition we have arbitrarily chosen to place

$$t_x = \frac{\mathrm{V}}{\mathrm{U}}, \text{ and } t_c = \frac{\mathrm{V}}{u}.$$

It is evident that these definitions meet the above requirement, so that with these definitions of time of contact the diffusion constants are the same no matter whether carrier or extractor are under consideration.

It will be shown later that the diffusion constant, k, increases with increasing velocity of extractor. The data on this point is inadequate, but seems to justify as a preliminary assumption the relationship,

$$k = \mathrm{K} = \beta\left(\frac{u}{\mathrm{A}}\right)^2,$$

where A is the cross section of the extraction system, and β a constant the value of which depends entirely upon the carrier, extractor, and solution involved, the *fineness* of the particles of carrier, the temperature of the extraction, etc. The value of β must be determined for each specific case.

Inserting these values in (9) there results,

$$(9a) \qquad \log\left[1 + \frac{c_1}{x_0}(\rho - \alpha)\right] = \frac{\beta u\mathrm{V}}{\alpha\mathrm{A}^2}(\rho - \alpha).$$

INTRODUCTION OF NEW TANKS

The calculation of a counter-current system for extracting a solid carrier with a liquid extractor is rendered complicated by the fact that it is impossible to realize perfect counter-current conditions. To secure absolute counter-current flow both carrier and extractor must enter the system at a uniform rate. In the extraction of a solutum from a solid carrier, the carrier is usually put into a tank, and at definite intervals of time, tanks of fresh carrier are introduced into the system. The system is then run with continued addition of extractor, but without the addition of further carrier until the next tank is inserted into the system. To allow for this lack of continuity in extraction, in any exact way, would be very difficult, but an approximation can readily be made, which will introduce no greater error than the other assumptions we have been compelled to use. When a new tank of fresh carrier is inserted into the system, the inflow of extractor at the other end of the series is changed from that tank which is most nearly extracted and into which fresh extractor has been running, to the next in the series, and the extractor continues to flow into this tank until the next change of tanks in the system, *i. e.*, throughout one cycle of operations. At the beginning of this cycle the top of this tank is the head of the system. At the end of this cycle the top of the next tank becomes the head of the system, and therefore it will not involve serious error if we assume that during this cycle the average position of the head of the system has been at the middle of this tank. In other words, during this cycle only one-half of this tank has really been an effective part in the counter-current extraction system.

Considering now the tank which has just been inserted into the series, at first, extract from the previous tanks flows into this tank until all the voids have been filled; until this stage is reached this tank is not in any way a part of the real counter-current system. When this state is reached the tank becomes active in a sense, but, on the other hand, during a large part of the rest of the time the liquid in this tank is merely being displaced by inflowing liquid and no extraction in the tank starts until this displacement is completed. It is possible to estimate when this displacement is finished, but, on the other hand, in general, this tank will be for so slight a time a really effective part of the counter-current system that in general the whole tank may be neglected. If we do this, this means that both this tank and one-half of the first tank are not in actual operation, and the net length of the counter-current system may be approximated by subtracting from the total number of tanks in operation 1.5. Inasmuch as one tank is out of the system entirely, being refilled, this means that 2.5 less than the total number of tanks in the system are in effective operation at any one time.

Furthermore, the liquid obtained as effluent from the last tank of such a system cannot be considered as having the same concentration as that which is obtained from the true counter-current system itself.

The reason for this is that the liquid flowing from the real counter-current system into the tank of fresh material first mixes with that material, dissolves the solutum from that material, and then delivers the product of the system as a whole before a new tank is inserted into the series. While the product of the counter-current extraction system is not of constant composition on account of the discontinuity of operating conditions, we may without serious error, assume it to be of a definite *average* composition which we shall call c_1. The composition of the liquid in the fresh tank obtained by admixture of the fresh charge with the liquid necessary to fill the voids flowing upon this charge from the true counter-current system we shall call c'. The concentration of the solutum on the carrier as it enters the system originally is x' and of the solutum on the carrier as it enters the counter-current system from the last tank x_1. We shall now assume that there is no adsorption of solutum on the carrier, but that the solutum is held in the voids within the carrier itself. As soon as the extractor from the true counter-current system enters a new tank of carrier which has just been inserted into the series, this extractor completely dissolves all the solutum in the carrier and forms a solution which we shall assume to be homogeneous both in the voids of the carrier itself, and in the voids between the particles of carrier in the tank. Unquestionably, in the majority of cases this is practically what happens, and the following equations apply only to these cases. The equations are merely an expression of the equality of input and output to the last tank in the series and to the series as a whole.

S = volume of product
P = volume of each tank actually filled by solid carrier
Q = volume of each tank occupied by voids in carrier
R = volume of each tank occupied by voids between carrier
P + Q + R = the total volume of each tank not including excess space above the top of the mixture
D = wt. of solid carrier per unit volume of the carrier itself
d = wt. of liquid extractor per unit volume of the solution

In each cycle the total carrier entering the system is enough to furnish the product, S, and fill the voids within the carrier Q. The ratio ρ, of extractor to carrier, is therefore

$$(a) \qquad \rho = \frac{(\mathrm{S} + \mathrm{Q})^{1}}{\mathrm{PD}}.$$

If equilibrium exists between carrier and extractor, the concentration, c, of solution in all the voids both within and around the carrier will be the same. The amount of solutum in the voids within the carrier will therefore be $d\mathrm{Q}c$, the corresponding weight of carrier itself being DP. Since, however, the concentration, x, of solution in the carrier is to be expressed as parts by weight of carrier, it must be true that

$$\mathrm{DP}x = d\mathrm{Q}c, \text{ or } \frac{\mathrm{DP}x}{d\mathrm{Q}} = c, \text{ or if } \frac{\mathrm{DP}}{d\mathrm{Q}} \text{ be called } \alpha,$$

$$(b) \qquad c = \alpha x.$$

Equations (*a*) and (*b*) hold in all cases.

Three cases arising in industrial practice must now be differentiated:

CASE I, S = R: When a tank of fresh carrier is inserted into a series the cycle through which it passes before the insertion of another tank can be divided into two stages: in the first, liquid entering from the previous tank fills all the voids in the charge. This liquid enters at a concentration c_1, bringing in an amount of solutum $d(\mathrm{R} + \mathrm{Q})c_1$, and dissolves all the solutum on the carrier, $\mathrm{PD}x'$, filling all the voids with a uniform solution of concentration c'. Hence

$$(c) \quad (\mathrm{R} + \mathrm{Q})dc' = (\mathrm{R} + \mathrm{Q})dc_1 + \mathrm{PD}x'$$

or

$$d(\mathrm{R} + \mathrm{Q})(c' - c_1) = \mathrm{PD}x'.$$

All of the solutum extracted from the carrier during the total

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[1] At this point one must keep clearly in mind the distinction between motion of both carrier and extractor past a section of constant concentration and motion of carrier and extractor relative to each other. The first is the essential in determining ρ. In the case under discussion the carrier remains stationary, so that motion of the extractor past a fixed point in the apparatus is greater than the value of ρ would indicate.

process is equal to DP multiplied by $(x' - x_0)$, the difference in the concentration of the solutum on the carrier at the beginning and at the end of the operation. The solutum extracted is also equal to dS multiplied by $(c' - c_0)$ the difference in the concentrations of the solutum in the extractor at the beginning and the end of the operation. The concentration of the solutum in the extractor is generally zero at the start of the extraction; therefore,

$$(d)\quad dSc' = DP(x' - x_0).$$

CASE 2, $S > R$: In this case during a cycle a fresh tank passes through three stages: *First,* a volume of effluent from the true counter-current system sufficient to fill the voids enters at a constant concentration c_1, bringing in a weight of solutum $dc_1(R + Q)$, dissolving the solutum on the charge x'DP, and producing a solution of concentration c', such that, as before,

$$(c)\quad d(R + Q)(c' - c_1) = DPx'.$$

Second, after the tank becomes full the product begins flowing from the tank, and a volume, R, is collected at the concentration c'. *Third,* in order to make up the total product, S, further volume, $S - R$ is removed as product at the concentration c_1. The solution removed as product is therefore the sum of the two, or,

$$(d)\quad c'dR + c_1d(S - R) = PD(x' - x_0).$$

This equality represents the equality of input and output in the extraction system as a whole.

CASE 3, $S < R$: In this case, during a cycle a fresh tank also passes through three stages. When the tank enters the series the solution of concentration c' has not been completely displaced from the previous tank. There therefore enters the tank a volume, $R - S$, at concentration c', and the tank is then filled with a solution $Q + S$ at concentration c_1, giving

$$(c)\quad (R - S)dc' + (Q + S)dc_1 + DPx' = (Q + R)dc', \text{ or}$$
$$d(c' - c_1)(Q + S) = DPx'.$$

Inasmuch as the product has a constant concentration, c',

$$(d)\quad dc'S = DP(x' - x_0).$$

By means of these equations one can estimate the conditions at both ends of any counter-current system for which sufficient data are available.

WASHING OF GASES

We have now completed the consideration of the extraction of a solid carrier by a liquid extractor. It will be remembered that we pointed out that the extraction of a gaseous carrier by a liquid extractor was in all essentials similar. The calculations in this latter case are indeed simplified by the fact that true counter-current conditions are usually realized in industrial practice.

The equations expressing the rate of extraction of a gas by means of a liquid are very similar to those previously derived for the counter-current extraction of a solid by means of a liquid.

$$(14)\quad \frac{dc}{dt_c} = k(p - \alpha c). \qquad (15)\quad \frac{dx}{dt_x} = -K(p - \alpha c).$$

α is the solubility constant, *i. e.*, the ratio of the partial pressure in the vapor to the concentration in the liquid.

If the pressure in the apparatus be chosen as unity then

$$p = \frac{x}{1 + x}.$$

$\frac{x}{1 + x}$ is the mol fraction of absorbable component in the gas at any point in the system.

If x be small in comparison with $1 + x$ we may assume $p = x$.

The equality of input and output requires that $(x - x_0)U = (c - c_0)u$.

Inserting these values in Equation (14) and integrating we obtain,

$$\log\frac{x_0 - \alpha c_0}{x - \alpha c} = \log\frac{x_0 - \alpha c_0}{x_0 - \rho(c_0 - c) - \alpha c} =$$
$$\frac{kV}{u}(\rho - \alpha) = \log\frac{p_0 - P_0}{p - P},$$

or as for $V = V_1$, $c = 0$

$$(16)\quad \log\frac{x_0 - \alpha c_0}{x_0 - \rho c_0} = \frac{kV_1}{u}(\rho - \alpha).$$

Experimentally it is found that $k = \frac{\beta U^2}{A^2}$.

$$(16a)\quad \log\frac{x_0 - \alpha c_0}{x_0 - \rho c_0} = \frac{\beta VU}{\rho A^2}(\rho - \alpha) =$$
$$\frac{\beta Ul}{\rho A}(\rho - \alpha) = \log\frac{x_0 - \alpha c_0}{x}.$$

If $\alpha = 0$, without neglecting x in the denominator of the mol fraction,

$$(17)\quad \log\frac{x_0\,(1 + x)}{x\,(1 + x_0)} = \frac{\beta UV}{A^2} = \log\frac{f_0}{f} = \frac{\beta Ul}{A},$$

where f may be either the fraction or the per cent of the absorbable gas at the points indicated. This is the equation to use where chemical combination of solutum with extractor occurs, *e. g.*, for the absorption of NH_3 by H_2SO_4.

Equation (16*a*) becomes indeterminate for $\rho = \alpha$. In this case, and indeed whenever ρ and α are nearly equal, (16*a*) simplifies to

$$(16b)\quad \frac{c_0}{x} = \frac{kV}{u} = \frac{\beta Vl}{\rho A}.$$

The equation for the washing of gases can be written as follows:

$$\log\frac{P_0 - p_0}{P - p} = kV\left(\frac{1}{U} - \frac{\alpha}{u}\right)$$

But from (7), $U(P - P_0) = \frac{u}{\alpha}(p - p_0)$

$$\text{whence}\quad \frac{1}{U} = \frac{\alpha}{u}\left(\frac{P - P_0}{p - p_0}\right).$$

$$\text{Hence}\ \log\frac{P_0 - p_0}{P - p} = \frac{kV\alpha}{u}\left(\frac{P - P_0}{p - p_0} - 1\right) =$$
$$\frac{kV\alpha}{u}\left(\frac{P_0 - p_0 - P + p}{p - p_0}\right) = kV\frac{[(P_0 - p_0) - (P - p)]}{u(c - c_0)};$$
$$\text{or}\ u(c - c_0) = kV\frac{[(P_0 - p_0) - (P - p)]}{\log\frac{P_0 - p_0}{P - p}},$$

or the amount extracted per unit time equals the diffusion constant k, times the volume of the apparatus V, times the logarithmic mean of the pressure differences of the solutum in gas and liquid at the two ends of the apparatus.

We have, therefore, the amount of solutum transferred proportional to the logarithmic mean of the pressure difference, an expression strikingly similar to the law for the flow of heat between bodies, in which case the logarithmic mean should also be employed. It is helpful to consider an extraction system as in all respects similar to a system for the transfer of heat, and indeed apparatus for the transfer of heat from one body to another which embodies the counter-current principle can be looked upon as a counter-current extraction system in which the solutum is not matter but energy in the form of heat.

It is very important to keep in mind the fact that the equations developed from the differential expression involving the rate of transfer of solutum from carrier to extractor—and involving therefore the diffusion constants k and β—are equations having to do only with the velocity of interchange of solutum from one phase to the other. They are, therefore, the equations which determine the *extraction capacity per unit volume* of the system in question. If a given system is operating entirely satisfactorily from this point of view of capacity per unit volume, and it is merely desired to change extraction capacity of the system as a whole not by changing the concentration relationships at different points in the system, but by enlarging the system proportionally at every point, it is unnecessary to involve any of the equations containing the constants k or β. Equations involving the constants k or β are necessary only where it is desired to modify the performance of the system by changing the concentration relationships at comparable points within the system.

Where, therefore, a given system is operating satisfactorily and it is merely desired to build a larger or smaller system to accomplish the same purpose on a correspondingly larger or smaller scale, it is merely necessary to see to it that in the new system the values of time contact t_x and t_c, the ratio of extractor to carrier, and the velocity of the liquid phase through the system, *i. e.*, u/A in the case of the extraction of a solid by a liquid, and U/A in the case of the washing of a gas, remain constant. It would be unnecessary to maintain the velocities constant were it not for the fact that these velocities so greatly change the value of the extraction constant k.

To avoid misunderstandings in the use of the preceding formulas, the following tables of definitions of the quantities involved are appended.

NOMENCLATURE

ca = carrier *so* = solutum *ex* = extractor

SYMBOL	SIGNIFICANCE	DEFINITION FOR EXTRACTION OF Solid by a Liquid	Gas by a Liquid
c	Concentration of *so* in *ex*	Ratio of weight of *so* to weight of *ex* in which it is held at any point in the system	Ratio of mols of *so* to weight of *ex* in which it is dissolved
x	Concentration of *so* on *ca*	Ratio of weight of *so* to weight of *ca* on which it is held at any point in the system	Ratio by volume of *so*, in *ca*, to *ca* at any point in the system
p	Partial pressure of *so*		Partial pressure of *so* in the liquid *ex*, total pressure in the apparatus being taken as unity
α	Solubility constant	Defined by the equation $x = \alpha c$ which holds when *so* on *ca* and *ex* are in equilibrium. (Does not hold for adsorption)	$p = \alpha c$
u	Velocity of *ex*	Weight of *ex* per unit of time	Weight of *ex* per unit time
U	Velocity of *ca*	Weight of *ca* per unit of time	Mols of *ca* per unit of time
V	Total volume of extraction system	Units of volume	Units of volume
t_c	Time of contact of *ex*	$t_c = V/u$	$t_c = V/u$
t_x	Time of contact of *ca*	$t_x = V/U$	$t_x = V/U$
ρ	*Ex* employed per unit amount of *ca* treated	$\rho = u/U$	$\rho = u/U$
β	Diffusion constant	$\beta = kA^2/u^2$	$\beta = kA^2/U^2$
K k	Diffusion constants	Where k and K are identical; value depends on the particular system	
S	Volume of product	Units of volume	
P	Volume of apparatus filled by carrier	Units of volume	Partial pressure of *so* in the gaseous carrier, total pressure in the apparatus being taken as unity
Q	Volume of apparatus filled by voids in *ca*	Units of volume	
R	Volume of apparatus occupied by voids between carrier	Units of volume	

It will be apparent that throughout this discussion the functions of carrier and extractor will be reversed if the concentration or pressure differences be of opposite sign.

EXPERIMENTAL INVESTIGATION

Preliminary work was carried out by Mr. A. W. Kenney in the spring of 1913. The system employed consisted of porous coke saturated with sodium hydrate solution. Work with this indicated in a qualitative way the lines which the investigation would have to pursue, but no quantitative results of value were obtained. During the next year Mr. Kenney[1] followed up the work with a study of a counter-current extraction system, removing SO_2 from a gaseous mixture by the use of water as an extractor. At first mixtures of SO_2 and air were employed, but the oxidation to sulfuric acid was excessive and vitiated the results. Finally mixtures of SO_2 and CO_2 were used. A great deal of difficulty was encountered in obtaining satisfactory concentration gradients; this was ultimately traced to variations in temperature. The solubility of SO_2 in water changes very rapidly with the temperature and very slight temperature changes profoundly influence the shape of the concentration curves. It was ultimately found necessary to maintain the whole extraction system at constant temperature by air jacketing and to saturate the gas entering the tower with moisture by bubbling through a wash bottle in order to avoid the cooling effect due to water evaporation into the dry gas which otherwise occurs. The results obtained are given in tabulated form below, but at the time it was impossible to get satisfactory constants from these results by any method of calculation, and the problem seemed almost hopeless. Nevertheless, during the next year the work was taken up by Mr. V. A. Stewart, who studied the absorption of CO_2 by solutions of caustic soda in excess, using the same absorption system as that employed by Mr. Kenney. The results of Mr. Stewart's[2] work are also given in tabular form and again it was found impossible to reconcile the results and to obtain from different runs constants in any way concordant. During the last year a careful study of Stewart's results called our attention to the fact that the absorption was much more rapid the higher the velocity of the gas through the system. In all previous calculations no allowance had been made for variations in gas velocity, but this was now taken into consideration and it was found that the absorption coefficient K was proportional to the square of the velocity of the gas. Recalculating both the results of Kenney and of Stewart on this assumption we obtain the constants shown in the last column of each table. Realizing that these constants were obtained by methods of calculation, the significance of which was not appreciated until more than a year after the data were collected, and that the variations in conditions in the absorption system were very

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[1] Thesis submitted in partial fulfilment of the requirements for the S.M. degree at the Massachusetts Institute of Technology, 1914.

[2] Thesis submitted in partial fulfilment of the requirements for the S.B. degree at the Massachusetts Institute of Technology, 1915.

wide, the degree of coincidence is remarkable. We believe that the results of this work substantiate the accuracy of our assumptions and the reliability of our method of calculation.

TABLE I—REMOVAL OF CO_2 FROM AIR BY EXCESS NaOH

Number of Sections	Mol-fraction CO_2 = $x/1 + x$ f	Mols Air per hour U	V	β
0	0.205	...	...	....
1	0.045	27.48	260	0.000092
2	0.010	...	340	0.000080
0	0.083	15.60	...	....
1	0.030	...	260	0.000109
0	0.252	...	...	....
1	0.164	11.34	260	0.000063
2	0.082	...	340	0.000072
0	0.152	...	...	....
1	0.065	11.88	260	0.000120
2	0.015	...	340	0.000141
0	0.150	...	...	....
1	0.093	12.30	260	0.000065
2	0.024	...	340	0.000108
0	0.124	...	...	....
1	0.046	12.72	260	0.000130
2	0.034	...	340	0.000074
0	0.080	16.98	...	....
1	0.030	...	260	0.000097

TABLE II—REMOVAL OF SO_2 FROM CO_2 BY WATER

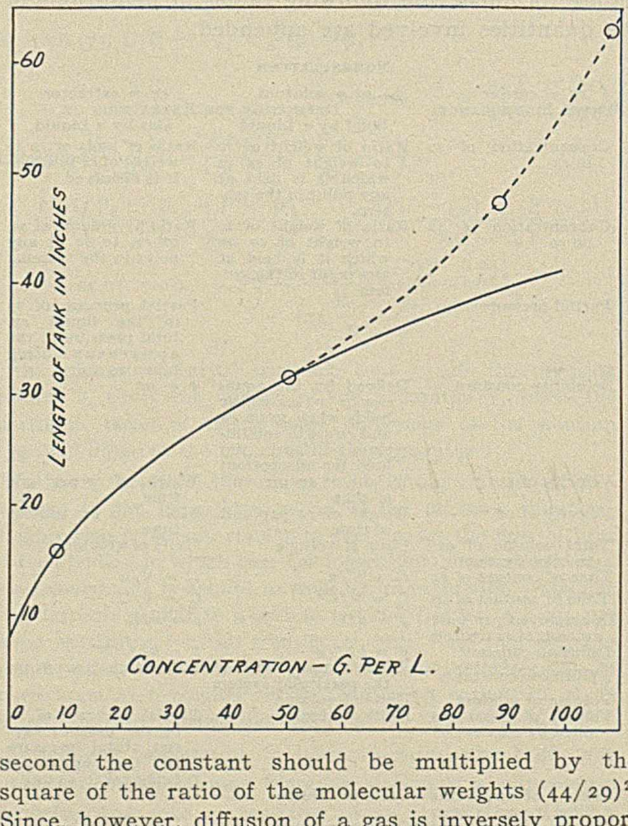
U	u	c	T	α	x_0	% loss	Volume	β
3.05	0.702	0.0988	21	0.532	0.0625	12.5	0.260	....
..	...	0.0955	..	...	..	..	0.340	....
..	...	0.0870	..	...	..	..	0.320	0.000162
2.23	0.555	0.1057	24	0.531	0.0624	22	0.260	....
..	...	0.1012	..	...	..	..	0.340	....
..	...	0.0917	..	...	..	..	0.320	0.000201
3.86	0.621	0.1160	25	0.535	0.0635	1	0.260	....
..	...	0.1083	..	...	..	..	0.340	....
..	...	0.1000	..	...	..	..	0.320	0.000166
2.89	0.711	0.1106	21	0.531	0.0665	9	0.260	....
..	...	0.1080	..	...	..	..	0.340	....
..	...	0.0922	..	...	..	..	0.320	0.000216
3.40	0.577	0.1150	22	0.532	0.0677	11.5	0.260	....
..	...	0.1110	..	...	..	..	0.340	....
..	...	0.1010	..	...	..	..	0.320	0.000124

At the same time another investigation was being carried on by Mr. T. C. Pond[1] on the extraction of sodium carbonate solution from wood pulp as is necessary in the soda pulp process. One of the concentration gradient curves obtained by Mr. Pond is given here. The experimental points represent the values as determined by Mr. Pond; the dotted curve connecting those points represents the actual concentration gradient and the full curve represents the concentration gradient as calculated from our equation. Mr. Pond had only four tanks in series in his system so that the insertion of a new tank into the system introduced decided variations in the concentration gradient, the flattening out of the curve being emphatically shown in the divergence of the actual from the theoretical curve in the fresh tanks in the series. This divergence, while very large in the fresh tanks in which the concentration gradients have not yet been established, is negligible in the rest of the system where the concentration gradient is relatively unaffected by the introduction of a new tank. In a longer system divergence would be much less than in the short system employed by Mr. Pond.

UTILITY OF EQUATION

We believe that these figures offer experimental justification of our method of calculation. On the other hand, it cannot be too strongly emphasized that under ordinary operating conditions it is almost impossible to get a concentration gradient which satisfies our expression. The reason for this is that the concentration gradient is very sensitive to changes in conditions such as temperature, rate of flow, etc., and these must be carefully controlled if theoretical results are to be obtained. None the less, our equations do indicate the nature of the process involved and while they are not applicable directly to the concentration gradient existing in commercial systems they should and in our opinion do apply to the *average* conditions existing in any continuously operated system. The diffusion constant K for our equation must therefore be determined from the known results of a system operating under commercial conditions, taking for the concentrations the average values obtained for a relatively long period of time. In order to determine the constant in our equation it is unnecessary to determine the concentration gradient through the system, but average values of the constant will be obtained from the known average performance of the operating system. Using these constants it will be possible to predict the effect of change in the performance of the system resulting from increase in size, change in velocity of flow, or variation in the amount of extractor employed.

It will be noted that the average value of the constant from Table I is 0.000096, and from Table II, 0.000174. In the first case, however, the inert gas was air and in the second CO_2. Evidence points to the assumption that the thickness of stationary film is determined by the *weight* of gas passing the surface, rather than by its linear velocity, *i. e.*, to compare the results in the first case with those in the second the constant should be multiplied by the square of the ratio of the molecular weights $(44/29)^2$. Since, however, diffusion of a gas is inversely proportional to the square root of its molecular weight, a



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[1] Thesis submitted in partial fulfilment of the requirements for the S.B. degree at the Massachusetts Institute of Technology, 1915.

further correction factor of $\sqrt{44/64}$ must be applied. Corrected in this way, the constant in the first table becomes 0.000183 as compared with 0.000174 in the second. In other words, it is apparently possible to use a single constant for the rate of absorption in two such diverse cases as SO_2 in water and CO_2 in NaOH solution, even with different diluent gases, provided differences in the densities and diffusion velocities be allowed for. While too much weight must not be put upon the checking of these two constants, it is still confirmatory of the correctness of our assumptions and method of calculation.

If data are to be obtained in the laboratory for the design of commercial systems as is of course necessary when new processes are under investigation, the laboratory conditions must duplicate on the small scale, as nearly as is possible, the conditions which it is anticipated will obtain in actual operation. We do not, however, recommend the laboratory method for determining the value of the diffusion constant in our equation where it is possible to get data from a large system in actual commercial operation. The main value of our equations will be to predict the effect of adding new tanks to the system, of increasing the rate of flow of extractor through the system, of using more extractor, and of all such changes in commercial operation.

EFFECT OF VELOCITY

The most striking fact brought out in this investigation is the marked influence of velocity on the rate of extraction. Throughout our work on extraction for those cases where the distribution of solutum between carrier and extractor is linear, we have found that the coefficient of diffusion K in our formulas is proportional within the experimental error to the square of the gas or liquid velocities. This means that the more rapidly the extractor is forced through the system the more rapid and indeed the more perfect will be the extraction. This statement would not apply to a gas washer using a spray, inasmuch as the drops of spray are carried with the gas and the relative velocity of the spray past the gas remains practically unchanged, whatever the velocity of the gas. In any system in which the carrier is stationary our results should apply. This means that in the design of counter-current extraction apparatus where gas washers or ordinary extractors are used, provision should be made to have the relative velocity of carrier and extractor as high as it is possible to make it. We do not claim that this rule, that rate of extraction is proportional to the rate of the velocity of the extractor, holds under all conditions. It is merely the empirical result of our experimental work, but it is in keeping with our concept of the extraction process. If the rate of extraction be limited by diffusion through a stationary film on the surface of the carrier, then high velocity should tend to remove this film and make it thinner, thereby greatly increasing diffusion. This result is in striking accord with all we know regarding the influence of velocity upon flow of heat and diffusion processes in general, but the proportionality between K and the square of the velocity is probably limited in its application.

ILLUSTRATIONS

A single illustration of the method of employing these equations will suffice. Assume that a part of the SO_2 is being removed from waste sulfur gases by washing with water. The tower used is 50 ft. high. The gases enter with 10 per cent SO_2 at 77° F., and at present one-half the SO_2 is removed. The tower at present treats 70,000 cu. ft. of inert gas per hour, using therefor 30,000 gals. of water. How much higher would it be necessary to build this tower to recover 70 per cent of the SO_2 instead of 50?

The equation to be employed is

$$\log \frac{x_o - \alpha c_o}{x} = \frac{kl}{u}(c - \alpha) = (\text{const.})l.$$

The latter form may be used because it is not proposed to modify the velocity of gas through the apparatus nor the amount of water used to dissolve the gas.

Where the gases enter the system the ratio of SO_2 to inert gas, or x_o, is 10 : 90, or $x_o = 0.1111$. At present half the SO_2 is removed, or at the other end of the tower $x = \frac{0.1111}{2} = 0.0556$.

From the solubility tables it is found that at the average concentration and temperature in the tower the partial pressure of SO_2 is such that a solution of 1 g. mol per liter exerts 0.530 atmospheres. 1 g. mol per gram, which is the same as 1 pound mol per pound, the unit of concentration in these equations, will therefore exert a thousand times as much, or $\alpha = 530$.

The tower is treating 70,000 cu. ft. of inert gas or 10/90ths as much SO_2. Multiplied by the ratio of the absolute temperatures, (460 + 32)/(460 + 77), the volume of SO_2 is reduced to standard conditions. Divided by the pound molecular volume under standard conditions, 359 cu. ft., gives the pound mols of SO_2, 1/2 of which is recovered.

This SO_2 recovered, divided by the pounds of water used, 30,000 times the pounds per gallon, $8^1/_3$, gives the concentration, c_o, of the solution obtained.

$$c_o = \frac{(70{,}000)(10)(492)}{(90)(537)(359)(2)(30{,}000)(8.33)} = 0.0000397.$$

Hence,

$$(\text{const.})(50) = \log \frac{0.1111 - 530(0.0000397)}{0.0556} = 0.210$$

$$(\text{const.}) = 0.0042.$$

Under the proposed conditions, x_o and α will remain the same, but x will fall to 0.3 x_o while c_o will rise in the ratio of 7 to 5, as 70 per cent of the SO_2 will now dissolve in the water which at present takes up but 50 per cent. Therefore

$$\log \frac{0.1111 - 530(0.0000397)\frac{7}{5}}{0.3(0.1111)} = 0.0042l,$$

whence $l = 93$ ft., or the tower must be made 43 ft. higher.

SUMMARY

We have developed formulas which show the influence of the size of any extraction system, the amount of extractor employed per unit amount of carrier treated, and the velocity of flow of carrier past extractor in any counter-current system for the extraction of solids by liquids or of liquids by gases or *vice versa*, and we have presented experimental evidence which we believe demonstrates the applicability of these formulas and justifies us in recommending their use in the interpretation of data collected in the study of any extraction system and in the design of new systems which it is desired to construct.

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A COMPARISON OF THE RELATIVE EFFICIENCY OF LABORATORY REFLUX CONDENSERS

By M. V. Dover and J. W. Marden

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Further than statements based upon qualitative separations, such as that made by Clowes,[1] in which he mentions that there is a considerable loss of ether when it is heated under a Liebig condenser used as a reflux, there has not been, so far as is known to the authors, any systematic comparison of the efficiency of different kinds and lengths of condensers.

Much important chemical work demands the use of this apparatus, and it seemed worth while to compare the efficiency of those most commonly used. The aim of this work is not to obtain great accuracy of results, but rather to gather data under the ordinary laboratory conditions which will aid in the choice of a reflux condenser, when it is necessary to heat a low-boiling liquid for some length of time. When fat is extracted by means of a Soxhlet apparatus, the ether is boiled for about 16 hrs. Should the condenser used show an efficiency of 98 per cent per hr. (that is, if 2 per cent of the total ether were lost in 1 hr.), $^1/_3$ of the total ether used would be lost in the experiment. It is very obvious that an efficiency of even a fraction of 1 per cent per hr. in the condenser is well worthy of consideration.

Not long since, one of us was asked to select a condenser for use with the Soxhlet apparatus and no preference could be given. Many indeed are the claims for great efficiency of the various types now in use. At that time the various kinds at hand were roughly tested, using gasoline as the volatile liquid. One hundred grams were boiled for 1 hr. under different condensers. The source of heat was then removed and the flask allowed to cool and reweighed. The efficiency of the condenser was calculated as the per cent of gasoline remaining after the experiment.

Table I—Efficiency of Reflux Condensers (Gasoline)

Gentle Boiling. Flow of Water 375 Cc. per Min.
Temperature at inflow = 20° C.; at outflow = 24° C.

Condenser	Allihn	Liebig	Ball Metal	Allihn	Liebig		Air Condenser Glass	Air Condenser Block Tin
Length, cm.....	30	80	....	15	48	40	150	100 (coil)
Efficiency per hr.	98.69	97.64	96.8	94.65	91.96	89.4	86.4	42.6

It is apparent that the length of the condenser makes considerable difference in its efficiency. In order to condense any large proportion of the gasoline vapor, the longest of the Allihn or Liebig condensers must be used. This method of comparison is, however, too crude, and in order to obtain results that show comparative values of the various condensers now on the market, more accurate methods of work were devised.

Experiments were made comparing the refluxing efficiencies of the following kinds and lengths of condensers: Liebig, 5 lengths; Allihn, 3; Spiral, 3; Hopkins, 2; Davies, 3; and Friedrichs, 1. The simpler form of the last named variety was used, not that having an outer as well as an inner water jacket.[2]

In each determination, 100 g. of liquid were boiled in a 250 cc. Erlenmeyer flask standing upon a concave asbestos wire gauze and heated from beneath by means of a ring burner. This burner and gauze insure equal distribution of heat upon the bottom of the flask. After boiling for $^1/_2$ hr., the burner was removed and an asbestos board slipped under the flask. It was allowed to cool for 5 min. before weighing, the water still flowing through the jacket. Duplicate determinations were made in every case.

A Woulfe bottle, carrying a thermometer, was placed between the water tap and the condenser, so that the temperature of the water flowing through the jacket might be observed. This temperature during all of these experiments did not vary more than about 3° (from 16 to 19° C.). The water was allowed to flow at the rate of approximately 500 cc. per min. The rubber stopper carrying the condenser was covered with tin foil to prevent any solvent action by the liquid.

It was found necessary, in every case, to bevel the lower end of the condenser tube so that the size of the drop and the rate of drop-back might be kept more nearly uniform. It was also found early in the work that the only way in which comparable results could be obtained, was to count the drop-back of the liquid used, as a measure of the rate of boiling.

The Liebig, Spiral and Allihn condensers were kept in a vertical position. The Davies, Friedrichs and Hopkins varieties were inclined slightly, because in these types the vapor traverses a space between an inner and outer jacket: this construction caused a drop-back when the condensers were held in a vertical position, both from the bottom of the inner jacket, and from the bevelled end of the tube. By tilting the whole apparatus, this drop from the bottom of the inner tube is made to fall upon the inner surface of the outer tube and run down to the bevelled tip, thus making the drop returning to the flask more nearly of the same weight as that in the case of the other condensers.

In order to obtain sufficiently accurate values, it was found necessary to correct for the amount of liquid remaining in the condenser after cooling. To estimate roughly the ether adhering to the walls of the tube, it was boiled under a reflux condenser which had been previously dried and weighed. (No water was allowed to flow through the jacket during these determinations.) When the vapor escaped freely from the top, the flask was allowed to cool for 5 min. and the condenser was again weighed as rapidly as possible. The sources of error in this crude method of procedure are at once obvious. The results given below are taken into account in Table V and seem sufficiently accurate for practical purposes.

Table II—Corrections for Ether in Various Condensers

Condenser	Friedrichs	Davies			Liebig			Spiral		Allihn	Ball (Copper)
Length, cm.	18	15	19	30	15	20	32	9	25	29	..
Ether, g.	0.07	0.06	0.07	0.06	0.01	0.03	0.09	0.06	0.04	0.06	1.7

A few trials were made, allowing the four liquids—water, chloroform, alcohol and ether—to drop back in equal quantities by volume. The number of drops

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[1] *J. Soc. Chem. Ind.*, **16** (1897), 979.

[2] *Z. angew. Chem.*, **23** (1910) 2425.

giving the same volume at the temperature of the boiling point of each were calculated from the respective surface tensions and densities given by Castell Evans[1] using the formula given by Findley.[2]

$$\frac{V_1}{V_2} = \frac{N_2 d_1}{N_1 d_2}, \quad \text{or,} \quad N_2 = \frac{V_1 d_2 N_1}{V_2 d_1}$$

where V_1 and V_2 = surface tension; N_2 and N_1 = no. drops; d_1 and d_2 = densities.

It is evident that different liquids could not be compared in the same condenser by using the same rate of drop-back in each case. The size of the drops is different for each liquid at a given temperature, the attraction of the glass varies, etc. Five drops of ether per second were here taken arbitrarily as a standard and the number of drops of the other liquids having the same volume, compared to this. These numbers are included in Table III.

TABLE III—EFFICIENCY WITH DROP-BACK IN EQUAL QUANTITIES BY VOLUME (LIEBIG CONDENSER)

No account was taken of the quantity of substance adhering to condenser tube

SUBSTANCE	B. P. ° C.	Drop Rate 20 cm. Jacket	PER CENT EFFICIENCY 20 cm.	24 cm.	38 cm.
Ether	34	5	Very low	98.4	98.76
Chloroform	61	7.6	93.6	88.5	98.16
Alcohol	78	4.5	97.9	98.5	98.42
Water	100	1.77	98.78	99.0	99.42

The percentage efficiencies in Table III indicated too great an apparent loss in the case of chloroform. Ether, boiling as it does at a lower temperature, would be expected to escape in larger quantities if conditions were in every way comparable.

When it was found that correct results could not be obtained by refluxing equal volumes of the respective liquids, a comparison was made by weight. In order to determine the number of drops of each liquid having the same weight, the respective weights of one drop of each were determined, the temperature being as near the boiling point as was practicable. Twenty drops were in each case drawn from a given orifice and weighed. The weight of one drop of water, divided by the weight of one drop of any of the other liquids, gives the number of drops of each having the same weight. These values appear in Table IV, Column 1,

TABLE IV—RELATIVE EFFICIENCY OF LIEBIG CONDENSERS OF DIFFERENT LENGTHS

SUBSTANCE	Drop-back	B. P.	PER CENT EFFICIENCY 15 cm.	20 cm.	24 cm.	37 cm.
Water	1	100	98.8	98.17	99.15	99.42
Alcohol	2.5	78	97.3	97.9	98.9	98.4
Chloroform	2.3	61	97.0	97.3	98.8	99.0
Ether	3.34	34	94	94.3	96.4	97.0

Table IV shows the influence of the length and also the influence of the boiling point of the liquid upon the efficiency of the Liebig condenser. As would be expected, the longer the condenser, and the higher boiling the liquid, the greater the efficiency. It is noteworthy, too, that the values are very largely dependent upon the rate of boiling. There are many sources of error in the above method. A small error in counting the rate of drop-back may account for the irregularity in the efficiency of the 37 cm. Liebig shown in Table IV for chloroform. There is also an irregularity in this table in the values for efficiency in the case of ether. Slight changes in external conditions such as draughts, etc., cause considerable variation in the efficiency of the shorter condensers. It was found by trial, that if a small plug of glass wool was placed in the upper end of the 24 cm. Liebig, the efficiency was changed from 96.4 per cent up to about 98.7 per cent. Considerable saving of ether in the Soxhlet or similar apparatus can be effected if air currents are prevented, as these which carry away the vapor.

The relative efficiencies of a number of condensers have been compared at two different rates of drop-back, *viz.*, 3.3 and 5 drops per second. Results at the latter rate are given to show that with a rapid rate of boiling the very short condensers cannot be used to advantage. As might be expected, our results checked best at the lower rate of drop, partly no doubt because it is rather difficult to count accurately, drops at the rate of 5 per second or 25 in 5 seconds. The results in Table V express the total *condensing efficiency* of the condensers enumerated.

TABLE V—A COMPARISON OF RELATIVE EFFICIENCY OF VARIOUS KINDS OF CONDENSERS FOR ETHER

Rate of Drop-back, 5 drops per second				Rate of Drop-back, 3.3 drops per second		
CONDENSER	Length Cm.	Per cent Efficiency	Price	CONDENSER	Length Cm.	Per cent Efficiency
Hopkins	37	99.03	$3 to $4(?)	Hopkins	30	98.82
Friedrichs	18	98.98	$5.00	Graham	9.5	98.7
Liebig	37	98.87	$1.20	Allihn	29	98.60
Graham	25	98.80	$2.40	Allihn	20	98.58
Davies	30	98.14	$6.00	Friedrichs	18	98.5
Hopkins	27.5	98.02	$1.75	Graham	16	98.5
Allihn	29	97.74	$1.50	Hopkins	27	98.48
Davies	20	97.64	$5.00	Hopkins	37	98.4
Liebig	32	97.63	$1.00	Graham	25	98.3
Davies	15	97.0(?)	$4.50	Liebig	32	98.17
Allihn	20	97.16	$1.20	Liebig	37	98.0
Graham	16	97.12	$1.35	Liebig	20	97.86
Graham	9.5	97.0(?)	....	Liebig	15	97.78
Ball	(*a*)	96.64	$3.20	Liebig	20	97.60
Liebig	20	73.23	$0.75			
Liebig	15	0.00	....			

(*a*) Drop-back 3.2 per second. Highest rate attainable with this metal condenser.

The weight of a drop of ether in the case of the copper ball condenser was not determined. Apparently it is larger than in the case of glass tubes; therefore the efficiency of this condenser may be greater than is at first sight apparent, *i. e.*, the ether may be boiling much faster than is necessary to obtain, in the case of glass, a rate of 5 drops per second.

Evidently, at a slow rate of boiling the lengths of these condensers is of little moment. The rate of boiling, rather than the length or kind of condenser, seems to be the determining factor in efficiency.

CONCLUSIONS

I—It has been found that in order to obtain comparable results, the rate of drop-back of the liquid must be in approximately equal weights per second.

II—In order that drops of equal weight may return to the flask the end of the condenser tube must be bevelled so that the drop returns from one point only.

III—The rate of boiling has very marked influence upon the efficiency of the condenser.

IV—The bore of the condenser tube has influence upon the efficiency of the condenser, as has also a

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[1] "Physical Chemical Tables," **2** (1911), 725, Chas. Griffin & Co., London.

[2] "Practical Physical Chemistry," **1914**, p. 94, Longmans, Green & Co., New York.

narrowing at the tip or a constriction anywhere in the tube. (Noticed in the spiral type where the spiral is fused on to the inner tube.) These conditions tend to cause choking and when this occurs the loss is always disproportionately great.

V—The length of the condenser is a factor in its efficiency (especially in the case of the Liebig) for low-boiling liquids. In the case of the other forms the length of the jacket has less influence than seems to be commonly supposed.

VI—In experiments where a long condenser can be conveniently used, the Liebig seems to be preferable because it is a much less costly condenser and can be easily cleaned. Where a short condenser is required, the Friedrichs seems best.

VII—The short Liebig or Allihn can be used to advantage only when the rate of condensation is not greater than from 2 to 3 drops per second, or when some means is used, such as a glass wool plug in the top of the condenser or a test tube inverted over the top of the condenser to prevent too rapid a carrying away of the vapor by air currents.

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CHAIN SCREEN DOORS

By Henry H. Wiegand

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Whenever the ordinary door of an oven or furnace is opened a stream of intensely heated gases pours out of the upper part of the opening, while at the bottom an equivalent volume of cold air rushes into the furnace, chilling contents and walls, entailing damage thereto and loss of heat. Time is also lost, as the interior must again be raised to the requisite temperature.

Many makeshifts have been devised to avoid the adverse conditions arising from the opened furnace door, but until the advent of the ingenious Wiegand chain screen door, nothing properly served the purpose. What was demanded was a door or shield that would permit a clear, unhampered view of the interior of the furnace or oven; would not in any way interfere with the free manipulation of the tools required to care for the interior; yet a door that would keep the heat in and the cold air out; in other words, a door which should possess at the same time the qualities of opaqueness, transparency and penetrability. This was a seeming impossibility until the chain door was devised by a Baltimore inventor.

These chain screen doors, in the form used mostly around metal, glass and chemical furnaces, consist of a multitude of freely hanging individual strands of steel chain suspended close together from a bar in a manner to form a continuous sheet or curtain of chain, not unlike the familiar Japanese screen. This curtain of chain, hung before the uncovered opening to a furnace and looking like a coat of mail, effectively hinders the heat, glare, gases and sparks from leaving the furnace and checks the entrance of cold air. The loosely hanging strands of light chain are parted with ease and pressed aside by the tools or other objects projected into the furnace, only to fall together again when entrance has been effected. The interstices in the links of chain permit an unhampered view of the interior—in fact a better survey may be obtained than under ordinary conditions, as the glare is toned down and the effect is similar to looking into a furnace through a piece of wire gauze. This is particularly noticeable with those installed on electric furnaces.

In some plants, when it is necessary to work in front of the naked fire, the workmen are obliged to stand back a great distance from their work and protect their bodies from the heat and glare with large sheet-iron shields which are supported by one hand while the other manipulates the tools. This seriously handicaps the workman and cuts his efficiency in half. In some industries the men are obliged to protect their eyes with dark goggles and their bodies and hands with extra heavy coverings. All such devices impede the men in the performance of their work. In those plants where the new chain screens have been employed the workman has both hands available for his work and may, with comfort, freely manipulate his tools while standing within a few inches of his work.

In glass working, the heat of the uncovered furnace is intense. Measured on the thermometer it shows a temperature of 600 to 1000°, yet when one of these chain screens is placed in front of the opening the temperature is lowered to such an extent that the bare hand may be held without danger or discomfort within an inch or so of the protecting transparent screen.

In a boiler room where the Wiegand chain doors have been employed for about three years, experiments were made to obtain an idea of the effectiveness of the device in avoiding the losses arising from the frequently opened stoking door. A thermometer was fixed on a standard in the fire room at a point opposite this door and 10 in. therefrom. This position was chosen as being near to the one usually taken by the fireman when stoking or cleaning the fire. When the ordinary fire door was thrown open and the incandescent fire bed exposed, as is the case whenever the furnace is coaled or cleaned, the thermometer rose to 400° F. On covering the furnace opening with the auxiliary "chain door," the temperature dropped to 135° F., and the bare, unprotected hand could be held anywhere in front of the screened opening without discomfort. This drop of 265° on the application of the screen indicates that a great quantity of heat lost by radiation and convection, through the ordinary uncovered furnace opening, may be saved by the employment of such a device.

These chain screens have a great field of usefulness in connection with glass furnaces, porcelain ovens, pyrites roasters, chemical, shrapnel and annealing furnaces, and cupolas for melting iron and other metals. Their use around the electric furnace has added much to the comfort of the operatives, when pouring.

Chain screen doors are supplied in "automatic" and "non-automatic" forms. The automatic is employed mostly on boiler furnaces and is so constructed that the opening of the fire door trips a catch, which permits the screen to unroll from a cylinder, and fall in front of the furnace opening. When it is desired to close the fire doors again, the screen is rolled up on its cylinder, which is permanently mounted above the furnace opening. The "non-automatic," much used on ovens and other furnaces that are not so frequently opened, is much simpler in construction. The chains forming the screen are suspended from a bar and may be raised out of the way by a hand chain running through a pulley overhead. When needed the screen is lowered into supporting brackets fixed at the sides of the opening. In some plants, whose furnaces are provided with vertically moving doors, the chain screen is permanently attached to the bottom of the ordinary vertical door. When the latter is raised to uncover the entrance, the chain door rises and takes its place.

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EXAMINING COMMERCIAL BROMINE

By Elwyn Waller

Received June 7, 1916

Recently a sample of commercial bromine was brought to the writer's laboratory for examination. The impurities likely to be present are not very numerous. If the material has been recovered from by-products in the manufacture of substances from aromatic and other organic compounds, a material amount of organic substance may be present, *e. g.*, Reymann[1] mentions finding 10 per cent bromoform in one case. Ordinarily, only a small amount of grease, wax or paraffin, which has been used in sealing the container, is all of the organic impurity present. The presence of SO_3 or H_2SO_4 is possible, but the amount is usually insignificant. The presence of Br hydrates may perhaps occur, but that branch of the subject does not seem to have been investigated. The occurrence of Cl is naturally the chief impurity, both on account of the association in nature, and also on account of the usual methods of manufacture.

In testing, some manufacturers determine the purity by taking the specific gravity in a specially constructed apparatus, and by reference to a table (made up, I know not how) read off what they claim is the true per cent of Br in the sample. Apparently it is assumed, in the construction of the table, that Cl is the only impurity. The possible influence of other impurities would seem to render this method a rather uncertain one, especially as the authorities[2] are not altogether in accord, varying from 2.966 to 3.1872.

The sample referred to showed sp. gr.	at 5–6° C.	3.0286
	at 25° C.	3.0135
A sample marked C. P. from a well-known dealer	at 25° C.	3.1021

Titration of a known quantity with standard $Na_2S_2O_3$, is one method recommended by many. The objection to it is that this permits of working on only a small quantity, and the assumption must also be made that only Br and Cl are present.

Friedheim and Meyer[1] suggest the application of Dechan's process,[2] which was devised for the examination of brines, mineral waters, etc. It depends on the following: With a mixture of bromides and chlorides, addition of a large excess of $K_2Cr_2O_7$ and positive acidification with H_2SO_4, on boiling gives off Br but no Cl unless it is allowed to become very concentrated, when CrO_2Cl_2 may distil over. By the aid of a current of steam passed through the boiling solution, all the Br can be driven into the distillate, and in the residual solution the Cl can be determined with $AgNO_3$. To apply the process in the case of commercial Br, 0.5 to 1 g. of the sample is weighed out in a thin glass bulb, which is broken under the surface of NaOH solution. When all Br has been taken up, 50 cc. of a 3 per cent solution of H_2O_2 is added, and the excess boiled out. Transfer to a distilling flask, add 10 g. $K_2Cr_2O_7$ in crystals, and 20 cc. H_2SO_4 (1 : 1 by vol.). Distil until the distillate gives no reaction for Br, avoiding a concentration beyond what would be equivalent to 8 cc. concentrated H_2SO_4 in 100 cc. of liquid. Then dilute the contents of the flask, and precipitate an aliquot portion with $AgNO_3$.

The process was tried but proved unsatisfactory. To obtain the necessary reagents absolutely free from chlorides, is, at this time especially, a difficult matter. It was also found that unless the concentration is brought to a certain point, no Br whatever will distil over, though much still remains, consequently constant attention is necessary to keep the degree of concentration in the flask between the proper limits. The results obtained were irregular and not concordant.

Erchenbrecher[3] treats 6 g. of the sample with 25 cc. of $N/5$ solution of KBr or NaBr, evaporates on the water bath, finally in a weighed dish, ignites gently and weighs. The Cl of the sample displaces the Br of the salt, and by use of a table the proportion may be found.

To weigh out precisely 6 g. or any other prescribed quantity of Br is a troublesome operation, so that the use of a table would hardly seem to be of advantage in this connection. The principle involved can, however, be applied as will be seen later.

Kubierschky[4] applies the same principle by shaking 25 cc. of the sample in a flask with 25 cc. of N KBr, settling and taking the specific gravity of the supernatant aqueous solution. With pure Br he states the specific gravity should be 1.227, and he has made a table showing the gravities corresponding to different percentages of Cl.

The application of the above principle proved to be a convenient mode of conducting the test. The method pursued was to weigh out 6 to 8 g. of the sample in a small stoppered flask. This was then poured and rinsed into a 350 cc. beaker containing about 70 cc. of water. The object in using so large a beaker

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[1] *Ber.*, **8**, 792.

[2] Judging from the statements in Watts' Dictionary, I, 676.

[1] *Z. anorg. Chem.*, **1**, 407.

[2] *J. Chem. Soc.*, **49**, 682.

[3] *Z. angew. Chem.*, **1894**, 636.

[4] *Loc. cit.*

was to avoid loss when boiling out the Br. To this was then added, by means of a pipette, 20 or 25 cc. of a solution of pure NaBr of 7 to 10 per cent strength. At the same time, *using the same pipette*, the same amount of NaBr solution was pipetted into a weighed dish to serve as a blank.

The beaker containing the Br was placed on the boiling water bath, and allowed to remain there until the Br had all boiled off, and most or all of it had been expelled from the solution, when the solution of mixed bromide and chloride was transferred to another weighed dish, and both that and the blank were evaporated to dryness, the last traces of moisture expelled by heating in air bath at about 130°, ignited gently and weighed. The salts obtained from the "mixed" is less than that from the "blank" by an amount equivalent to the difference between the combining weights of Cl and Br.

In other words, Blank — Mixed = Diff., and since

$$(\text{Br})\ 79.92 - (\text{Cl})\ 35.46 = 44.46$$

$$44.46 : 35.46 = \text{Diff.} : \text{Cl present.}$$

For most purposes, 80 per cent of the difference in weights gives the Cl.

The contents of the dishes should be dissolved separately, and each diluted to some convenient bulk (say 250 cc.), and aliquot portions tested by titration with standard $AgNO_3$. The halogen equivalent in the two masses of salts should be the same if no losses have occurred.

Applied to the sample submitted the results were:

Taken	Wt. of "Blank"	Wt. of "Mixed"	Diff.	= Cl	% Cl
6.7249	1.5884	1.3206	0.2678	0.21364	3.18
7.2330	1.3983	1.1257	0.2726	0.21747	3.06
8.4340	2.0737	1.7434	0.3303	0.26349	3.12

Material from a dealer in laboratory supplies marked as Bromine C. P. was found to contain 0.19 per cent Cl.

159 Front Street, New York City

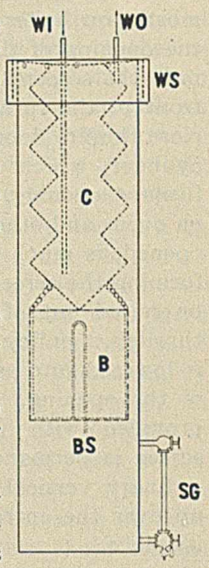
A NEW TYPE OF EXTRACTOR

By James B. McNair

Received May 22, 1916

The accompanying diagram illustrates an original type of extractor which has been used successfully in extracting plant material with 86° Bé. gasoline. Like many other extractors, it consists of three main parts, *viz.:* a container for the solvent, a container for the material to be extracted, *B*, and a condenser for the solvent *C*. This machine, however, has advantages (which the illustration makes apparent) over some other extractors; it is easily cleaned, lacks complications, retains almost all of the solvent, etc. The diagram is drawn proportionally for a machine which has been efficiently used with 86° Bé. gasoline. The use of another solvent, due to a different specific heat, etc., might necessitate a re-proportioning of the parts, *e. g.*, a greater proportionate condensing area or the use of a different variety of substance in the condenser (in this case, copper).

The container is a long copper cylinder with a water boiler gauge, *SG*, attached to its vertical side near the base. Surrounding the top of the cylinder is a gutter to serve as a water or mercury seal. This water seal tends to prevent explosions and the escape of the solvent. The bucket, *B*, for the material to be extracted, has a siphon, *BS*, and an inside wire gauze bucket nearly the same size as *B*. The bucket is suspended by chains to hooks attached to the lower part of the condenser, *C*. The condenser, *C*, consists of a series of truncated cones attached (as illustrated) to a lid. The water inlet is a small pipe, *WI*, and the water outlet a shorter pipe, *WO*.



In operating the machine the solvent is first poured into the container; then the condenser with its attached bucket is lowered into the container. Heat is applied at the bottom of the container. The number of extractions may be observed by the variations in the level of the liquid in the solvent gauge, *SG*.

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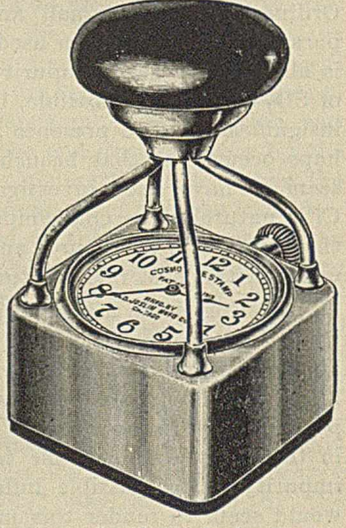
A SIMPLE AUTOMATIC TIME RECORDER

By Max Morse

Received February 4, 1916

No one appreciates more than the laboratory worker any device which eliminates the personal responsibility when many determinations are running at the same time. The accompanying figure concerns one such device, namely, an instrument which accurately keeps account of the recording of time of beginning experiments, the receipt of samples, etc. The clock, mounted in a nickel frame, operates a rubber dial on the back. Being rubber, there is little incentive to damage the clock, as happens sometimes with those bearing copper dies by jamming the works when making an impression. Dials are furnished either in 12- or 24-hr. cycles. A key is furnished, operating the setting and winding, so that one may wear it on his chain or bunch of keys and have sole access to the clock as to winding and setting, for the key is individual. The low cost of the apparatus, as compared with the ordinary cumbersome, nonportable type of recording clock—a difference of $27.50—is an item for the budget. The clock has been used to advantage in this laboratory.



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ADDRESSES

INTERPRETATION OF COAL ANALYSIS: WITH SPECIAL REFERENCE TO NONCOMBUSTIBLES[1]

By E. G. Bailey

The purpose of a test on coal or any other material is to arrive at definite conclusions by a short cut, and yet with sufficient accuracy that the results of the test may form the basis of comparison for the purchase or use of the material tested. The old saying "The proof of the pudding is in the eating thereof" strictly applies to the burning of coal. There is no test, nor, can there be any test, that will replace results obtained from actual practice. But it is impossible to burn two coals under the same conditions at the same time, and it is unnecessary to state that in actual practice conditions do vary, so that comparisons based upon actual service results alone are often unfair to one coal or the other, or at least they lead to indefinite conclusions.

Another kind of test where the operating conditions are more nearly under control is a road test, where a great many data covering operating conditions are accumulated in addition to the consumption of coal per ton-mile, so that should the conditions vary from one test to another, certain allowances can be made. No criticism can be made of carefully conducted road tests, but they require time and are very expensive, and it is desirable to have some quicker and cheaper method of checking up the comparative values of different kinds of coal or different shipments of coal from the same company.

For this purpose, the chemical analysis of coal has been very widely used during the past ten or twenty years by practically all coal consumers in the country.

The purpose and value of coal analysis should be better understood. The chemist, as a rule, passes his figures on to the purchasing agent or superintendent of motive power with little or no comment or interpretation. The man who is responsible for the buying or burning of the coal is most interested in making a comparison of it with other coals which he has used or which are available. He accepts the figures from the chemist for the purpose of such comparison, and proceeds to draw certain conclusions as to the relative value of the two coals, based upon one or two constituents, such as the percentage of ash, sulfur or B. t. u., according to his own ideas of what the chemist's figures really mean. Very often these conclusions are not borne out by the practical road tests or the actual use of the coal in regular service. That theory and practice do not always agree, has often been repeated when the results obtained in the actual burning of the coal did not bear out the figures of the chemical analysis as interpreted by the person making the comparison. But theory and practice should and do agree when they are both right. Too often one is based upon erroneous data, incomplete results, or else failure to duplicate conditions.

It is regretted that too often the results of the chemical analysis are wrong, not by insignificant fractions of one per cent, but by several per cent or several hundred B. t. u. Very frequently the trouble is in the sampling, where the original sample is not large enough to be truly representative, or else it may not have been properly reduced and pulverized. The sampling question is of much greater importance than it has usually been considered. This phase of the subject will not be treated here except to impress upon each person who has any occasion to depend upon coal analyses, that no matter how sure he may feel that his present method is right, he should look up the methods of sampling and analysis recently proposed by committees of the *American Society for Testing Materials*[2] and the *American Chemical Society*. One of the most obstinate hindrances to progress along any line is the characteristic of human nature for people to feel confident that their own way is the best. It may be all right for a poet or a musician to have distinctive peculiarities of his own, but it does not work out well in chemistry nor in the sampling of coal. The best standards should be rigidly followed.

HEATING VALUE

In the case of coal used for the generation of steam, whether in stationary, locomotive or marine practice, the primary factor is the heating value of the coal. In other words, all coal for these purposes has as its principal object the generation of heat to evaporate water. The matter of primary consideration is to evaporate a given amount of water at the lowest cost; and it should be remembered that the cost of fuel alone is not the entire item, for the character of the fuel has a great deal to do with the cost of repairs to grate bars, furnace linings and arches; and of very great importance in the case of locomotive practice is the question of the capacity which can be obtained.

With the introduction of calorimeters for determining the heating value of coal, many chemists considered that the whole question of fuel value was summed up in the one item of B. t. u., and consequently comparisons were drawn between different coals upon the B. t. u. basis, allowing no consideration for their other characteristics. It was soon learned, however, that such results do not always agree with results of practice, consequently many practical men have become skeptical of the value of coal analysis for giving them the dependable information which they desire.

A more careful insight into this problem shows that the real cause of the difficulty was that the comparison was limited to the one factor of heating value. While this may be the item of primary importance, yet the effect of the noncombustibles upon the action of the coal in the firebox had such a modifying influence that very frequently the coal with the higher heating value gave the poorer results. Anyone who has depended upon coal analyses without the proper interpretation, and has not given full weight to the effect of the impurities which accompany the heat-producing elements, has not been able to secure very much benefit from coal analysis.

The usual analysis of coal gives the percentage of moisture, volatile, fixed carbon, ash and sulfur, in addition to the heating value. The ultimate analysis, dividing the constituents up into their elements, gives carbon, hydrogen, oxygen, nitrogen, sulfur and ash. This is very seldom used, first because the analysis is more expensive, and second because the analysis really gives less information than the usual proximate analysis. Let us therefore confine our attention to a study of the proximate analysis.

The moisture is of course a noncombustible. It produces no heat, but is, on the other hand, an absorber of heat, as it must be vaporized and sent from the boiler as superheated steam at the stack temperature. Assuming a stack temperature of 700°, the total heat required to vaporize and superheat 1 per cent of moisture amounts to only $^1/_{10}$ per cent of a 13,000 B. t. u. coal. This of itself is not a serious matter, so that the principal importance of moisture is that it acts as so much inert matter, which is paid for at the same price as coal. This applies only to the moisture which is in the coal at the time of its being weighed. It must be remembered that the percentage of moisture as shown by the usual analysis does not in-

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[1] Presented before the 8th Annual Meeting of the International Railway Fuel Association, Chicago, May 15 to 18, 1916.

[2] Proceedings American Society for Testing Materials, Vol. XV, Part 1; also Year Book 1915.

clude all of the water or H_2O compound present in the fuel, for there is a considerable amount of water that cannot be dried from the coal even at 220° F., but remains in chemical combination probably as a carbohydrate, and can only be driven off with the volatile. Therefore, a considerable percentage of impurities is included in the volatile, although it is usually considered that the moisture, ash and sulfur are the only impurities present.

BASIC IMPURITIES IN COAL

The real basic impurities in coal are oxygen, nitrogen and ash, so far as generating heat is concerned. Sulfur is generally classed as an impurity because its heating value is so low that the heat produced does not compensate for its detrimental qualities. According to the best authorities all of the oxygen which occurs in coal is combined with hydrogen, either as moisture, combined water, or in the form of a carbohydrate, and that which is not shown in the analysis as moisture is included in the volatile.

The following tabulated data of a typical West Virginia gas coal give the division of the volatile matter into its different elements, hydrogen, oxygen, carbon, nitrogen and sulfur. It is noted that in the volatile there is a total of 5.38 per cent of the total coal, or about 13 per cent of the volatile, that is water, besides some nitrogen and sulfur as noncombustibles.

ANALYSIS OF A TYPICAL WEST VIRGINIA COAL

				Heating Value per Pound	Calculated B.T.U.	B.T.U. by Calorimeter
Moisture	2.01	H 0.22	2.01 water	None	..	
		O 1.79				
Volatile	37.31	H 4.86	5.38 water	None	..	
		O 4.78	4.26 available H	62,000	2,641	
		C 26.65		14,500	3,464	
		N 0.23		None	..	
		S 0.79		4,050	32	
Fixed Carbon	52.13	C 49.18		14,500	7,131	
		N 1.20		None	..	
		S 1.75		4,050	71	
Ash	8.55			None	..	
					13,339	13,811

Making a similar division of the proximate analysis of a typical Illinois coal, we find that 9 per cent of the total coal occurs in the volatile in the form of water, or 25 per cent of the volatile itself is noncombustible. In the case of lignite and peat, the percentage of volatile which is noncombustible proportionately increases. So that in this we see that volatile itself is not an indication of rich locomotive fuel, for much depends upon the nature of the volatile, and how much of it is impurities and how much combustible. Then in the combustible itself there is considerable variation, depending upon the relative percentages of available hydrogen and carbon.

MOISTURE—The percentage of moisture retained in coals varies widely with the characteristics of the coal. Lignite and sub-bituminous coals carry a much higher percentage of moisture than do the bituminous and semi-bituminous. Anthracite coal, on the other hand, carries a slightly higher percentage of moisture than does semi-bituminous.

This point should be taken into consideration in comparing coals from different fields. Many people have considered that the percentage of moisture was such a variable quantity, depending upon weather conditions, etc., that the only true comparison was on a dry basis, and they therefore reduce all analyses to this basis, and make their comparisons on it. This is likely to lead to very erroneous conclusions. For instance, take Illinois coal, which may run normally with say 12 per cent moisture, and a bituminous coal from the Pittsburgh or West Virginia district, which would run normally 3 per cent of moisture. If these are both reduced to a dry basis, the Illinois coal will show an apparent advantage of about 9 per cent better than it should.

In order to get a more uniform basis of comparison it is all right to compare different shipments of coal from the same region on a dry basis, but it is not right to compare coal of one character with another coal from another region of different character on any other basis except with their normal moisture content that is fairly representative of the different districts.

A coal which normally has a high moisture content usually has a relatively large percentage of its volatile matter in the form of combined water, and is therefore just as inert and nonproductive of heat as if it showed up as moisture in the regular analysis. The only practical way that this can be taken care of is through the B. t. u., for such coals show lower heating value per pound of combustible, or on a basis free from moisture and ash.

ASH—The impurity which is always present in coal, and the one which is of the greatest importance, is the ash. The ash is a very different proposition from the moisture, for it is not only inert and nonproductive of heat, but it may have very marked effect upon both the rate and efficiency of combustion. If the ash in all different kinds of coal were similar in its composition and characteristics, it would be possible to make comparisons on a B. t. u. basis alone with much greater certainty than is actually the case.

The composition of ash varies widely. In all cases it is a very complex compound, consisting of alumina, silica, iron, lime, magnesia, titanium, alkalies, etc. Practically all of these compounds are always present. The relative percentages of each varies widely, and the effect of them upon the action of the coal in the firebox varies according to such a complicated law that it is practically impossible for this analysis to be used as a reliable means of determining the character of the ash for comparative purposes.

ANALYSIS OF A TYPICAL ILLINOIS COAL

				Heating Value per Pound	Calculated B.T.U.	B.T.U. by Calorimeter
Moisture	12.39	H 1.38	12.39 water	None	..	
		O 11.01				
Volatile	36.89	H 4.47	9.01 water	None	..	
		O 8.01	3.47 available H	62,000	2,150	
		C 23.19		14,500	3,363	
		N 0.10		None	..	
		S 1.12		4,050	46	
Fixed Carbon	41.80	C 38.10		14,500	5,525	
		N 0.90		None	..	
		S 2.80		4,050	113	
Ash	8.92			None	..	
					11,197	11,399

An ash which does not clinker gives very little trouble, and is not much, if any, more detrimental than so much moisture. It is merely an inert substance that does not produce heat. It does not seriously obstruct air passages and can easily be shaken through the grates. But an ash which melts into a clinker is more difficult to get rid of, and while remaining on the grates it obstructs the flow of air to a serious extent, and oftentimes it adheres tightly to the grates and obstructs the air so completely that the heat of the fuel bed is conducted to the grate bars and causes them to burn.

The question of clinkers is one of the very vital problems in locomotive practice, and heretofore practically the only means of getting any line upon this important characteristic of fuel was the actual trial. At the same time, it has always been realized that some firemen would make more clinkers than another, both using the same coal, so that such results obtained from actual practice were not always a safe comparison so long as the fireman was a factor in the problem.

A very thorough study into this phase of the fuel problem some years ago led the writer to conclude that the whole question of clinkers could be summed up in the *fusing temperature of the ash and the temperature to which this ash is subjected.* The composition of coal ash is very similar to the composition of different kinds of clay from which brick are made. We have all varieties of clay, from that used in manufacturing the best grade of firebrick down to ordinary building brick. The latter will not stand the lowest furnace temperature without melting into a clinker. In the case of coal ash, some ash has such a high fusing temperature that there are practically no fuel bed conditions that will produce troublesome clinker from it. Another ash with a little lower fusing temperature will sinter together and form a porous, spongy clinker which does not form a serious obstruction to the flow of air, nor is it difficult to remove. The ash with a still lower fusing temperature, say 2,100°, will not only become melted in the average firebox, but it will be heated several hundred degrees above its melting temperature, in which case it runs down like overheated iron until it spreads out in a thin sheet over the grate bars.

To a certain extent the action of a clinker depends upon its fusing temperature, but equally important is the temperature to which the ash is subjected. When a coal is burned, the ash is not entirely liberated until it reaches the lower part of the fuel bed, where the incoming air keeps a lower temperature than in the zone 4 to 6 in. above the grates. So it is often possible to get satisfactory results from a coal having a fusing temperature of 2,300 and yet carrying a fuel bed temperature of 2,500. Some clinker, of course, will be formed, but it is not of the extremely objectionable character if the firing is properly done. Clinker accumulates gradually, and is more or less open and does not obstruct the air beyond the critical limit. But if another fireman should handle the same coal differently, slicing or working the fire, and causing the ash, which has already been liberated from the coal in the lower and cooler part of the fuel bed, to be again thrown up into the hotter zone, it will melt into a very fluid mass and spread out over the grates in a thin sheet, and obstruct the air flow to a serious extent.

SULFUR—Many people have considered that the percentage of sulfur was a true indication of the clinker property of a coal. The sulfur determination, however, is one of the ideas that has been passed on from the steel chemist. In his case sulfur was extremely detrimental, but in the case of steam coal it is of minor importance. It is true that in some coal fields the variation in the clinkering property of coal received from different mines does follow the percentage of sulfur to a certain extent. Sulfur is an indirect cause, however, for it is really the iron which has the effect upon the fusing temperature, and the percentage of iron usually increases or decreases with the sulfur. There are so many exceptions to the relation between sulfur, or even iron, and the clinkering property of coal, however, that a dependence upon either is apt to lead to erroneous conclusions.

One of the very lowest sulfur coals in the United States is found in Rhode Island, where the percentage of sulfur will run less than one-quarter of 1 per cent, yet the fusing temperature and the clinkering property of this coal class it among the very worst in this respect.

FUSING TEMPERATURE OF ASH

Several of the largest stationary power plants in the country are making fusing temperature determinations in addition to the regular analysis on each shipment of coal. In many respects the clinker problem is of more serious consequence in railroad practice that it is in stationary boilers. The matter of fusing temperature determination has not as yet been standardized from a laboratory standpoint to the extent that the regular analysis and B. t. u. determinations have been. The value of this determination has been demonstrated so conclusively that there is now under way a definite movement to work out the fundamentals of this problem and decide upon a method which can be adopted as standard for comparison. It is the writer's opinion that the method which will ultimately prove most valuable for this determination is the one which stays closest to practice, so far as duplicating the actual fuel bed conditions is concerned.

One of the big difficulties with the whole question of coal analysis has been that the chemist was carried away with the idea of getting scientifically accurate results. The percentages of the various constituents and the determinations which he made were largely a matter of tradition, passed on to him from the needs of an entirely different line of work, and he has left the interpretation of these results to the person interested in the purchase or use of the coal. The original form of analysis did not fill the bill, and the next step was to include other factors, such as the B. t. u., and later on the fusing temperature of the ash, in an effort to strike the key to the situation that would give the factor essential for comparing the relative values of different coals. It is doubtful if there ever will be found any one factor that can be depended upon in drawing conclusions regarding a substance so complex as coal that is used under the severe conditions that exist in a locomotive firebox. It is therefore essential that the most important factor be taken as a basis of comparison, and consider the other factors as having modifying influence.

While the heating value of a coal may be considered the essential element, yet it means very little unless the percentage and character of the impurities existing in the coal are fully considered. It is therefore necessary to determine the amount and nature of these impurities. After they have been determined and allowed for, it is found that the heating value per pound of combustible is practically uniform for all coals from any one district, practically the only exception being in the case of crop coal.

Therefore it would seem in comparing one shipment of coal with another from the same district, that the determination of the heating value was the least important; the percentage of moisture is often beyond control, and it is very difficult to determine accurately at the time the coal is weighed, so the question resolves itself largely into the percentage of ash and its clinkering property, as being the critical factors to be considered in comparing the commercial value of different fuels of the same character.

When it comes to comparing coals of different character, taking lignite and semi-bituminous coals as extremes, it is practically impossible for a safe conclusion to be drawn from any chemical analysis, no matter how complete. In such cases practical tests are the only reliable means of arriving at comparative results, and then comparative information regarding different shipments of coal from any one region can best be obtained from the percentage of ash and its fusing temperature.

Bailey Meter Company
141 Milk Street, Boston

COAL-TAR PITCH

By John Morris Weiss

Received June 19, 1916

Much has been written on the subject of coal-tar pitch, largely in Germany, but most of the extant publications are very restricted in scope and consider only a method of testing, a specification for some particular purpose, or a description of a particular grade of material. To make a complete review of the literature would be a difficult task and would be of little practical value for the purpose the writer has in mind. The object of this article is: (1) To treat in a rather general way the crude material for, and the manufacture of, coal-tar pitch; (2) to present the known physical and chemical characteristics of coal-tar pitch in a somewhat concise and definite form; (3) to consider the present uses of the material in industry—all from the point of view of United States practice.

MANUFACTURE OF COAL-TAR PITCH

Coal-tar pitch is the residual product from the distillation of coal tar, and tars are ordinarily distilled with the character of residue obtained as the primal object. The tar is taken in a horizontal, sometimes vertical, steel still fired by coal, oil, or gas (depending on local conditions), and distilled with air, steam, or mechanical stirring. Light oil and water are first separated, then carbolic oil and finally creosote oil. The distillation is continued until the residue in the still is of the desired degree of consistency. Sometimes, where the pitch is being run very hard, anthracene oil is also separated toward the end of the creosote run, but this is exceptional, any anthracene oil obtained going for the most part along with the creosote oil. American practice has been very well set forth in an article by R. P. Perry[1] and the writer would refer to this paper, for a more complete and exhaustive study of manufacturing methods.

The characteristics of pitch are mainly dependent on two factors: The character of tar with which the still is charged, and the percentage of total distillate removed. The more oil removed, the higher melting the pitch becomes. Factors such as type of still setting and method of running also affect the character of the pitch, but to a minor degree compared to the first two mentioned variants.

Crude coal tars may vary widely depending on the coal used for carbonization, the type of installation in which the carbonization takes place and the degree of superheating to which the developing tar vapors have been subjected. In a paper by S. R. Church, read before the Southern Gas Association,[2] there are given comparative analyses of a number of typical coal tars and it can be readily seen that there are wide differences in the characteristics of crude tars.

ANALYSES OF TYPICAL TARS

(All tests on dry tar)

	Gas Retort				Coke Oven		
	Horizontal		Inclined	Vertical	United Otto	Semet-Solvay	Koppers
Sp. gr. at 15.5° C.	1.266	1.293	1.238	1.153	1.207	1.188	1.186
Free carbon (insol. in C_6H_6)....	28.9	37.5	24.3	....	13.3	10.7	6.8
Sp. viscos. (Engler at 100° C.).	21.8	30.0	14.9	2.1	3.4	3.0	2.1
Oil to soft pitch 60° C., m. p. (% by vol.).....	13.2	....	14.3	28.8	21.2	21.8	35.3
Refractive index at 60° C. (taken on oil)......	1.5932	....	1.5807	1.5755	1.5987	1.6122	1.6139
Sulf. res. (% taken on oil)......	0.4	....	2.4	4.3	0	0	0
Tar acids (% taken on oil)...	14.0	....	21.0	29.0	12.0	4.0	0
Pitch res. 60° C., m. p. (% by vol.).....	86.8	....	85.7	71.2	78.8	78.2	64.7

These variations are in turn imparted to the pitch produced and are largely dependent on the nature of the basic tar bitumens.

It may be set forth as an axiom that grades of pitch suitable for all purposes cannot be produced from a single source of tar. An admirable product for a particular purpose may be produced from each single tar but in general it is safe to say that the best results are obtained by blending tars from various sources and altering the still mixtures to suit the purpose for which the residual pitch is designed.

PROPERTIES OF PITCH

In considering the properties of coal-tar pitches it may be said that all the testing methods, peculiar to the tar industry, have been given in detail by S. R. Church[3] and any references to specific properties not specially noted may be taken as determined by the methods given in this article.

PHYSICAL PROPERTIES

(1) MELTING POINT—The term "melting point" is really a misnomer. Bitumens, such as pitch, which consist of a complex mixture of hydrocarbons cannot be said to have a melting point in the sense that this term is usually applied to pure compounds. When pitch is heated it gradually softens, passing by imperceptible degrees from the solid to the liquid phase and the so-called melting point is merely an arbitrary figure taken for commercial purposes and representing the temperature at which a cube of pitch softens sufficiently to drop from a wire, when heated at a prescribed rate and under rigidly controlled conditions.

The melting points of coal-tar pitch vary from 37.5° C. (100° F.) in water up to 174° C. (345° F.) in air. These are really the practical limits of manufacture. A material melting below 37.5° C. (100° F.) could hardly be called a pitch, but would rather come under the class of distilled tars, where the distillation has merely removed the water, light oil and possibly a small portion of the carbolic oil fraction. Very hard pitches can be manufactured if desired, but ordinarily the hardest pitches made have an air melting point of not over 130° C. (266° F.).

(2) SPECIFIC GRAVITY—The specific gravities of coal-tar pitches vary from about 1.200 to 1.290 at a melting point of 37.5° C. (100° F.) and from 1.250 to 1.350 at a melting point of 88 to 93° C. (190–200° F.) Specific gravity is of comparatively little importance of itself. When an unknown pitch is examined, the specific gravity determination may give an indication of adulteration with pitches from other sources such as oil or water-gas tars. These are of lower specific gravity for the same melting point than coal-tar pitches and any considerable adulteration will usually be reflected in the figure found.

(3) EFFECT OF HEATING—The effect of heating and melting of coal-tar pitch is at most a slight hardening due to volatilization of oil. Trials on various grades at temperatures up to 205° C. (400° F.) showed only minor changes and there was no evidence of cracking and decomposition. Pitches that have been hardened by frequent heating, unless badly overheated, can readily be brought back to the original consistency without altering their essential properties, by fluxing with a high-boiling creosote oil.

(4) SOLUBILITY—Coal-tar pitches are soluble in benzol, carbon bisulfide, chloroform, carbon tetrachloride and glacial acetic acid. Of course the free carbon does not dissolve but can be brought into suspension by shaking. Coal-tar pitches are only partly soluble in petroleum naphthas, turpentine, grain alcohol and wood alcohol and any solution of coal-tar pitch in one of the materials which dissolve it, may be partially precipitated by the addition of an excess of one of the later named solvents. This is of considerable importance in the thinning of paints containing a coal-tar pitch base.

(5) TENACITY AND DUCTILITY—In the examination of bitumens these two properties are usually determined simultaneously. A cylinder of material of definite cross section is pulled apart under rigidly controlled conditions. The force necessary to do this is taken as a measure of the tenacity, and the lineal extension before rupture occurs as a measure of the ductility. These properties vary with the melting point of the pitch and the temperature at which the material is tested. To give detailed tests would take up much space and carry the writer outside the scope of this paper. The two properties are somewhat in inverse proportion. As tenacity increases, ductility tends to decrease. However, comparing coal-tar pitch with other bituminous materials of like tenacity, it is almost invariably of markedly greater ductility.

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[1] THIS JOURNAL, 5 (1913), 151; reprint from *Proc. 8th Intern. Congr. Appl. Chem.*

[2] *Gas Age*, May 15, 1913.

[3] THIS JOURNAL, 3 (1911), 227; and 5 (1913), 195.

(6) ADHESION—This quality of pitch is its faculty to adhere to other materials such as stone, felt or wood, and it possesses this in a very high degree. This is of prime importance in many of the practical applications of pitch.

(7) COMPRESSIBILITY—It is well known that pitches will flow under pressure. Recent tests made in our laboratory by subjecting discs of bitumens to a smooth even pressure under rigidly controlled conditions of temperature have shown that coal-tar pitches show more compressibility at lower temperatures than other bitumens which apparently are less susceptible to changes of temperature as evidenced by the ordinary testing methods. Harder pitches will flow at temperatures considerably below their brittle points. They give under the smooth even pressure and do not splinter and crack as might be supposed.

(8) ELECTRICAL PROPERTIES—Tests made in our laboratories show the puncture voltage of pitch to be from 80,000 to over 100,000 volts per inch. Other tests showed the specific resistance to be so high that accurate measurements could not be obtained, the results varying from 168,000 megohms for 1 in. thickness, to infinity.

CHEMICAL PROPERTIES

(1) CONSTITUTION—Very little is known of the actual nature of the compounds making up coal-tar pitches but it is a generally accepted fact that these belong to the aromatic series. It is undoubted that some coal-tar pitches contain oxygenated hydrocarbons and all have some sulfur-containing bodies as part of their make-up. Nitrogen bodies are also present. It is possible that the nitrogen and oxygen contained in pitches are present in the form of higher homologues of the basic and phenolic bodies found in coal-tar creosote oils. C. R. Downs[1] has published some ultimate analyses of briquette pitches in which one of the three pitches tested showed a notable amount of oxygen and all, considerable quantities of nitrogen and sulfur. There is always a greater or lesser percentage of carbon, which is apparently not present in combination but which is in the free state and is therefore called "free carbon." This is usually considered as the portion of the pitch insoluble in hot benzol and toluol. This insoluble matter is not pure carbon but is very largely made up of this element. The nature of "free carbon" has been very extensively considered by the writer in a previous article.[2] The amount of free carbon in a pitch materially affects its physical properties but no definite quantitative relation can be shown. It has been held by some that the free carbon not only affects the pitch *per se* but also by virtue of the nature of the bitumens which normally make up a low or a high carbon tar. The percentage of free carbon may vary from 10 to 50 per cent in various pitches. If a coal-tar pitch is ignited there is left but a small quantity of mineral ash, almost invariably under 1.0 per cent and usually under 0.2 per cent.

(2) RESISTANCE TO ACID—Concentrated nitric and sulfuric acids char and decompose coal-tar pitch. Dilute sulfuric acid up to a strength of 40° Bé. seems to have very little action. Dilute nitric acid has more effect, but weak solutions are very slow in disintegrating the material. Hydrochloric acid, concentrated or dilute, is very well resisted by coal-tar pitches, and heating the acid has little effect, provided the heat is not sufficient to melt the pitch. Glacial acetic acid dissolves coal-tar pitch, the solution being purely physical, more dilute solutions not affecting it.

(3) RESISTANCE TO ALKALI—Most coal-tar pitches resist the action of caustic soda, caustic potash, lime and ammonia. A very few, derived from tars of high phenoloid content seem to be somewhat attacked by alkali, apparently due to the withdrawal of material soluble in this agent. For purposes requiring alkali-resisting strength it is always possible to obtain a coal-tar pitch derived from tars, which does not present this feature.

(4) AIR AND WATER—These two common reagents have practically no chemical effect on coal-tar pitches even after prolonged exposure. In the case of softer pitches exposed to the weather there is a gradual drying out of oil and consequent hardening. In a paper by S. R. Church and the writer[3] the results of a year's exposure of pitches to atmospheric conditions are given, and it is shown that the alterations due to this exposure are of little importance.

(5) OTHER CHEMICALS—Coal-tar pitches have been shown to resist very well the action of concentrated bleaching powder solutions and solutions of many inorganic salts. In general, it is a very resistant material so far as inorganic chemicals are concerned and is not readily oxidized.

In the paper by S. R. Church and the writer,[3] experiments are presented which indicate that coal-tar pitch is affected to a lesser degree than bitumens from other sources by illuminating gas and gas drips. Illuminating gas from leaky mains frequently affects bituminous pavements, and both the gas itself and the liquid condensate have a serious effect on bituminous waterproofing below city streets.

(6) COMBUSTIBILITY—All coal-tar pitches are inflammable, but have such high flash points that risk from this source is comparatively small. Coal-tar pitches of 135° F. melting point have flash points of above 193° C. (380° F.) and fire points upward of 243° C. (470° F.) when tested in an open dish on a sand bath. These high flash and fire points mean that there is a negligible risk in handling coal-tar pitches at the temperatures necessary for the application of the material.

USES OF COAL-TAR PITCH

(1) ROOFING—The use of coal-tar pitch for roofing purposes is too well known to give it more than passing mention. A roof composed of coal-tar saturated felt with coal-tar pitch mopped between the plies and surfaced with coal-tar pitch and gravel or slag has stood the test of time, has been approved by the Underwriters' Laboratories as a fire-retardant roof, and has been adopted as a standard high-class roofing by architects and engineers throughout the United States. Its resistance to atmospheric conditions, its impermeability to water and its adhesive qualities are of prime importance in this field.

(2) WATERPROOFING—Pitch is also used for underground waterproofing, on bridges, and in tunnels in very much the same way that it is used on roofs, that is, mopped between and on the surface of the plies of saturated felt. This use is also well known to architects and engineers, and coal-tar pitch waterproofing has been used widely with markedly favorable results. The qualities required here are about the same as for roofing purposes, but owing to the fact that such high temperatures are not generally encountered, a softer grade may be used. In this connection, the comparative resistance of coal-tar pitch to gas drips and illuminating gas is of considerable advantage.

(3) PAVING—Coal-tar pitch has found wide application in the construction of pavements of various types. Probably the most important, although of comparatively recent development, is the use of very soft pitch as a binder in the construction of bituminous concrete and tar macadam roads. In brick pavements, granite block pavements and wood block pavements, the proper grades of coal-tar pitch have found wide application, both as a filler between the blocks, and as an expansion joint at the curb line. Many municipalities have issued specifications covering the quality of pitch to be used for these purposes. Pitch for this work is usually somewhat softer than that used for roofing materials.

The ability of pitch to give under pressure is of advantage, especially in its use as a filler in wood block pavement. With expansion of the blocks the pitch squeezes out and does not crack and allow moisture to penetrate the joints of the pavement.

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[1] THIS JOURNAL, 6 (1914), 206.

[2] *Ibid.*, 6 (1914), 279.

[3] "Experiments on Technical Bitumens," *Proc. A. S. T. M.* (1915).

In general the adhesion of pitch to all sorts of surfaces makes it very valuable as a joint filler.

(4) BRIQUETTING—The use of coal-tar pitch for briquetting fine coal or coke breeze has been developed abroad further than in the United States. There are two types of briquetting processes, one where the coal or coke is mixed hot with the pitch and the other in which the pitch is ground and mixed cold with the coal before pressing. In the first case a soft pitch is used which can be readily melted and in the second process the pitch must be sufficiently hard to be readily pulverized. For this purpose the binding strength and waterproofing effect of the pitch makes it particularly advantageous.

(5) CORE COMPOUNDS—This serves as an outlet for harder pitches than are used in briquetting work. Here the pitch is used as the binder for sand cores used in making castings of iron and steel. For this purpose a bituminous binder of low ash content is desirable and coal-tar pitch serves the purpose admirably.

(6) PAINTS AND PROTECTIVE COATINGS—Solutions of coal-tar pitch in tar solvents comprise the main ingredients of the best tar paints. These are used for the protection of structural iron and steel, for waterproofing of interior walls, where it is desired to plaster directly over the paint, for acid-proofing and alkali-proofing paints and many other diverse uses. The reputation of tar paints has suffered much by poorly and improperly made materials. If properly compounded they are the equal if not the superior of many more expensive preparations for many purposes. That they can be completely ruined by thinning with noncompatible thinners, is referred to in an earlier part of this paper.

(7) MISCELLANEOUS USES—Other uses which may be given passing mention are as a pipe dip, in the manufacture of ready roofings, as a cement in the joints of stoneware pipe, and as a constituent of various rubber and other compounds used for insulating purposes. Hard pitch is also used in the manufacture of electric light carbons and in the manufacture of "clay pigeons" or "flying targets." Of more recent development is the use of ground-hard pitch as a fuel in the same manner as powdered coal. This has been found of advantage in some metallurgical processes.

It is probable that an intimate knowledge of all the industries of the United States would develop many other important uses for this class of bitumens. Wherever a bituminous or plastic substance is used there is the possibility of the advantageous substitution of coal-tar pitch. Because of the great diversity in the nature of the crude tars it is possible to vary the characteristics of the residual pitches so as to make them cover a wide field of usefulness. In all chemical industry there is the possibility of its use and it may be that only the unfamiliarity of many chemists and engineers with the real properties and characteristics of coal-tar pitch, has prevented its wider application in our industrial establishments.

THE BARRETT COMPANY
17 BATTERY PLACE, NEW YORK CITY

THE HIGH CHARACTER OF THE MANUFACTURED FOODS OFFERED THE PUBLIC TO-DAY[1]

By A. V. H. MORY

Received May 3, 1916

In view of a disposition in certain quarters to weaken the confidence of the people in the food they eat, it is thought that a summary showing the character of the foods examined during the past few years in the laboratory of a food distributing house, might be of interest.

To begin with, it should be pointed out that the attitude of the chemist who would safeguard the reputation of his house must of necessity be different from that of the food official who would successfully prosecute violators of the law. The official is under the necessity of proving his case in court, which means that very fine distinctions may not ordinarily be taken into account; the food house chemist is seldom justified in overlooking any discrepancy, no matter how small, since he cannot be sure that somewhere in the country there may not be some one who would take exception to what appears to him to be a very small matter.

With the fact clearly in mind that the examinations made were thorough and the criticisms hair-splitting, the following may be of interest:

Out of the 585 samples of miscellaneous manufactured foods analyzed, representing prospective purchases as well as samples taken from stock, there were found, all told, 497 samples, or 85 per cent, which were entirely free from any form of adulteration or misbranding.

Of the 15 per cent of adulterated or misbranded samples about one-sixth, or 2.7 per cent of the whole number, might be held to be deleterious to health. These possibly deleterious samples represented the following products: Flour bleached with oxides of nitrogen, catsup containing sodium benzoate, junket tablets preserved with boric acid, and dried fruits and gelatine bleached with sulfur dioxide. The rest of the 15 per cent were found wanting for the most part because they gave constants not in full accord with the U. S. Department of Agriculture *Circular* 19, though probably not enough out of line to warrant a charge of proved adulteration. There were also a few cases involving fraud only.

These 585 samples represent the output of many producers from different parts of the country, and while it must be admitted that in almost every case these producers are well known and reputable, still, since the most of them are also very large producers, their output represents a considerable part of the manufactured food of the country.

The point must not be lost sight of that the above data were mostly obtained from the examination of products known to be more likely to be found deficient. If uniformly frequent examinations had been made of all varieties of food products sold, the showing would be many times as good as that indicated by the above figures.

It would thus appear that among manufacturers of food products who are considered reputable, the number of cases representing adulteration and misbranding is very small and the number representing a serious menace to health is practically negligible.

The fact is that for some years past about the only service the laboratory of the distributing house referred to has been able to render, is that of helping the expert buyers to select the best from among a number of perfectly legal and wholesome products submitted for consideration. And this in spite of the fact that evidences of adulteration and misbranding have been carefully and persistently sought.

It is a serious question whether the production of food products has not reached a plane far above that of other lines equally susceptible of sophistication, and approached very near to the point where the criminally inclined, who always have taken and always will take chances in the violation of law, are about the only offenders.

This encouraging state of affairs has plainly come about through our food laws, the enforcement of which has enabled the majority, inclined naturally toward fair dealing, to compete on a higher plane with the less scrupulous minority. Efficient law enforcement has thus found a ready champion in the reputable producer and distributer, whose influence is bound to be favorable to even greater efficiency in law enforcement and to a continued improvement in the character of our food supply.

SEARS, ROEBUCK & COMPANY
CHICAGO, ILLINOIS

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[1] Read at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, April 18–21, 1916.

RESEARCH, SCIENTIFIC AND INDUSTRIAL IN THE COAL-TAR DYE INDUSTRY[1]

By Bernhard C. Hesse

The coal-tar dye industry as it stands to-day is the result of the methodical and systematic following up of a side-issue of a scientific research in 1856. It is the composite result of the coördination of science, industry and merchandizing. The purpose of this paper is to consider the contribution of chemical research to this net result and to compare, in some manner, the contributions of investigations in institutions of learning with those of investigations in industrial establishments.

POPULAR VIEW OF COAL-TAR DYE RESEARCH

Chemical research is, without doubt, the real underlying source of the origin, development and growth of this industry; on account of the great brilliancy of the intellectual achievement in synthetically producing on a commercial scale a thing theretofore derived wholly from vegetable sources, namely, alizarin, and of producing so many beautiful and useful things from such an unsightly mess as coal tar, the part played by research in this development has come to be regarded by the public as distinctive of and peculiar to this industry and naturally this has lost nothing in the retelling; so it is not to be wondered at that research in coal-tar dyes came to be spoken of by both laymen and scientists as something of an extraordinary nature. This view has become very wide-spread and deep-rooted. From the time I first became acquainted with coal-tar dye chemistry at the University of Michigan in 1888, until I was graduated from the University of Chicago in 1896, I somehow acquired from the literature and from my instructors the idea, amounting almost to conviction, that there was something almost uncanny about coal-tar dye research and the methods employed in it.

GERMANY AND THE UNITED STATES

Directly after graduating from the University of Chicago in 1896, I entered the employ of the largest coal-tar dye works in the world at its plant in Germany and indeed in one of its research laboratories. This was my first trip outside the United States and it was, of course, an event of the first magnitude for me to be in Europe, and, as a chemist, to be in Germany, in a German coal-tar dye plant, and to cap it all in its research laboratory—a real *sanctum sanctorum* for chemists. In a short time the daily routine wore the novelty off my experience and I then settled down to calm analysis and dispassionate appraisal of my surroundings and to compare what was actually before and around me with my expectations. I found that the general laboratory equipment was no better than what I had been accustomed to; that my colleagues had no better fundamental training than I had enjoyed nor any better fact—or manipulative—equipment than I; that those in charge of the work had no better general intellectual equipment nor any more native ability than had my instructors; in short, there was nothing new about it at all, nothing that we did not have back home, nothing—except the specific problems that were engaging their attention, and the special opportunities of attacking them. Those problems were of no higher order of complexity than those I had been accustomed to for years, in fact, most of them were not very complex from a purely intellectual viewpoint. There was nothing inherently uncanny, magical or wizardly about their occupation whatever. It was nothing but plain hard work and keeping everlastingly at it. Now, what was the actual thing behind that chemical laboratory that we did not have at home? It was money, willing to back such activity, convinced that in the final outcome, a profit would be made; money, willing to take university graduates expecting from them no special knowledge other than a good and thorough grounding in scientific research and provide them with opportunity to become specialists suited to the factory's needs. However, we then had numerous men at home, who put their money behind investigational enterprises but they had selected subjects different from coal-tar dyes; for example, sewing machines, agricultural implements, typewriters, shoemaking machinery, incandescent lamps and many others, where the sums invested, the high-grade specialists employed, the scientific, systematic and methodical development and merchandizing lose nothing whatever by comparison with what is done in coal-tar dyes in Germany. This was my first conclusion 20 years ago and it has since been confirmed by comparison with conditions on both sides of the Atlantic and has long since become a firm conviction with me, fortified as it is by close and intimate contact with a number of large enterprises at home and ten different trips to Germany, covering a total of 36 months' residence in Germany, where and when I checked up my views. Also, I have met competitively and collaboratively coal-tar dye chemists and researchers, not only of Germany, but of Austria, France, Switzerland and England as well, and have worked side by side with them in three different research laboratories, two in Germany and one in England. Each trip brought me home more convinced than ever that neither Germany nor any of these other countries had anything fundamental to teach us in the way of research even though, as a people, we did have much to learn, particularly from Germany, in determination to know how to make everything count to its utmost profitably realizable capacity, and to make specialists out of university graduates—in other words, national teamwork.

In short, we have as good educational institutions, as good chemical instructors, as good chemical investigators, and as good native ability as has Germany or any other country, but with us these are not as widely diffused.

In the final analysis "Research" is made up of "I want to know" and "I am going to find out,"—two qualities which the American people, inclusive of its chemists, have always had in abundance and to spare, but not always coördinated nor efficient. Desire to know cannot have practical effect unless opportunity to find out be available. To-day's opportunity was generally yesterday's impossibility. If opportunity ever presents itself in this country to find out about coal-tar dyes, I am confident that we will find out all that such opportunity can be made to make available and without going beyond our own borders for the men or the "know-how." What we do not have now, our own educational institutions are fully capable of supplying, if and when called upon. But in this, as in all like things, the time element is one that must be taken into serious account.

Like coal-tar dyes, our sewing machines, incandescent lamps, agricultural, writing and shoemaking machines are not natural products and had to make their own way in the markets of the world; they too had to be created and developed; as in coal-tar dyes every other country had the same initial opportunity to make the same kind of machines that we did, but we created those industries and we have maintained our supremacy against the world. It is nothing unheard of or new for us to create new things, overcome long-standing prejudices and to conquer foreign markets.

Fundamentally then, we have done all the things that made the coal-tar dye industry, but our efforts have been along other specific lines; it merely remains for us to decide definitely to attack that particular problem, it is no harder to solve than many others that we have solved. It is not, and probably never has been, a question of whether we can or cannot make coal-tar dyes or whether we could learn how, but rather a question of when we did do it would it be worth our while; could we not do something else to better advantage?

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[1] Address at the Chemistry Conference, 25th Anniversary University of Chicago, June 5, 1916.

THE COAL-TAR DYES

In the coal-tar dyes industry as it is to-day, all but two of those dyes are without counterpart in nature; they are as much man-created as is a sewing machine or a typewriter. Two of the dyes now made from coal tar were, prior thereto, secured entirely from vegetable sources and had been used for centuries as dyestuffs: these two are alizarin and indigo. The coal-tar product is identical with the vegetable product in both cases. It was chemical research that pointed the way for the founding and development of this industry in both the above branches.

As applied to chemistry, research may be scientific, empirical or industrial; it is as impossible to draw the dividing line between these three classes as it is to designate the precise instant of time when night ceases and day begins, or the reverse. The scientific research of to-day is the empirical research of to-morrow and the industrial research of the day after.

INDIGO AND ALIZARIN—In the case of both indigo and alizarin, scientific research first of all had to determine the chemical constitution of these substances and confirm them by a synthesis; then empirically, and guided by the spirit and method of scientific research, the commercially possible syntheses had to be explored and then industrial research had to adapt one or more of these methods to commercial use—a general procedure fundamentally familiar to Americans in many other lines.

Scientific research attempted to solve the chemical constitution of alizarin as early as 1848; in 1852 a constitution, since recognized as erroneous, was assigned to it but in 1869 its correct constitution was deduced and its synthesis from anthracene accomplished; its commercial introduction was accomplished within 1 year; empirical research, in less than 6 months from the discovery of the first synthesis, developed the method which, with but few nonfundamental changes, is the one used to-day, and shortly after its discovery the annual value of its production was $8,000,000; that is, 20 years were required to solve the scientific research, and less than 1 year was needed for commercial introduction. Vegetable alizarin was practically conquered in less than 2 years of commercial effort, or a total of 22 years.

Scientific research into the chemical constitution of indigo began in 1841 and was not concluded until 1882; in 1890 empirical research led to the present-day commercial process, but it was not until 1897 that the industrial research was concluded; it required 5 years in addition to conquer vegetable indigo; that is, the scientific research required 41 years to complete its task, empirical research 8 years, industrial research 7 years, and commercial exploitation 5 years, or a total of 61 years. The annual value of vegetable indigo in 1882 was about $20,000,000.

The contribution of scientific research was not limited to the ascertainment of the constitution of these two substances. In the case of alizarin the use of caustic-alkali melt of sulfoacids for the making of hydroxyl derivatives was discovered in the course of scientific researches in France and in Belgium in 1867, and applied in Germany and in England almost simultaneously in 1869 for making alizarin.

For indigo, liquid chlorine—in 1890 an industrial fact—was the direct offspring of a scientific research (though carried out in an industrial establishment) into the conditions under which chlorine can be liquefied and into the properties of liquid chlorine itself; the conversion of phthalimid into anthranilic acid was accomplished in 1890 in Holland by applying to phthalimid a reaction originally applied in Germany in 1882 to acetamid and thereafter largely developed by chemists in Holland and elsewhere; the use of phenylglycine and of its carboxylic acid as an indigo intermediate was discovered in Switzerland in 1890; the use of mercury in connection with sulfuric acid for oxidizing organic substances controllably, as well as to complete oxidation, was discovered in 1883 and is of Danish origin, but was not applied to the oxidation of naphthalene until 1896. Therefore, scientific research also blazed the way for the commercial alizarin synthesis and provided the direct fundamentals of four of the necessary things in the first commercially successful indigo synthesis.

Furthermore, before the makers of synthetic alizarin and of synthetic indigo could afford to commit themselves definitely and heavily to the production of these two things, it was necessary to make reasonably sure that the particular method to be operated was as cheap as any as would be likely to be developed by others and above all that there were no "next-door-neighbors" chemically known as isomers, homologues and substitution products, that would be better than these two substances or either of them. Here is where the results of scientific research through its achievements in determining the possible number of isomers, homologues and substitution products enabled the empirical investigators to delimit and circumscribe the field to be investigated with reasonable assurance as to accuracy and certainty that nothing had been overlooked, that nothing was left for those who came after to create unwelcome effective competition—and in these empirical investigations the laboratory, investigational and reasoning methods of scientific research were liberally drawn upon.

MAGENTA AND ITS CONGENERS—Passing now to those coal-tar dyes not to be found in nature, *i. e.*, the created dyes of this industry, it may be said that for the great majority of them the chemical constitution is assumed as known, based upon the methods of their production and the rules in relation thereto which scientific research established; to some of these dyes no chemical constitution has been assigned and for some even the chemical composition is not known.

Magenta was first discovered in Russia in 1856; chemists in France and England from 1858 to 1860 developed and patented various methods of manufacture from the commercial anilin of that day; but it was not until 1864 and 1866 that it was discovered that pure anilin or pure para- or orthotoluidin when treated by these methods would not yield magenta but that a mixture of these three is needful; it was not until 1878 that its constitutional formula was determined. Long prior to this the industrial method of to-day had been found by empirical or exploratory research; the constitutional formula, however, gave greater certainty to the conclusion of the industrial men that the limit of successful further investigation had been reached for at least a reasonably long period of time. In this case, knowledge of the constitution did not itself point to any commercially new or useful results; it merely confirmed the conclusions as to temporary finality of the work of others.

Long before the constitution had been determined it was definitely ascertained empirically by men in France and England, and to a lesser extent in Germany, that there were three amido groups in magenta, and long before that, that there were replaceable hydrogens in magenta and the empirical workers had exhausted the then available means of treatment of magenta for its substitution products and had worked out substantially all the commercially useful products which included red, blue, violet and green, both basic and acid, of the present day.

As a direct result of the scientific investigation for the constitution of magenta came the investigation of condensation products of benzaldehyde with tertiary amines and from that the use of benzaldehyde and of substituted benzaldehydes in the making of dyes which have since acquired great commercial importance. Once the direction was given, it was only necessary to prepare the various substituted benzaldehydes and the substitutes for dimethylanilin employed in making the pioneer of this class in 1878 and systematically to exploit the field thus marked out. In 1878 it was recognized that nitration and reduction might yield new dyes but attempts in this direction then failed only to become commercially successful about 10 years later.

In a scientific investigation into the constitution of rosolic acid in 1878 it was found that dioxybenzophenone combines with phenol to produce aurin. Michler's Ketone, a "next-door-neighbor" of dioxybenzophenone, was discovered in 1876; its production on a commercial scale was realized in Switzerland in 1883, in which year it, like benzaldehyde in 1878, was treated, also in Switzerland, with dimethylanilin and gave a violet. From then on it was only needed to treat Michler's Ketone with all the substitutes for dimethylanilin and to work out the commercially useful dyes in the field thus laid out—a labor not completed in the 33 years that have since elapsed.

THE PHTHALEINS—All of these investigations reflect the influence of the scientific researches begun in 1871 on the behavior of phthalic acid with phenols in which the trihydric phenol, pyrogallol, was first examined, then the dihydric phenol, resorcin, and, finally, phenol itself; the commercial introduction of the first did not take place until 7 years later, while the second required 3 years, this delay being due to the difficulties encountered in commercially making the intermediates, namely, phthalic anhydride and the phenols; the bromination products of fluorescein, though discovered in 1873, were not marketed until 1874; these were thereupon followed by iodination, methylation, chlorination and nitration products of fluorescein, but it was not until 13 years later, or in 1887, that alkylated amidophenols were investigated in their behavior towards phthalic acid and yielded most valuable dyes; still, not until 1894 or 7 years later was it discovered that this reaction proceeded in a two-stage manner, combining first in equimolecular proportions and this result then reacting with the second molecule of the amidophenol, although such behavior was foreshadowed in the work done in the scientific investigation of the constitution of magenta and the synthesis of the benzaldehyde dyes and the dyes from Michler's Ketone just considered. While in this particular case, failure to recognize the two-stage character of the reaction did not result in the loss to the art of really valuable dyes, yet our knowledge of the mechanism of this reaction was by that much retarded. In the case of tartrazine, which was discovered in 1884 and marketed in 1885, although its two intermediates were known to scientific investigators wholly as the direct result of abstract scientific work as far back as 1879, the two-stage nature of its synthesis was not observed until 1893, or 9 years later; in this case the two-stage process enables the production of commercial dyes of real value not theretofore available.

Methylene blue, discovered in 1876 and marketed in 1877, was manufactured in three different ways before conclusive answer was obtained as to the mechanism of any of these reactions by scientific examination, in 1889; no method of manufacture, at all new in principle, grew out of this investigation.

THE AZO DYES—The reactions underlying the azo dyes were exhaustively treated, scientifically, in researches begun in 1860 and completed in 1870; the reactivity of diazo compounds with amido compounds was discovered in 1864 and with phenolic compounds in 1870. The first of the azo dyes appeared on the market in 1861 and was followed in 1863 and 1875 by two others, but it was not until 1876 that this reaction began to be exploited to any considerable extent and here again the reason was the difficulty of obtaining the intermediates in commercial quantities. All products of this class were direct dyes for wool or mordant dyes for cotton and none of them was a direct dye for cotton until 1884, when benzidine, itself described in scientific literature as early as 1846, was found to be capable of producing direct cotton dyes; but these first benzidine dyes were not very fast to acids, alkalis or light and the chase for phenolic or amido or amidophenolic substances which, when combined with benzidine or benzidine substitutes, would yield fast colors, was on! In this chase scientific investigators contributed little of effective specific help; they had marked out the field, provided the general implements, intellectual and manipulative, but the magnitude of the problem was too great for any individual and one wholly unsuited to university treatment; its solution called for careful preparation of the individual materials, combining them with benzidine and benzidine substitutes, to yield direct cotton dyes, examining these dyes in their behavior towards cotton and other fabrics under service conditions or their substitutes and, profiting by whatever they showed, forecasting further work with the help of the general scientific rules and laws of structure of these materials and to take up the task anew. A heart-breaking, desolate and uninspiring lot for the isolated worker, not in the confidence of those who know commercial conditions as to the availability, immediate or remote, of the materials needed to make these new intermediates, and of the commercial requirements of the dye markets, but a task full of zest and excitement when carried out in coöperation and collaboration with those who were conversant with all these details—for it was clear that there could be but few victors, the laggards would be beaten. Surely, the university and the individual investigator were hopelessly outclassed in this particular chase for only the worst kind of a fluke could lead to a useful result; true, new results could be obtained, but differing to the uninitiated in such subordinate and seemingly trifling details as to make the work actually sheer monotony. Yet the greatest skill and knowledge was required of the men who actually carried out this work in the industrial establishments.

In the middle of the eighties investigation by individual investigators and by institutions of learning began to cease contributions of pioneer value to this industry and except for the brilliant glycine synthesis of indigo in 1890 the scientific researchers have done nothing since which specifically and directly approaches pioneer work. By that time research in this field had settled down to the humdrum task of sifting out from the hundreds of thousands of millions of possible dye combinations those that could survive in the world's markets. The work theretofore done by the university investigator was now done in industrial establishments and the new types of commercial dyes since then introduced have emanated from these industrial establishments themselves and as a direct result of industrial conditions themselves, and not from any real scientific experimentation, reflection or deduction by university investigators, as such.

RETROSPECT

However, looking backward, it does seem that industrial investigators could have developed the industry faster and that university investigators could have pointed out new fields a little more quickly than they did. For example, sulfonating as a means of rendering dyes better adapted for animal fiber, was discovered as early as 1862, yet Martius' Yellow, discovered and marketed in 1856, was not sulfonated until 1879, nor was magenta, also marketed in 1856, sulfonated until 1877; anilin yellow was not sulfonated until 1877, although on the markets in 1859; as early as 1876 it was known that sulfur could be substituted for the imido group to produce new dyestuffs, but this substitution in the indigo group was not tried until 1905, although all needful materials were known as early as 1890, and the real development of the indigoid dyes did not begin until well after 1900, although most of the materials had then been available for upwards of 10 years. Instances like these could be given in great numbers.

Of course, after things have been done it is not only very easy but most ungracious to say that they should have been done sooner or better, but these comparisons are not here made for any purpose of criticism or fault-finding; they are made in the hope that calling attention to a few opportunities now easily recognized as having been overlooked in the past, may sharpen our foresight and increase our powers of intellectual penetration and deduction and hearten university investigators so that they may again be the pioneer leaders in a field which is without limit and whose future cannot but be far brighter than its past, however glorious that has been. The opportunities for applying constructive imagination and selective judgment to the logical and systematic development of this field for pioneer work along the lines of types and subtypes are far greater today than they ever were and the chances of success are certainly no smaller than they were in the days when the university investigator was the guiding spirit in this industry. A comprehensive and useful answer to the question as to the causal relationship between tinctorial properties and chemical constitution has still to be given; no more powerful intellectual instrument than this could be devised and the university investigator has an almost equal chance, so far as materials, facts and facilities go, with his industrial brother, and so far as surroundings in sympathy with such work are concerned the industrial chemist or researcher is very greatly at a disadvantage; an insight of this kind should be as powerful in this branch of chemistry as the calculus is in engineering; the fact that more than 40 years have passed since the first attempts were made in this direction should not discourage—centuries before Newton and Leibnitz the world had many mathematicians of undoubted ability and power.

CONCLUSIONS

It would be idle to suppose that in the foregoing anything more than a mere fragmentary outline sketch of the relative contributions of research and its various subdivisions to this industry have been given; nevertheless, the essentials are there, and they justify the following general statements:

I—The coal-tar dye industry had its origin in an accidental occurrence in the course of a purely scientific research.

II—For the first 8 years the development was wholly through empirical research with no scientific or very clear guide to the field.

III—When scientific investigation had established certain fundamental scientific data the development proceeded more rapidly than theretofore and with greater certainty.

IV—The first individual success of real commercial magnitude and permanence owed its conception and execution wholly to scientific research.

V—Empirical investigation, both in institutions of learning and in industrial establishments, profiting by and taking advantage of purely scientific achievements and results, reached its conclusions and completed its labors more speedily and certainly than it otherwise would and made the commercial venture less hazardous than it otherwise would have been.

VI—The industrial research needed for the industrial application, itself, depended for much, and in some cases for all, of their material upon scientific research in no way connected with dyes or anything relating to them.

To return, then, to the beginning and fulfil the avowed purpose of this paper, namely, comparison of researches carried out in institutions of learning and in industrial establishments.

The university and like men for the first 30 or 35 years, by the development of the general and specific laws of chemical constitution, placed in their own and in the hands of industrial researchers means more powerful than ever existed as helps in chemical research; as a result, new methods of manufacture, new dyes and new types of dyes were made foreseeable long before the industrial researcher and chemist could get around to the experimental testing of the material thus laid bare.

The industrial chemist and researcher has not provided his university or scientific brother with any such broad general helps but he has contributed an enormous amount of fact-material and has discovered a multitude of new manipulative methods but all of them more or less disconnected and not coördinated; the successful methods of industrial research were all borrowed from scientific research; for the past 25 or 30 years the industrial researcher has accomplished all new advances himself but in so doing he has drawn very heavily and without stint upon the results of scientific research not at all connected with the subject of dyes.

Who shall say which is the more important achievement? Both are wholly essential to progress; neither can develop to its fullest extent without the other; the scientific investigator needs access to an amount of fact-material which it is beyond his strength to gather; the industrial researcher needs rules, laws, generalizations, experimental and manipulative methods which his surroundings usually make impossible for him to discover or to devise; the coal-tar dye industry never would have existed without both.

This answer is probably the only one that should have been expected, yet the general and wide-spread opinion was and is otherwise. This answer portrays approximately the conditions existing in whole or in part in our own chemical, mechanical and electrical industries and in every application of science to every-day life, and why should chemistry applied to coal-tar dyes be different? The answer is that it is not.

Since our success as a nation in chemical, mechanical and electrical endeavor is in part, at any rate, based upon essentially the same attitude towards their respective purely scientific branches and their commercial application, is not that a complete warrant for the conviction that we also have the ability to build up a coal-tar dye industry? Our institutions of learning have long been prepared competently to make their contribution should our industrials make the call. Will our industrials send forth the call?

25 Broad Street, New York City

THE AMERICAN TEXTILE MANUFACTURER: HIS ATTITUDE TOWARD AMERICAN-MADE DYES[1]

By Frederic Dannerth[2]

So much has been said during the past two years regarding the attitude of American textile manufacturers toward American-made dyes that it seems necessary to correct some current impressions.

One of the principal, if not the most important, reason for using German-made dyes in the United States was the fact that nearly all the sunfast and laundryproof dyes available were and are still made in Germany. The dyes used for printing colored stripes on men's cotton shirtings are the well-known vat dyes which occur in commerce under the distinctive names of Helindone, Algole, Indanthrene, Cibanone. Then, too, there are a large number of "acid" dyes which are characterized by unusual fastness to light when applied to wool and silk fibers. These acid dyes if applied to silk fabrics can be exposed to direct sunlight for a period of 40 days, in a latitude of 41 ° North, during July and August, without showing any appreciable "fading." For the benefit of such research chemists as may be interested in developing dyes of this character, I have appended a list of some sunfast dyes together with the index number under which they appear in Schultz' "Farbentabellen" (1914 edition). This might well serve as a basis for advanced dye investigations in our organic chemical laboratories.

Sunfast Dyes on Animal Fibers

(865)	Alizarin cyanin green GX
(864)	Anthrachinon green GXN
(863)	Anthrachinon blue-green BXO
(862)	Alizarin blue-black B
(861)	Anthrachinon blue SR extra
(860)	Cyananthrol G
(859)	Cyananthrol R
(858)	Alizarin Saphirol B
(853)	Anthrachinon violet B
(852)	Alizarin Irisol D
(851)	Alizarin direct blue B
(850)	Indanthrene blue WB
(639)	Gallanil violet RB
(303)	Brilliant yellow
(249)	Crocein scarlet 3B

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[1] Presented at the One Hundredth Meeting of the National Association of Cotton Manufacturers, Boston, April, 1916.

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These and a score of others including such well-known dyes as Cloth Red and Naphthol Green are dyes which are to-day of importance to the textile manufacturers of the United States. To the list given might be added such dyes as Patent Blue (Hoechst) and Rhodamine (Elberfeld), which stand entirely in a class by themselves in the matter of brilliancy. The dyes mentioned have all been tested out in this laboratory and have been found to possess the properties mentioned.

In view of the extensive discussion of tariff protection for our American dye industry it seems that attention should be called to one of the important factors which has heretofore received no consideration in discussions of this measure. The industry of coal-tar dyes is based on the science of organic chemistry, and this is a branch of chemical research which is at present being taught to only a limited extent at our American colleges. This statement is based on an inspection of the catalogue of five leading universities located in the Atlantic States, and is supported by a personal contact with graduates of these institutions. It therefore seems timely to call attention to this deficiency in our educational system, and if possible provide ways and means for altering these conditions. The points which require emphasis are:

(1)—The supremacy of the German dye-manufacturing industry at the present day is probably due primarily to the advanced instruction in organic chemistry which is offered to students in German universities and technical colleges.

(2)—The manufacture of modern *sunfast* and *laundryproof* dyes in the United States cannot begin until there are in the country a sufficient number of men with an adequate education in the methods of organic chemical research.

(3)—Until this instruction is given in our American colleges, the extension of our dye factories and the invention of new and useful dyes must of necessity be very limited. Even if our college courses are revised to-day, it will be three or possibly four years before adequately trained men are available. The past twenty-five years of activity in our American dye factories bear abundant witness to the fact that our dye manufacturers are not inclined to spend time or money in the development of dyes of especial "fastness." This, however, is the particular point which European chemists have emphasized in all their dye developments and any rational consideration of tariff protection must take this point into consideration. The mere investment of capital will not insure for us an American dye industry.

(4)—The numberless complaints which have already been made with regard to the "fastness" of American-made dyes, demonstrate conclusively the present state of the industry in the United States, after an unhampered development of forty-six years.

(5)—An investigation will show that European chemical laboratories, in the majority of cases, have their doors open from seven o'clock in the morning until six o'clock in the evening. Which of our American universities can say as much?

The textile manufacturers of the United States have been variously accused by some of our less conservative collegiate professors, of favoring English and German dyes to the exclusion of American-made dyes. The answer to this accusation has already been given. All that the American dyer asks is that he be supplied with *modern dyes* which shall equal in brilliancy and in "fastness" the products which are now made by foreign manufacturers. It is also fair to assume that this will not be possible until students are given the necessary basic instruction in our colleges.

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CURRENT INDUSTRIAL NEWS

BRITISH SUPPLY KIESELGUHR AND TUNGSTEN ORES

It is satisfactory to learn, says the *Times Engineering Supplement*, that the supply of diatomite, more familiarly known as kieselguhr, much of which was formerly obtained from foreign sources, will, in future, be obtained from sources within the British Empire. Diatomite is not only used in the production of dynamite but also in sugar refining and other industries, and it is important to have regular supplies in times of peace as well as in war times. It seems from the results of research carried out at the Imperial Institute, London, that valuable sources of supply have been found in Victoria and New South Wales. Attention has also recently been directed to the question of supplies of another important raw material, tungsten powder. Now that the technical problem in connection with the production of tungsten has been solved, it is necessary that the new industry should be assured of supplies of raw material to keep the new plants in regular operation. It is probable that, as in the case of diatomite, resource will be had to the large supplies of ores which are known to exist in Australia, and it has been suggested that a sound policy would be to erect concentration machinery in close vicinity to the wolfram deposits so that the ore, shipped to home manufacturers, might contain a conveniently high percentage of tungsten.—A. McMillan.

NEW ZEALAND CHINA CLAY

According to a report in the *Chemical Trade Journal*, what will eventually prove to be a valuable industry has been started in New Zealand despite the war. For some months past developments have been proceeding on a large reef of china clay at Ngaruawahia in the north island. Analysis made by the government analyst has shown the material to be very similar to the china clay of Cornwall.—M.

REVISED MINING REGULATIONS IN COREA

H. M. Consul at Seoul has furnished a translation of a Mining Ordinance issued by the Governor-General of Corea, to take the place of the mining law of July 12, 1906. The ordinance, which is to take effect upon a date to be determined by the Governor-General, consists of 64 articles and is based on the Mining Law of Japan. The main feature of importance is that, in future, foreigners, as individuals, will be prohibited from obtaining mining concessions in Corea. The grant of mining interests by the new regulation is to be limited to Japanese subjects or juridical persons established in accordance with Japanese law. Mining rights already in existence and held by foreigners are not to be interfered with but foreign juridical persons in order to succeed to such rights must become juridical persons established in accordance with Japanese law, and must have their head office in Corea. Priority of application will probably no longer ensure the grant of mining rights although this is not expressly stated in the ordinance.—M.

SIAM BENZOIN

According to a report from Bangkok, one of the staple products of Siam is gum benzoin (the resinous exudation of a tree closely related to the Styrax benzoin of Sumatra). Siam benzoin is collected in the northern forest regions of the country and is very highly esteemed for its delicate odor. It is used to some extent locally for the preparation of toilet water and allied preparations. During the year ending March, 1915, 52,251 lbs. of benzoin were available for export and with a value of $27,918. Most of the benzoin exported went to the United Kingdom but a large quantity went to Germany before the outbreak of the war.—M.

PETROLEUM DISCOVERY IN CHILE

According to a report in the *British Board of Trade Journal*, a telegram from Punta Arenas states that splendid samples of petroleum have been extracted from borings at Rio Amarillo and the existence of this oil in considerable quantities can be taken for granted in that district.—M.

SULFUR PRODUCTION IN RUSSIA

At the foothills of At-Chagyl, alongside the salt lake of Kukurt-Ala, 62 versts (40 miles) from Krosnovodsk, the exploitation of an immense deposit of sulfur has been begun. The deposit is said to consist of 90 per cent pure sulfur.—M.

POWER TRANSMISSION UNDER WATER

International power transmission, says a contemporary, by submarine cable has now been established between Sweden and Denmark, having been put into use in January. The cables run from Palsjo just north of Elsinore, Denmark, the underwater distance being 3.35 miles, the transmission voltage 25,000, and the energy transmitted 5,000 kilowatts. The two power cables are laid parallel to each other 100 m. apart while a protecting steel cable with a breaking strength of 40 tons is run parallel to the power lines and 100 m. from the nearest. Iron towers 25 m. high on either shore warn vessels against attempting to anchor near the cables. These towers carry green lights at night. A steam station on the Denmark side serves as a reserve in case of interruption on the submarine line.—M.

EFFICIENCY OF GAS-FIRED FURNACES

A wide range of gas-fired furnaces for melting and annealing metals is described in a list recently published by a Birmingham firm. The crucible melting furnaces are fitted with Wright-Brayshaw burners and use gas at ordinary pressure with an air blast at a pressure of 3 lbs. per sq. in. A comparative test, extending over 4 working days, has been carried out between one of these furnaces and a coke-fired furnace at a brass foundry. The coke-fired furnace was able to melt an average weight daily of 592 lbs., the number of melts being 13, each requiring 53 min., while the total fuel used was 300 lbs. The average weight of brass melted with the gas-fired furnace was 910 lbs., the number of melts 20, each requiring 34.5 min. and the total fuel consumption being 2,076 cu. ft. The gas-fired furnace proved the cheaper as the average cost of the castings produced was 0.3 cent, while for the coke furnace the cost worked out about double that amount. Furthermore, with the coke, the cost for crucibles was more than twice as much as with gas and the gas-fired furnace crucibles are able to stand regularly 90 to 100 melts. The best result obtained during the tests was the melting of 45 lbs. brass in 15 min. with a consumption of 67 cu. ft., or 1.49 cu. ft. of gas per lb. of metal melted. In the annealing furnace, a reducing, neutral of oxidizing atmosphere can be obtained at will. Gas at ordinary pressure is employed with air at 2 to 4 in. water-gauge pressure and a temperature of 1400° F. is readily obtained. Other types of furnaces are referred to, for the heat treatment of high-speed steel tools, for heating and mixing chemicals and for heating rivets.—M.

MOLYBDENITE AND ZINC IN NEW ZEALAND

H. M. Trade Commissioner in New Zealand has forwarded extracts from the local press relating to reported discoveries of deposits of molybdenum and zinc ores in the Dominion. The deposit containing the molybdenum has been discovered at Takata and the samples assayed were found to contain 50 per cent MoO_3. Ore declared to be pure sulfide of zinc has also been discovered at Wangapeka, 53 miles distant from Nelson. The reef is from 4 to 5 ft. wide and the ore is said to run 18 per cent zinc.—M.

ANNEALING OF ALUMINUM

In a recent report to the Faraday Society, London, on the annealing of aluminum, Messrs. Seligman and Williams describe some interesting anomalies in the behavior of the metal. Hard-worked aluminum seems to be more readily soluble in nitric acid than the annealed metal and, if the hard-worked sample be heated to 125° C., a definite change in the rate of dissolution is brought about. A specimen of hard-worked metal which lost 56 mg. per 100 sq. cm. per 24 hours in nitric acid (sp. gr. 1.42), lost only 39 mg. when similarly exposed after being annealed at 500° C. (a decrease of 30 per cent). On annealing for 10 hours at 125° C. there was a decrease of 5.3 per cent in the rate of dissolution, whereas it had been anticipated that if the heating were prolonged, the decrease in the rate of dissolution might be augmented. If samples were heated for 80 hours at 152° C., the rate of dissolution was very much the same as if no prolonged heating had been used at all. These facts do not seem to tally with the observations of other workers. A release of strain should certainly be accompanied by reduction in the rate of dissolution but this release of strain would not account for the subsequent increase. The behavior of aluminum as described above does not seem to fall in with any theories which have yet been put forward.—M.

A NIGERIAN COALFIELD

It is possible that the recent discovery of coal at Udi, in Southern Nigeria, may mark a new and important epoch in the history of West Africa, as it may start many industrial developments in that little-known country. The discovery was made in the course of a mineral survey of Southern Nigeria. According to the *Engineer*, **122**, No. 3157, steps have been taken by the government to work the field, following a favorable report from the Imperial Institute, London, and 10,000 tons of coal have already been mined and stacked for use. The coal field is in the immediate proximity of the New Nigerian railway from Port Harcourt, whence the distance is only 150 miles; when this line is opened for traffic—some time this year—transport can begin at once and the coal be at the service of the whole of Nigeria. Many specimens of Udi coal have been fully examined and it has been subjected to exhaustive trials on the Nigerian railway, the reports upon it as a locomotive fuel being entirely favorable. The total area of the Udi deposits is, as far as can be at present estimated, not less than 2100 sq. mi. and in places the seams are 5 ft. thick.—M.

ZINC BRONZE

Bulletin 59 of the Technological Series of the British Bureau of Standards gives an account of an investigation of standard test specimens of a zinc bronze (Cu 88, Sn 10, Zn 2) by Messrs. C. P. Carr and H. S. Rawdon. The authors draw the following conclusions: (1) The addition of a small percentage of zinc does not affect the theoretical microstructure of the alloy; (2) the method of casting, pouring temperature, etc., affect the structure only indirectly by influencing the rate of cooling, amount and distribution of enclosures; (3) the microstructure offers an explanation for the characteristic appearance of the tensile bars after testing; and (4) of the various microstructural properties affecting the physical properties, oxide films must be considered to exert by far the greatest influence. The best type of test bar where the metal is to be cast in sand is the cast-to-size shape and if the metal is poured at a temperature ranging from 1120 to 1272° C., uniformity of tensile strength and ductility are obtained. The advantage of the cast-to-size shape is that it is easy to mould and inexpensive to machine into the shape and size required for testing. It is recommended as the form which should be adopted as standard for general foundry practice.—M.

MINING DEVELOPMENT IN PERU

According to a report from the British Vice-Consul at Callao published in the *Mining World*, **91**, No. 2362, there seems to be considerable activity towards the development of mining throughout Peru. Work in the gold placer claims of the Peruvian Exploration Co. on the Marañon River has forged ahead rapidly and there is a working staff of 300 men, including experts in hydraulic operations, while new machinery has been obtained. At Cerro de Pasco, investigations have been made and proposals put forward in regard to the possibility of working the ore dumps by the cyanide process. The low-grade silver ore tailings scattered over the pampas amount to something like 15,000,000 tons running 15 oz. of silver to the ton, and it is suggested that this ore might be treated at a total profit of over £6,000,000 ($30,000,000), which would make Cerro de Pasco a silver producer of considerable magnitude as well as a copper producer. The Morococha Mining Co., a subsidiary of the Cerro de Pasco, although in a preliminary state of development, is producing from 80,000 to 90,000 tons copper a year which is shipped to La Fundicion for smelting. The Morococha region is one of the most actively worked mining zones in Peru. For some time past, satisfactory investigations have been made on properties some 35 miles from Cerro de Pasco and exploration work on a large scale has been determined upon. At present, machinery is in process of erection, but operations have been somewhat checked by the war. At a later date, it is intended that a smelter shall also be erected and, from indications, it is thought that the output from these mines should then rank with that of the biggest copper producers of this region. Practically the only tungsten properties so far discovered in Peru are now being developed in the Conchucos district of the department of Ancachs and that of La Libertad, but owing to lack of funds no great progress has been made.—M.

BRITISH BOARD OF TRADE

During the month of July, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

American cloth
Asbestos, A. P. jointing
Batteries for pocket flash lamps
Brackets, spring, for cycle lamps
Bricks, magnesite
Burners for cycle lamps
Cardboard containers for office paste
Celluloid ring cases
Cerium stones for pocket lighters
CHEMICALS:
  Alum
  Green copperas
  Manganese dioxide for Leclanché batteries
  Quinoline
  Sodium silico-fluoride
Combs, horn and noninflammable
Duplicators, composition
Dyes, henna powder
Electrical novelties
Electrolytic iron
Fiber, vulcanized, red
Gelatines, high-class for photographic purposes
GLASSWARE:
  Arc lamps, inner and outer globes
  Lamp chimneys
  Glass stoppered bottles
  Glass screw cap jars, 1 lb. and $1/2$ lb. capacity
Glue, fish, liquid, genuine
Glycerine substitutes
Grasses, artificial
Honey sections glazed
Helmets, papier maché
Hollowware, cheap, enamelled for West African market
Insulators, steatite
Kettles or pans, brass, as used in West Africa for rubber
Lamp burners, cheap, for Indian markets
Locks, small for fancy boxes
MACHINERY FOR:
  Bronzing, vacuum, hand
  Flattening and heading nails
  Knitting gas mantles
  Making dominoes
  Making calcium carbide
  Making metal tubes for tooth paste
  Graduating glassware
  Making spectacle and eye-glass ear-pieces
  Making gramophone needles
Mactear furnace for making hydrochloric acid
Magnets, tungsten-steel, permanent magnesite
Monazite sand
Metal plates, enamelled for domestic use
ORES AND MINERALS:
  Celestine
  Strontianite
Razors and safety-razors
Steel sheet, perforated like grater
Steel castings, electric
Syringes, hypodermic 10 per cent and 2 per cent
Vices, hand
Vacuum flasks
WIRE:
  Bismuth, 0.1 mm. diam.
  Silver, 0.0165 mm. diam.
Wire-netting (rolls) 2 ft. × 50 yds.

—M.

CASE HARDENING OF MILD STEEL IN GAS

Such work as is described by Mr. C. M. Walter in a recent paper on this subject, says the *Journal of Gas Lighting and Water Supply*, should be given a wider circulation among steel manufacturers. Little work has seemingly been done on the use of town gas as a carburizing or case hardening agent, but Mr. Walter's experiments show that its use for this purpose in the case of mild steel is highly effective and a good commercial proposition. His results confirm the classical researches of Prof. A. H. White and Mr. H. T. Hood, who were able to show efficiency of quality of product and controllability such as cannot be realized with the solid agents ordinarily employed for the purpose. It is important in this carburizing work that the rate at which the gas is passed through the apparatus should be slow, as this affects the quality of the carburizing.—M.

NITRATES FROM ATMOSPHERIC NITROGEN

The statement, *Nature*, **97** (1916), 408, that since the war began Germany has succeeded in obtaining her full supply of nitrates by fixation from atmospheric nitrogen, lends additional interest to an account given in *Dagens Nyheter* (June 8) of a Swedish Company formed for the same purpose. The method of obtaining nitrogen from the air by means of an electric arc is relatively expensive and its success as a commercial project depends on the local price of electrical energy. It has further been calculated that, even if all the waterfalls of Europe were to supply energy for this purpose alone, this would be hardly sufficient to cope with the increasing demand for fertilizers throughout the world. The Swedish Company employs a method invented by Th. Thorssell (formerly head of the fertilizer and sulfuric acid works in Malmö), which method depends purely on chemical processes and demands only the special treatment of easily accessible raw material. No details of the process have as yet been given. The chief products of the factory are ammonia, ammonium nitrate and cyanide compounds, saltpetre and sulfuric acid. The process is said to be of such a nature that factories can be installed in most places without requiring any large supply of energy. Experimental work in connection with the process seems to have been started in the autumn of 1911, and during the summer of 1912 the results were approved by outside experts. The company was then set going and is now preparing to deliver its products in large quantities and has decided to raise its capital from 3.7 million to 8 million Kroner.—M.

OILSEED INVESTIGATIONS

An article in the *Indian Trade Journal* (Feb. 11, 1916) deals with the report of the Imperial Economic Botanist, more particularly with two crops, *Carthamus tinctorius* and "rai," *Brassica juncea*. The former, safflower, is distributed widely in different parts of India and has been under investigation at Pusa for six years. Twenty-four different types have been separated and closely studied. The coloring matter, carthamin, is absent in some types and in others only feebly developed. The plant has been investigated regarding its dyeing properties by an expert who found that the best color varieties are eight times as strong as the weakest. As a rule the percentage of oil in the seeds varied between 22.77 and 30.19 and a high percentage of oil and a high color yield could be found together. Rai or Indian mustard, when studied in the pure culture, gave a large number of varieties. No fewer than 102 pure types were separated and these varied in height from 30 in. to 10 ft. The writer of the report is of the opinion that, in the case of safflower and Indian mustard, by careful selection, any types desired may be produced and, by the distribution of these types, the crops may be greatly improved both with regard to yield of seed and oil content.—M.

ALLOYS USED FOR ZEPPELINS

A French chemical journal has published analyses of the alloys used in the construction of a Zeppelin brought down recently in France. The angle brackets were found to contain aluminum to the extent of 90.27 per cent, while zinc and copper were present to the extent of 7.8 and 0.73 per cent, respectively, together with small amounts of iron, manganese, silicon and tin. For the channel sections an alloy composed of 88.68 per cent aluminum, 9.1 per cent zinc and about the same quantities of the other elements as for the angle brackets, was used. The braces seemed to be composed of commercial aluminum, as that element was found in their composition to the extent of 99.07 per cent.—M.

NITRATE OUTPUT

The total nitrate production for the year just ended, *i. e.*, July to June, reached about 57,850,000 quintals (a quintal = 100 lbs.) against 34,000,000 quintals for the previous year, when the total available production, after deducting oficina consumption and merma, proved to be about 33,500,000 quintals and against 62,300,000 and 62,000,000 quintals for the year ending June 30, 1914. Shipments during the past year have been about 55,000,000 quintals against 32,000,000 quintals for the year ending June 30, 1915, and 58,750,000 quintals for the year ending June 30, 1914. Mr. Thomson Aikman, in his annual report on the nitrate position, says that as no figures of European deliveries have been available during the war, it is impossible accurately to ascertain what the world's consumption has been, but it may be estimated that the total which has disappeared throughout the world has been approximately about 48–50,000,000 quintals, which is a figure greater than generally looked for. The principal features have been the continued demand for refined quality for explosive purposes (which has been considerably greater than generally anticipated), and the very large shipments to the United States and other countries outside Europe. As regards the latter, however, the excess over the normal is also probably due to the demand for explosives. The demand for agricultural purposes is understood to have been somewhat disappointing due to a variety of causes but, probably, principally on account of the difficulty of getting supplies when required and the necessary high price through excessive freights. The International Institute of Agriculture has published an extensive table showing the world's production of fertilizers, but the figures are carried down only to 1913. The following, however, are the figures for the production of sulfate of ammonia in the different countries for the years 1914 and 1915:

	1914 Tons	1915 Tons
France	91,500	42,000
Italy	14,323	15,000
Sweden	1,510	....
United Kingdom	433,235	429,768
United States	166,015	192,323
Germany	413,837	....

Italy and Norway produced 22,500 and 14,670 tons cyanamide, respectively, in 1914.—M.

ELECTRICAL TREATMENT OF TIMBER

The *Builder*, 110 (1916), 405, quoting from a Swiss contemporary, refers to methods of treating timber electrically. When a current is passed through freshly cut timber a chemical change is stated to occur which renders it more able to withstand attacks of fungi. By using the "Nodon" process, it is claimed that the effect in a few hours is equivalent to months of ordinary drying in free air. Since moisture assists the flow of the electric current, the process is best applied after the tree is felled and in this way the transit weight is reduced. The electric power required is 3 kilowatts to 6 kilowatts per cubic meter.—M.

MANUFACTURE OF VISCOSE

Two French inventions of recent date deal with the manufacture of viscose. The first concerns the precipitating bath for the preparation of the thread, and the use of a saturated solution of a double sulfate of ammonium and sodium has been patented. The solution is used as the precipitating liquor at a temperature of 30 to 40° C. and, if it is made slightly acid by means of an excess of bisulfite of soda, the ammonia is not lost, but if the liquor be raised to a temperature of 80 to 90° C. the xanthate of cellulose becomes transformed in half an hour to the hydrate and the sulfur and alkaline polysulfides retained by the threads are eliminated. The second patent is somewhat different and refers to the preparation of a saturated solution by dissolving xanthate of cellulose in aqueous solutions of acid salts. The acid salts recommended for use are bisulfite of soda in proportion 10 to 15 per 100 parts of cellulose, bicarbonate of soda and diphosphate of soda. Under these conditions a solution of viscose is obtained in a state like that of the neutral xanthate not containing free alkali but only a certain proportion of alkaline salts derived from the acid salts employed.—M.

MOTOR CAR CONSTRUCTION

To introduce anything approaching a right-angled bend in the immediate vicinity of the exhaust part of motor car engines, says the *Autocar*, is obviously an erroneous practice. Yet, this is exactly what is done in the case of internally exhaust manifolds where the deflection of the gases from their transverse direction of emergence into a longitudinal direction can be effected only within the limited dimensions of a *monobloc* casting by what almost amounts to a right-angled bend. In the case of a new and clean engine with a fairly free exhaust and carbureter conditions to suit, fair results may, for a little while, be achieved, but there generally comes a time when a permanent carbureter blow-back sets in and defies the majority of experts.—M.

RAPID DRYING PAINT

In the March-April number of the *Bulletin de la Société d'Encouragement*, a report is given of a rapid drying paint. As many as three coats can be given in one day. The rapid drying is obtained by using, instead of refined linseed oil, linoxine or linseed oil solidified by oxidation such as is obtained in linoline manufacture. This is dissolved in a small quantity of slightly acid amyl alcohol and then a considerable quantity of turpentine added. When this solvent evaporates, the paint is completely dry since the oil has been oxidized in advance. What the lasting qualities are time alone can tell, but, in one case, walls coated with the paint show no signs of deterioration after five years. The price in normal times would be a little higher than that for ordinary zinc paint, but the advantages in quick drying would more than make up for the extra cost in many cases where quick drying is an important factor.—M.

USE OF REFUSE

In a paper recently published by the Bureau of Mines it is reported that within the last five or six years marked progress has been made in Europe in the utilization of various waste material not ordinarily thought of value. The manufacturers of producer gas report the successful use of a large variety of fuels including wood-shavings, wood-blocks, sawdust, excelsior, coffee-husks, rice-husks, cocoanut shells, straw and spent tan bark. The figures in fuel consumption reported by the main factories are as follows: With reasonably dry wood (say, mixed oak, ash and elm) the consumption has been as low as 2 lbs. per brake horse-power hour; with sawdust the average consumption is $3^{1}/_{2}$ lbs. per brake horse-power hour, and with spent bark containing 50 per cent moisture, it is about $4^{1}/_{2}$ lbs.—M.

FUSEL OIL FROM CANE MOLASSES

It is opportune, says the *Int. Sugar Journ.*, to remind readers who have the control of cane molasses distilleries that fusel oil is a material very much in demand at the present time and that high prices for it are now ruling. Previous to the war the cost of raw fusel oil seldom fell below about $1 per gal., and $1.80 could perhaps be taken as a normal figure. At the moment, however, that product cannot be obtained for less than $2.52 to $3 per gallon, according to quality and it would seem that the price may be yet increased. Although the amount obtained from fermented cane molasses is less than in cases of sources such as grain, potatoes or the "inarc" of grapes and in pre-war days its recovery may have been unfavorably considered in cane-growing countries, present conditions make the question worthy of consideration particularly where patent stills are in operation. Those interested may be reminded that fusel oil enters the British Isles free of duty provided it contains less than 15 per cent of proof spirit.—M.

CANADIAN WOOD-PULP INDUSTRY

According to information received in London, the consumption of wood in Canada for the manufacture of pulp has increased threefold during the past eight years and, in the same period, the value of wood consumed for this purpose has increased from slightly under $3,000,000 to nearly $9,500,000. Fifty mills reporting to the government show a consumption in 1915 of 1,405,000 cords of wood valued at $9,426,000 with an average value of $6.71 per cord. Canada produced pulpwood in 1915 valued at $15,590,000, of which $6,164,000 worth was exported. The province of Quebec leads in the number of mills and in the value of pulp-wood exported, possessing 24 out of the 50 mills in the Dominion and exporting $4,000,000 worth of wood-pulp.—M.

REMOVAL OF RESIN FROM SULFITE PULP

The *Paper-Maker*, **52** (1916), 53, quoting from a German contemporary, states that the removal of resin from sulfite wood-pulp is best effected by washing with hot water, not in the digester but in the stuff-chest outside the digester. The usual method of sprinkling has not much cleansing effect because the rinsing water tends to take the shortest path from the inlet to the outlet so that large masses of stuff escape the washing altogether. It is recommended that the stuff be diluted largely with hot water and stirred up and washed by blowing in large quantities of air. The inlet tube for the hot water is situated underneath the false bottom and filtered air at a pressure of 6 to 8 atmospheres is forced through a system of hard lead pipes to the false bottom. A charge of 15 tons of pulp can be washed in 37 minutes and the bleaching qualities of the pulp are improved by the treatment.—M.

PORTUGAL OLIVE OIL PRODUCTION

The *Diario de Governo* (Lisbon), of June 6, publishes an official statement giving the total production of olive oil for 1915 as 27,965,078 liters. The stock of oil on March 20, 1916, amounted to 33,904,475 liters. The above mentioned issue of the *Diario* contains detailed statistics of the production and stocks in each of the oil-producing districts of the Republic.—M.

TRADE OPENING IN BOLIVIA

The British Consul at Oruro (Bolivia) reports that there is a shortage of many goods, especially of those required by the mining industries. The greater part of the machinery and electrical fittings was in the hands of German importers up to the outbreak of war, and there is now an opening in Bolivia for manufacturers and exporters who wish to secure a good and profitable market for mining requirements. There has been a great boom in mining recently in the state.—M.

GREENLAND CRYOLITE

Cryolite, says the *Chemical Trade Journal*, **59** (1916), 45, has been found in commercial quantities at Ivigtut, an Eskimo hamlet on the southern coast of Greenland. The cryolite deposit is said to be a solid mass having surface dimensions of about 200 ft. × 600 ft.; it has been worked as an open cut to a depth of about 150 ft. The deposit widens with depth and the depth is unknown.—M.

NOTES AND CORRESPONDENCE

ON THE EFFICIENCY OF AIR DRYERS

Editor of the Journal of Industrial and Engineering Chemistry:

With reference to the letter of Mr. W. E. Wadman[1] relative to the efficiency of air dryers, Mr. Wadman states that the "consumption of heat in an 'air dryer' for evaporating purposes is a perfectly definite thing and just as definite as in the case of the steam boiler." In this Mr. Wadman is mistaken. Mr. Wadman states that it requires practically 1120 B. t. u. to evaporate 1 lb. of water in such a dryer under even the most ideal conditions, but to convince him of his error I propose to describe an air dryer so designed as to evaporate water at a much lower heat consumption than this, and if any inherent impossibility attaches to the proposed method it will clear up the matter to have it pointed out.

Assume a material which may be dried at a temperature of 160° F. without injury, but which can be dried successfully at a temperature even as low as 90°. Assume that the air supply is at 50° with a dew point of 40°, carrying 0.0052 lb. of water per lb. of dry air,[2] that the material to be dried enters at 60°, and that the specific heat of this material is negligible. Let the air leaving this dryer have a temperature of 160° and a dew point of 140°, carrying 0.1514 lb. of water per lb. of dry air. Instead of throwing this air away, let us use it as the heating element in another air dryer immediately beside the first, cooling the air to 100° and operating the dryer at 90°, thus having available a temperature difference between heating element and air in the dryer of 10° at the least, and with an average of much more than this. The air cooling to 100° will deposit 0.1090 lb. of water and give up 132.3 B. t. u. It is theoretically possible to reduce the heat consumption of the first dryer to 1102 B. t. u. per lb. of water evaporated (the heat of vaporization at 160° plus the heat necessary to heat up the water from 60°). The water evaporation per pound of dry air entering the first dryer is 0.1462, and the minimum heat consumption in this dryer is therefore 161.2 B. t. u. per lb. of dry air. The theoretical consumption in the second dryer is 1081 B. t. u., and it is therefore possible in this dryer to evaporate 132.3/1081 or 0.1223 lb. of water per lb. of dry air without the use of any additional heat. In the two dryers we have therefore evaporated 0.2685 lb. on a heat consumption of 161.2 B. t. u. or 600 B. t. u. per lb. This of course assumes perfection in each of the units employed, but we can sacrifice 50 per cent efficiency and still be far below the limit specified by Mr. Wadman.

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[1] THIS JOURNAL, **8** (1916), 755.

[2] These calculations are made with the use of Grosvenor's curves, *Supplement to Transactions of American Institute of Chemical Engineers*, **1** (1908).

It must be admitted that to secure a higher efficiency than corresponds to the figure quoted by Mr. Wadman, requires the condensation of the water evaporated and the recovery of the heat given up thereby. This amounts to an application of the principle of multiple-effect evaporation, but this principle can in theory at least be applied just as effectively in air drying as in ordinary evaporation. Furthermore, the only industrial obstacle to a realization of these conditions is the low heat conductivity from gas through solid separating wall to gas, a fact which necessitates an enormous heating surface.

In the discussion of several years ago a heat consumption resulting from a commercial test of a Ruggles-Coles dryer was quoted as below the figures stated by Mr. Wadman to be the theoretical minimum possible, and it was stated that such a result was impossible. Unlikely such a result may be, but it is not impossible, in the type of dryer employed. That dryer cools the gases to a remarkable extent, and under certain conditions the gases leaving the dryer coming in contact with the cold, wet material entering it are cooled below their dew point. This results in separation of moisture in the form of fog, which is carried along by the gases. It is easily possible for the heat given up upon condensation of this moisture to more than compensate for the fact that the gases are still higher in temperature than the air supply. Under such conditions the Ruggles-Coles dryer is effectively utilizing a part of the heat of condensation of the water once evaporated, and in this way is making use to a degree of the multiple-effect principle. While such conditions can arise only under unusual circumstances in that dryer, there is no inherent absurdity in the low heat quotation referred to, and it is readily conceivable that in the future that particular type of dryer may be perfected to the point where such re-utilization of the heat may become industrially practicable.

Just because it is possible to lay out a dryer using air under atmospheric pressure which will evaporate water at practically any heat consumption demanded, it must be admitted that there is no theoretical consumption for such an apparatus and therefore no meaning to the term "efficiency" as applied to air dryers. The writer feels very strongly that it is unfortunate to consider evaporation and air drying as unrelated, and that it is *not* true "that the two things are quite distinct;" on the contrary, the fundamental factors involved are identical while the differences are scarcely more than superficial, and appreciation of this is necessary to progress in the development of both types of processes.

Regarding Mr. Wadman's misunderstanding of the statement concerning the evaporation of solutions, I evidently failed to make the point clear in my first communication. As a specific illustration, assume a 34 per cent solution of caustic soda, boiling under atmospheric pressure at 120° C. Mr. Wadman evidently understands that the vapor coming from such a solution is at 100° C., but such is not the case. The vapor coming from a solution cannot possibly be at a temperature other than that of the solution itself. It is true that in this case the vapor must cool to 100° before condensation will take place. Furthermore, if a thermometer be inserted into the vapor space, its cooling action will cause condensation of vapor upon it, and it will therefore register 100° until that condensation has been re-evaporated. The vapor rising from the solution, being at 120°, must be compressed *isothermally* to 14 lbs. gauge in order to condense at slightly above 120°, its heat of condensation then being available for evaporation of more water from the original solution. The *work* consumption necessary to remove 1 lb. of water from the 34 per cent solution of caustic soda is therefore

$$W = nRT\ln p/p_0 = \frac{1}{18}(1545)(460 + 248)\ln(14.7 + 14)/14.7 = 40{,}600$$

foot-pounds of energy per pound of water evaporated. The process involved is truly isothermal throughout—solution, vapor, and condensed steam being at all times at 120°.

W. K. Lewis

Massachusetts Institute of Technology
Cambridge, August 17, 1916

SIR WILLIAM RAMSAY

Editor of the Journal of Industrial and Engineering Chemistry:

In the death notice of Sir William Ramsay, in your August issue, the fact is omitted that he studied for some time under Prof. Rudolph Fittig, in Tuebingen, where he also acquired his degree of Dr. Sci. Nat. He came to Tuebingen while Ira Remsen was there and he told me that he tried to enter the laboratory through a door seldom used, which was locked; after considerable knocking Remsen opened the door and promptly answered Ramsay's question in broken German, in English.

Pittsburgh, Pa. K. F. Stahl
August 23, 1916

ANILINE OIL POISONING

Editor of the Journal of Industrial and Engineering Chemistry:

A letter in This Journal, 8 (1916), 573, written by Messrs. Fiske and Green on the subject of aniline poisoning, has come to my notice and I commend it to the careful consideration of all manufacturers and users of aniline oil. It is with the hope that I may add a few details thereto, that I am writing this.

Soon after the outbreak of hostilities, this company realized that it could no longer depend upon overseas sources for its aniline and by November 1, 1914, we were manufacturing aniline in large quantities; since that date the plant under the writer's supervision has produced approximately 1500 tons without a single fatality due to aniline poisoning; our good fortune has not been a matter of pure luck but is the result of a persistent campaign to eliminate every possible source of danger and to care promptly for such cases of poisoning as have actually resulted.

The premonitory symptoms of aniline poisoning are as described by Fiske and Green, the severe cases showing dizziness, unsteadiness on the feet and finally unconsciousness; however, men who are working constantly in the plant and who have, in a measure, become immune to the effect of aniline vapor, show bluish lips and skin; the poisoning does not seem to go beyond that stage and the men are not inconvenienced in any way; it has been our experience that the severest cases, those most prompt in making themselves manifest, have resulted from the spilling of aniline, nitrobenzol, or aniline hydrochloride liquor directly upon the skin and on this point we seem to be at variance with Fiske and Green.

Realizing that poisoning may be caused either by inhalation of vapor or direct contact with liquid, our manufacturing precautions have been based upon these two points; the building is provided with suction ventilating fans in the roof; several 24-in. fans located in the exterior sidewall of the building play streams of air directly upon the men while they are at their operating positions; in clement weather the windows are removed, at other times satisfactory floor ventilation is provided; suction ventilating ducts are led directly to stuffing boxes and iron-boring feeders where there is always more or less escape vapor; the manufacturing system is closed so that at no point is it necessary for a man to handle open aniline; drinking men are excluded from the operating force; regular rations of milk are issued and their consumption insisted upon; showers are provided and a daily bath is compulsory; the company provides two clean working uniforms weekly per man; rubber boots are supplied; pumps, valves, stuffing boxes, etc., are inspected frequently and all leaks taken care of at once.

The necessity of replacing the stirring paddles in the aniline reducers has been the cause of many of the aniline poisoning cases in our plant; these repairs have been made by our general repair crew, composed of men not familiar with the handling of aniline and not inclined to observe the precautions dictated by experience; in spite of continued washing and steaming-out, there is sufficient aniline saturating the residual iron borings in the reducer bottom to make it inadvisable for men to remain in the reducer for more than a half hour.

Dr. Hamilton, in *Bulletin* 179, U. S. Bureau of Labor Statistics, "Industrial Poisons Used in the Rubber Industry," has written fully on the use of aniline in rubber manufacturing, while Drs. Hamilton and Luce, *Journal American Medical Association*, **66**, 1441–1445, have written of "Industrial Aniline Poisoning in the United States" from a purely medical standpoint.

The Goodyear Tire & Rubber Company
Akron, Ohio, August 8, 1916

W. W. Sanders

THE LIEBERMANN-STORCH COLOR TEST FOR ROSIN—A CORRECTION

The peculiar fugitive violet color formed by the action of sulfuric acid on a solution of rosin (or rosin oil) in acetic anhydride is usually said to be produced by only one other substance, the alcohol *cholesterol*, which is found in all animal glycerides. This substance, however, contrary to the usual statements found in textbooks, gives a deep blue color with the L.-S. reagents, quickly changing to a permanent green, and in addition usually occurs in such small amounts in animal oils that it is practically negligible.

There is, however, a resin which gives a color almost exactly like that of rosin, although the intensity is not the same in all varieties. This is the fossil resin known as "Kauri," which is obtained from New Zealand, and forms one of the most common "gums" used in varnish making. The varieties showing the color best are those having a milky core surrounded by a nearly transparent shell, while in the varieties known as "Swamp" or "Brown Kauri," where the resin has undergone oxidation through contact with air and water, the color is to a great extent masked by impurities. Kauri resin, like common rosin or colophony, was originally produced by a coniferous tree, hence we can see why this color-producing substance is common to both resins. It does not appear to be altered much on fusing the resin as is usually conducted in the varnish industry.

Below are given the color reactions of some of the principal resins used in varnish making. These specimens were all authentic and in unbroken pieces so that contamination with rosin was entirely out of the question. The test was conducted by treating about 0.25 g. of the finely powdered resin with about 10 cc. C. P. acetic anhydride on the hot plate until the mixture just began to boil. After cooling, a portion of the clear liquid was removed to a watch glass and a few drops of C. P. sulfuric acid (sp. gr. 1.53) allowed to run down the side of the glass, and the color noted.

Rosin	Deep violet-red color quickly changing to brown
Kauri Resin (Fossil)	
Amber (Succinite) (Fossil)	Deep wine-red, then brown
Manila, Pontianak, and Borneo Resins (Fossil) (*a*)	Dark brown color
Batavia and Singapore Damar Resins (Recent)	Deep wine-red color which does not change on standing
East India and Black Damar Resins (Fossil)	Deep wine-red color which gradually turns brown on standing
Cholesterol (Merck's C. P.)	Deep blue color which quickly changes to a permanent green

(*a*) Some specimens of Manila have been observed to respond to the L.-S. test.

In the routine testing of oil-resin varnishes for rosin it is easy to see why we sometimes get a positive reaction with the L.-S. test, although the samples had been guaranteed by the manufacturer to be free from rosin.

7606 La Grange Ave., N. E.,
Cleveland, Ohio

P. E. Jameson

THE OLD GUARD

The American Chemical Society complete forty years of existence this autumn; on June 1st it had 8,057 members. Of those still living who became members during the first ten years—which includes 1886, as all those in the list joined during the ten-year period—there are now but 37. They were about one-seventh of the membership then; they are one-two hundred and fiftieth now. The list is as follows:

1876
Baumgarten, F. M.
Chandler, C. F.
Doremus, C. A.
Goldschmidt, S. A.
Herreshoff, J. B. F.
Krause, O. H.
Munroe, C. E.
Niese, H. E.
Parker, T. J.
Ricketts, P. de P.
Sharples, S. P.
Terne, Bruno
Waller, Elwyn
1877
Geyer, W. E.
Hindley, R. C.
Prochazka, G. A.
Stursberg, J. A.
1878
Prentice, W. P.
1879
Doscher, Henry
Eimer, August
1880
Booraem, J. V. V.
Hale, A. C.
1881
Colby, A. L.
Dunham, E. K.
Hallock, A. P.
1882
Pitkin, Lucius
1883
Breneman, A. A.
Krause, G.
McKenna, C. F.
Tucker, W. G.
1885
Morgan, T. M.
Williams, J. T.
1886
Cawley, John
Drummond, I. W.
Geisler, J. F.
Sabin, A. H.
Schupphaus, R. C.

111 Broadway, New York City
August 14, 1916

A. H. Sabin

ILLUMINATING ENGINEERING LECTURE COURSE

A notice of the Illuminating Engineering Lecture Course to be held in Philadelphia, September 21–28, under the joint auspices of the Illuminating Engineering Society and the University of Pennsylvania, appeared in the Personal Notes of our August issue. The preliminary list of lecture subjects of this Course with the names of the lecturers is given below:

A—GENERAL

Illumination Units and Calculations. A. S. McAllister.
Modern Photometry. Clayton H. Sharp.
The Principles of Interior Illumination (Two Lectures). Committee: J. R. Cravath. *Chairman*, Ward Harrison and Robert Pierce.
The Principles of Exterior Illumination. Louis Bell.
Color in Lighting. M. Luckiesh.
Architectural and Decorative Aspects of Lighting. Guy Lowell.
Recent Developments in Electric Lighting Appliances. G. H. Stickney.
Recent Developments in Gas Lighting Appliances. R. Pierce.
Modern Lighting Accessories. W. F. Little.

B—SPECIAL LECTURES ON INTERIOR ILLUMINATION

The Lighting of Factories, Mills and Workshops. C. E. Clewell.
The Lighting of Offices, Stores and Shopwindows. Norman Macbeth.
The Lighting of Schools, Auditoriums and Libraries. F. A. Vaughn.
The Lighting of Churches. E. G. Perrot.
The Lighting of the Home. W. H. Jordan.
Railway Car Lighting. G. E. Hulse.

C—SPECIAL LECTURES ON EXTERIOR ILLUMINATION

Street Lighting (Two Lectures). P. S. Millar and C. F. Lacombe.
The Lighting of Yards, Docks and Other Outside Works. J. L. Minick.
Headlights, Searchlights and Projectors. E. J. Edwards.
Sign Lighting. L. G. Shepard.
Building Exterior, Exposition and Pageant Lighting. W. D'A. Ryan.

Subscription tickets for the Course and further information covering the same may be obtained by communicating with Clarence L. Law, Irving Place and 15th Street, New York City.

COOKING OF SODA PULP—CORRECTION

Editor of the Journal of Industrial and Engineering Chemistry:

In reference to my article in This Journal, 8 (1916), 601, I find that the curves shown in Fig. IV were mislabelled. They should be changed as follows: Cook 1 to Cook 5; Cook 2 to Cook 4; Cook 4 to Cook 2; and Cook 5 to Cook 1.

Madison, Wisconsin
August 3, 1916

S. D. Wells

SCIENTIFIC SOCIETIES

MEETING OF THE AMERICAN CHEMICAL SOCIETY AND THE SECOND NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

The Fifty-third Meeting of the American Chemical Society will be held in New York City, September 25 to 30, inclusive, in conjunction with the Second National Exposition of Chemical Industries. The American Electrochemical Society and the Technical Association of the Pulp and Paper Industry will also hold meetings in New York City during the same week. It is expected that 2000 to 2500 chemists will be in attendance during the week's exercises, and that this meeting of the American Chemical Society will be the banner chemical meeting of the world. The registration office will be open at the Chemists' Club, 52 East 41st Street, throughout the week. Society headquarters will be at the Chemists' Club; hotel headquarters at Hotel Astor, 43rd Street and Broadway.

CHAIRMEN OF LOCAL COMMITTEES

Executive: J. M. Matthews, 50 East 41st Street, New York City.
Finance: L. H. Baekeland, Snug Rock, N. Broadway, Yonkers, N. Y.
Registration: H. R. Moody, College of the City of New York.
Reception: To be announced.
Entertainment: E. G. Love, 124 East 15th Street, New York City.
Hotels: T. J. Parker, 92 William Street, New York City.
Press and Publicity: Allen Rogers, Pratt Institute, Brooklyn, N. Y.
Ladies' Committee: Mrs. L. H. Baekeland, Snug Rock, N. Broadway, Yonkers, N. Y.

GENERAL PROGRAM

Dr. Charles H. Herty, president of the American Chemical Society and chairman of the Exposition Advisory Committee, will open the Second National Exposition of Chemical Industries, at the Grand Central Palace, on Monday, September 25, at 2 o'clock in the afternoon, with an address reviewing the history of chemistry and the chemical industries in this country and outlining developments since the outbreak of the war in Europe. Dr. Francis A. Fitzgerald, president of the American Electrochemical Society, and Dr. Arthur B. Daniels, president of the American Pulp and Paper Association, will also make addresses, after which the assembled guests will visit the exhibits.

The Second National Exposition of Chemical Industries is already an assured success. The managers report that there are but a few spaces still remaining on the second floor for exhibits and that a third floor is being seriously considered and a diagram being prepared. The greatest part of the Exposition will be devoted to things that are made from coal, ranging all the way from phonograph records and aniline dyes to road building materials. Of intense and recent interest, there will be exhibits showing porcelains made in America from American clays as fine as any produced by the Royal Berlin Works and also American glass the equal of the celebrated Jena glass. By way of surprise, Mr. Arthur D. Little will exhibit some silken purses made from sows' ears, thereby disproving the old, proverbial saying that silken purses could not be made from sows' ears. Practically all the large chemical industries of America will have exhibits which will offer unexcelled opportunity for study to American chemists. There will be no entrance fee charged to members of the American Chemical Society and the American Electrochemical Society. The member's badge obtained at the registration desk will admit him at all times.

The American Chemical Society, the Chemists' Club, The American Institute of Mining Engineers, the American Electrochemical Society, and the Technical Association of the Pulp and Paper Industry will all have booths at the Exposition. The Bureau of Mines is preparing an elaborate working exhibit. The Bureau of Commercial Economics is collaborating in arrangements for a motion picture program.

Two other features of the Exposition that have been added this year are a large "Southern Opportunity Section," showing the opportunities that await the chemist in our South, and a section for the "Paper and Pulp Industry" composed of materials and machinery used in the manufacture of paper and other related products.

The American Electrochemical Society have planned a very interesting program and will open their meeting on Thursday, September 28, with a "Made in America" technical session devoted to a review of American progress in the electrochemical industry.

The official opening of the American Chemical Society Meeting will take place at the Horace Mann Auditorium, Columbia University, on Tuesday morning, September 26. The provisional program of the A. C. S. Meeting is as follows:

Monday, September 25

Afternoon: Official Opening of Exposition; Addresses by Dr. C. H. Herty, Dr. F. A. J. Fitzgerald and Dr. A. B. Daniels. Council Meeting, Chemists' Club.

Evening: Council Dinner, Chemists' Club. Council Meeting, Chemists' Club.

Tuesday, September 26

Morning: General Meeting of the Society at Horace Mann Auditorium, Columbia University. Addresses of Welcome by Health Commissioner Emerson of the City of New York and President Butler of Columbia University. Response by President Herty, followed by General Papers.

Afternoon: Public Meeting, Horace Mann Auditorium, Columbia University. Addresses (*speakers to be announced*). Presidential address by Dr. Herty.

Evening: Reception at Hotel Astor. Members American Electrochemical Society invited.

Wednesday, September 27

Morning: Divisional Meetings, Columbia University, Symposium on Colloids (Theoretical).

Afternoon: Industrial Conference, Chemists' Club, "American Dyestuffs Manufacture." Industrial Conference, Grand Central Palace, "Steel Alloy Metals: Electric Steel."

Thursday, September 28

Morning: Divisional Meetings, Columbia University. Symposium on Colloids (Applied).

Afternoon: Industrial Conference, Chemists' Club, "Industrial Alcohol, Acetone and Formic Acid." Industrial Conference, Grand Central Palace, "American-Made Glassware and Porcelain."

Evening: Invitation Smoker of American Electrochemical Society.

Friday, September 29

Morning: Divisional Meetings, Columbia University, Symposium on Occupational Diseases in Chemical Trades. Industrial Conference, Grand Central Palace, "American Pulp and Paper Manufacture."

Afternoon: Joint Industrial Conference with American Pulp and Paper Association, Grand Central Palace, "American Pulp and Paper Manufacture." Industrial Conference, Chemists' Club, "Medicinal Chemicals."

Evening: Subscription Banquet at Waldorf-Astoria, members and wives \$3.50. Guests at cost (about \$7.00). Members American Electrochemical Society and Technical Association American Pulp and Paper Industry invited, with cost same as to members American Chemical Society.

Saturday, September 30

Morning: Meetings of Divisions. Industrial Conference, Chemists' Club, "Oils and Motor Fuels." Industrial Conference, Grand Central Palace, "Miscellaneous Chemical Industries; Convertibility of Plant."

Evening: Exposition closes at Grand Central Palace at 11 P.M.

DIVISIONAL AND SECTIONAL PROGRAMS

The usual meetings will be held by all of the Divisions with the following special program:

Joint Symposium on Colloids by the Biochemical, Physical and Inorganic, and Industrial Divisions—two mornings.

Symposium on Occupational Diseases in the Chemical Trades by the Division of Industrial Chemists and Chemical Engineers. Prof. Charles Baskerville, head of the department of chemistry in the College of the City of New York, will preside. The symposium will consider the chemical trades, prophylaxis in chemical industry, diseases incidental to work in aniline and other coal-tar products, cedar lumber, mines and explosives, and will be followed with a general discussion by the leading authorities of the country: These will include Drs. W. Gilman Thompson, F. L. Hofman, J. W. Schereshewsky, G. P. Adamson, H. K. Benson, W. A. Lynott, Alice Hamilton and Mr. J. B. Andrews.

The Section of Rubber Chemistry, which has held no meeting since the meeting at Cincinnati, will gather for papers and a general conference on the progress of the Chemistry of India Rubber. The Section will be under the chairmanship of Mr. L. E. Weber, with Mr. J. B. Tuttle as secretary.

PAPERS FOR THE MEETING

All titles for papers should be in the Secretary's hands on or before September 11; or in the hands of the secretaries of divisions on or before September 9, with the exception of the Physical and Inorganic Division, for which titles of papers should have reached the divisional secretary by September 1, and the Secretary of the Division of Industrial Chemists and Chemical Engineers on or before September 5.

The Division of Industrial Chemists and Chemical Engineers have voted that the titles of all papers shall be sent to the Secretary of the Division, which title should be accompanied by an abstract; that any title sent without an abstract shall not be printed in the program, and that the time limit for the presentation shall be 5 minutes, unless special arrangements are made with the Secretary of the Division.

The Division of Physical and Inorganic Chemistry have voted that a committee of three, consisting of James Kendall, Belgrade Lakes, Maine, Secretary of the Division, W. D. Bancroft, 7 East Avenue, Ithaca, N. Y., and Colin G. Fink, 33 Carleton Street, East Orange, N. J., be appointed to arrange the program of the Division for the September meeting; that no paper exceeding 5 minutes in length shall be read before the Division, unless an abstract is received by the Committee and approved by them, and that no member shall present more than one paper before the Division unless an abstract of each paper be received and approved by the Committee.

By vote of the Council no papers may be presented at the meeting, titles for which are not printed on the final program.

If any member sending in a paper does not expect to attend the meeting, he should put the words "By Title" on his announcement, so that members may understand in advance that the paper will not be read.

ADDRESSES OF DIVISIONAL AND SECTIONAL SECRETARIES

Agricultural and Food Chemistry: G. F. Mason, H. J. Heinz Company, Pittsburgh, Pa.

Biological Chemistry: I. K. Phelps, Bureau of Chemistry, Washington, D. C.

Fertilizer Chemistry: F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.

Industrial Chemists and Chemical Engineers: S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

Organic Chemistry: H. L. Fisher, Landing, N. J.

Pharmaceutical Chemistry: G. D. Beal, Univ. of Illinois, Urbana, Ill.

Physical and Inorganic Chemistry: James Kendall, Belgrade Lakes, Maine.

Rubber Chemistry Section: J. B. Tuttle, Bureau of Standards, Washington, D. C.

Water Sewage and Sanitation: H. P. Corson, U. S. Public Health Service, Grove City, Pa.

ABSTRACTS OF PAPERS

In order that the meeting may receive due and correct notice by the New York Press, every member sending a paper is requested to send an abstract not exceeding 200 words to Mr. Allen Rogers, Pratt Institute, Brooklyn, N. Y. It is hoped that all members will aid the Society by so doing. A copy of the abstract should be retained by the member and handed to the Secretary of the special division before which the paper is to be presented in New York. Such abstracts will be printed in *Science*.

Members will especially note that by vote of the Division of Physical and Inorganic Chemistry and the Division of Industrial Chemists and Chemical Engineers, papers cannot be presented before these divisions unless abstracts are in the hands of the secretary of the division as before stated, in time to have the abstract passed upon before the paper is put on the program.

ENTERTAINMENT OF THE LADIES

The Committee headed by Mrs. L. H. Baekeland is actively at work arranging the program for the pleasure of visiting ladies at the time of the meeting. Ladies may come with the assurance that everything will be done for their comfort and pleasure. Details will be found in the final program.

RAILROAD RATES

No special reduced fares have been granted for the meeting. No special cars will be provided from any points by the general secretary. Special cars may, however, be arranged for by the secretaries of local sections, if desired.

HOTELS

The following list of hotels, with rates, was taken from a recent publication. There are, however, plenty of hotels in New York City—really first-class hotels that you never heard of—where you can be very comfortable at reasonable rates. If you wish special information, write to the Chairman of the Hotel Committee.

		Rooms with Bath		Rooms without Bath	
Name	Location	Double	Single	Double	Single
Algonquin	59 West 44th St.	$3.50	$2.50		
Astor	43rd St. & B'way	4.00 up	3.00 up	$3.00	$2.00 up
Belmont	42nd St. & Park Ave.	4.00 up	3.50 up	3.50 up	2.50 up
Biltmore	43rd St. & Madison Ave.	5.50 up	4.00		
Breslin	29th St. & B'way	4.00	2.00	3.00	1.50
Grand	31st St. & B'way	4.00 up	2.00 up	2.00 up	1.00 up
Hermitage	42nd St. & B'way	3.00 up	2.00 up	2.00 up	1.50 up
Imperial	32nd St. & B'way	4.00 up	2.00 up	3.00 up	1.50 up
Knickerbocker	42nd St. & B'way	5.50 up	3.00 up	4.50 up	2.00 up
McAlpin	34th St. & B'way	4.00 up	2.50 up	3.00 up	2.00 up
Manhattan	42nd St. & Madison Ave.	5.00 up	3.50		2.50
Martinique	32nd St. & B'way	3.50 up	2.50 up	2.50 up	1.50 up
Monticello	35 W. 64th St.	2.00 up	1.25 up		
Park Avenue	32nd St. & Park Ave.	4.00	3.00	2.00 up	1.50 up
Plaza	58th St. & Fifth Ave.	5.00 up	3.50 up		
Prince George	28th St. & Fifth Ave.	4.00 up			2.00 up
Seville	29th St. & Madison Ave.	3.00 up	2.50	2.50	1.50
Waldorf-Astoria	34th St. & Fifth Ave.	5.00 up	3.50 up	4.00 up	2.50 up
Wolcott	4 West 31st St.	5.00	2.50		2.00 up

FINAL PROGRAM

The final and complete program will be sent on or about September 18 to all members signifying their intention of attending the meeting, to the secretaries of sections, to the Council, and to all members making special request therefore to the Secretary's office.

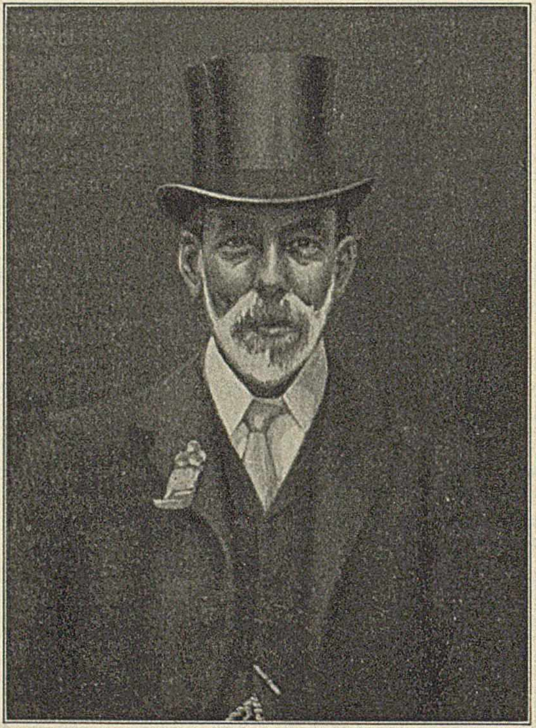
8100 MEMBERS

At the time of the Urbana Meeting, the Secretary started a campaign to obtain a membership of 8,000 this year. The Secretary already has 8,100 members. Owing to this great increase, journals for the early part of the year can no longer be sent to new members, but the Secretary has been authorized to begin membership for the present year with July 1 on the basis of payment of $5.00 to January 1, 1917, with journals from July up to that time and regular yearly dues beginning thereafter.

OBITUARIES

SIR WILLIAM RAMSAY

In considering the life of a man, we are apt, I think, to lay stress on what he has accomplished concretely, rather than on what he was abstractly. With the man of affairs it interests people in general to know what he has, rather than what he is, although we know that character is greater than accomplishment. With the scientists we reason the same, and look in the publications for a record of the man. Great as Sir William Ramsay was as a scientist, if we confine ourselves to that side of him we miss, I think, a great lesson of his life. He was not a one-sided man, but rather, a four-square, complete man, which is very different. It is not my purpose in this brief article to review his work. That has been done, and will be done, by far abler pens.



Sir William Ramsay

It was my good fortune to know him intimately, and it is to some of his less known qualities that I would draw attention, as his real greatness cannot be appreciated if that point of view be neglected.

Everybody knows he loved the truth. No man can be a great investigator otherwise. While his investigations carried him far afield, he differentiated strongly between hopes and facts, although well-grounded hopes were not easily set aside. He realized, as few men I have met have realized, that chemistry is in its infancy, and it would be a long time before it would even reach the age of manhood. Hence anything, not ridiculous on its face, was worth thought, and probably deep thought. Apropos of something said, I asked him once if he really believed in transmutation. His answer, "Why not?" was characteristic. It implied the possibility, while not assenting to the proposition. Dr. John W. Draper, my old preceptor, had progressed that far, without a tithe of the reasons of the modern chemist. Of course he did not teach it.

One of Ramsay's most charming qualities was his simplicity. He was full of fun and jollity. Years ago, he was at my St. Lawrence home when there was a house-party of girls, and he was the life of the party: full of pranks and schemes to amuse. You would lose sight of him a moment, and, behold, he would be quietly sketching the sunset, or some other feature of that beautiful region which filled his simple soul with delight. He was never idle. He was always doing something, generally with the idea of giving others pleasure. Those girls, I am sure, will remember him, not as a great man who overawed them, but rather as a jolly companion.

He was loyal to his friends. No one could be more so. He would go to any amount of trouble to do them a good turn. He was a royal guest, which is a great and rare virtue. He was a charming host, which is more common. His mind was clean and pure, and jealousy and unworthy thoughts could find no lodgment there. There was not a mean streak in him anywhere, that I could ever discover.

He had a great appreciation of humor. I sometimes think no man can be truly great who has not. He could even understand our American jokes, which is not always true of his countrymen. He was interested in everything that was going on about him, and could converse delightfully with anyone, no matter how humble might be his walk in life.

All the fine qualities which went to make up the man came to clearest view when he was stricken with a disease which leaves so little room for hope, and which requires such great patience. Suffering could not dim his courage, or deter him from the endeavor to make his last experience of value to others. To quote from Lady Ramsay's last letter to me: "The courage is not new; but the patience is almost heart-breaking." Writing in bed his last letter to me, he described the various experiments which he was trying on himself—not with any hope of the saving of his life, but with the yearning to arrive at some new knowledge which would help others, if taken in time.

Such, in brief, was the man. Endowed with a splendid constitution, and a wonderful mind, his whole life was spent in endeavoring to do all he could for the benefit of his fellows and the science which he loved so well. To those who knew him intimately, his memory will always be cherished; not so much for what he did, but because of what he was.

Wm. H. Nichols

PERSONAL NOTES

Dr. Charles H. Herty, professor of chemistry and dean of the School of Applied Science, University of North Carolina; Dr. W. R. Whitney, director of the research laboratory of the General Electric Company, Schenectady, N. Y.; Dr. Leo H. Baekeland, of Yonkers, N. Y.; and Mr. Warren K. Lewis, of Newton, Mass., have been appointed by the American Chemical Society to coöperate with the Committee of the National Academy of Sciences on the nitrate supply for the U. S. Government.

The Brown Instrument Company, Philadelphia, announce that they will occupy Section No. 306 in the Second National Exposition of Chemical Industries, and will exhibit a complete line of indicating and recording pyrometers, and also their new recording thermometers. They will be represented by Mr. John P. Goheen, sales manager, Mr. William Printz, assistant sales manager, and Mr. J. D. Andrews, New York representative.

The United States Civil Service Commission announces the following open competitive examinations: *Junior Fuels Chemist* (male), salary $1200 to $1500 a year, on September 20–21, 1916; *Junior Computer* (male), salary $1020 a year, September 20–21, 1916; *Assistant Examiner, Patent Office* (male and female), salary $1500 a year, September 13–15, 1916. Further information may be had from the U. S. Civil Service Commission, Washington, D. C.

The J. P. Devine Company have just received from the press and have ready for distribution copies of the following bulletins: Bulletin 101, covering the Devine line of vacuum chamber dryers, units adapted for the handling of materials that can be dried on trays or pans. Bulletin 102, covering the Devine line of vacuum drum dryers best adapted for all liquid solutions containing solids, drying same to a powder. Bulletin 103, covering Devine rotary vacuum dryers, used in connection with drying materials that can be mixed or tumbled in the drying. They have now on the press additional bulletins covering their entire line of equipment. The Devine Company maintain a laboratory fitted with every type of vacuum and nonvacuum dryer that they build, and where they will, without cost or obligation to the prospective customer, run such experiments as will put them in a better position to definitely determine the type and size of apparatus best adapted for the problem in hand.

R. Martens & Company have extended their export operations in Russia to non-mechanical lines, by creating a subsidiary company under the name of "Russia Trade Corporation of America," with general offices in the Maritime Building, 8–10 Bridge Street, New York City. The new concern will specialize on all kinds of general merchandise, and manufacturers are invited to write concerning the possibilities for selling their products in the Russian market. Mr. Frank G. Bolles, former manager of the export trade publication, *International Trade*, of Chicago, has been made vice-president and will be in immediate charge of the affairs of the Russia Trade Corporation of America. Offices have already been opened in several of the largest commercial centers of Russia and other branches will follow covering every field of importance in the Russian Empire.

The National Paint, Oil and Varnish Association will hold a convention at the Hotel Traymore, Atlantic City, October 9–12. Special information as to any detail can be obtained of D. W. Figgis, chairman of the Entertainment Committee, 447 West 14th Street, New York City.

The Society of Chemical Industry will hold their next annual meeting in Birmingham, England.

Dr. J. P. Longstaff, of Edinburgh University, has been appointed Secretary of the Society of Chemical Industry, and will take up his duties in September. Mr. C. G. Cresswell, who had been Secretary of the Society since 1884, having resigned, the Council has awarded him a superannuation allowance of £300 per annum.

M. C. Whitaker, professor of chemical engineering, Columbia University, has been granted leave of absence for the first term of the academic year 1916–1917.

Mr. L. P. Kyriakides, of the Detroit Organic Chemicals Company, Wyandotte, Mich., announces that he has changed his surname to Kyrides.

Mr. W. R. Hulbert, sales manager of the Goldschmidt Thermit Company, of New York, delivered an illustrated lecture on the theory and practicability of making thermit welds, supplemented with many practical demonstrations, to the members of the Clinchfield Railway Club, Erwin, Tenn., on July 25, 1916.

A. H. Ney, Inc., will continue the business of consulting chemists and chemical engineers, heretofore conducted under the name of A. H. Ney, Ph.D.

Mr. Wallace P. Cohoe, consulting chemist, announces that he has moved his office from the Chemists' Building, 50 E. 41st Street, to Trinity Building, 111 Broadway, New York City, and his laboratory to Bertrand Avenue, Perth Amboy, N. J.

The Oklahoma Producing and Refining Company, a Delaware Corporation, has certified that it has increased its capital from $2,000,000 to $5,000,000.

Frank L. May & Co., Perth Amboy, N. J., chemists and druggists, have been incorporated with $50,000 capital, by E. A. Reinhart, F. L. May and O. Larsen.

The Ninth Annual Meeting of the American Institute of Chemical Engineers will be held in New York City, January 10–13, 1917.

Mr. Newton D. Arnold, secretary-treasurer and general manager of the Rumford Chemical Company, and the oldest thirty-third degree Mason in the Northern Jurisdiction, died at Keekshaug, R. I., on August 13, 1916, in his seventy-third year.

George Anthony Hill, formerly assistant professor of physics at Harvard University, and author of a number of text books on mathematics and physics, died suddenly on August 18, in Cambridge, Mass., following a stroke of paralysis. Mr. Hill was born in Sherborn, Mass., August 25, 1842. He was a tutor of chemistry in Harvard, 1865–71; assistant professor of physics, 1871–76; and director of the Nolen Laboratory for college preparation in physics and chemistry, 1898–1914. Mr. Hill's last book, "Essentials of Physics," appeared in 1912.

Mr. H. A. Plusch, for the past seven years chief ceramic chemist for the Atlantic Terra Cotta Company, has resigned to take up the practice of consulting engineering. His office will be at Perth Amboy, N. J.

The Block Chemical Laboratories of Chicago were incorporated under the laws of Illinois on June 16, 1916, with the following officers: Dr. D. Julian Block, *president*, Prof. Robert M. Cole, *vice-president*, and Mr. H. B. Keeler, *secretary*.

The Elyria Enameled Products Company, Elyria, Ohio, has erected a new chemical laboratory equipped to carry on analytical and research work. Any problems relative to the use of glass enameled apparatus will receive careful attention.

Mr. R. H. Fash, formerly chief chemist and refiner of the Chickasha Cotton Oil Company, became the active vice-president of the Fort Worth Laboratories on September 1st.

The following promotions have been made in the chemistry faculty of the Johns Hopkins University: Joseph C. Frazer, professor of analytical chemistry; E. Emmet Reid, professor of organic chemistry; Paul B. Davis, associate in chemistry.

Electric welding of iron and steel will be one of the feature exhibits of the New York Electrical Exposition which will be held in Grand Central Palace, New York City, October 11 to 21, 1916. The exhibit is being arranged by the Arc Welding Machine Company, 220 West 42nd St., New York City, and Mr. O. A. Kenyon will be in charge. The public will have an opportunity of seeing all grades of welding accomplished in iron and steel, including structural pieces, plates and castings.

The United States Government is coöperating in the Electrical Exposition through the War, Navy and Commerce Departments, all of which will have comprehensive exhibits.

The Association of British Chemical Manufacturers, which had been under consideration for some time, was definitely formed at a recent meeting held in the rooms of the Chemical Society, London.

Prof. Alfred Stenzel has been placed in charge of a clinic at the hospital of the University of Pennsylvania for the exclusive study of industrial and occupational diseases.

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. Commerce 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 Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF STANDARDS

Effect of Certain Pigments on Linseed Oil. E. W. Boughton. Technologic Paper 71. 16 pp. "Since white lead, as supplied to painters and paint dealers, is almost always ground to a paste with raw linseed oil, it seemed desirable to determine whether or not the constants of the oil in the paste are materially changed during storage. Furthermore, it seemed desirable to obtain some numerical data regarding the extent to which certain pigments combine with linseed oil during the drying process, and also to make some experiments with drying paint films to determine the relative effect of different pigments on the rate of oxidation of the oil.

"The results as a whole indicate that white zinc combines with the free fatty acids of linseed oil more readily than does white lead. Of the three pigments, white lead, white zinc, and china clay, the former showed the greatest accelerative effect on the oxidation of raw linseed oil in films composed of pigment and oil, while china clay had the least accelerative effect.

"It is obviously unjustifiable to draw from the experimental part of this paper any conclusions regarding the relative values of the different pigments as paint materials. Such conclusions can be properly drawn only from the data afforded by exposure tests with painted panels and from general painting experience."

An Interlaboratory Photometric Comparison of Glass Screens and of Tungsten Lamps, Involving Color Differences. G. W. Middlekauff and J. F. Skogland. Scientific Paper 277. 23 pp. Interlaboratory comparison of photometric measurements involving color differences is discussed. It shows how close an agreement may be expected with experienced observers.

An Investigation of Laws of Plastic Flow. Eugene C. Bingham. Scientific Paper 278. 47 pp. The nature of plastic flow is described and theory involved is developed, showing that plasticity of a material depends upon its fineness of grain.

Distribution of Energy in Visible Spectrum of an Acetylene Flame. W. W. Coblentz and W. B. Emerson. Scientific Paper 279. 10 pp. This paper gives distribution of energy in visible spectrum of acetylene flame, based upon measurements made with three spectroradiometers. Results supersede data published in previous paper on this subject (Scientific Paper 191).

A Study of the Inductance of Four-Terminal Resistance Standards. Francis B. Silsbee. Scientific Paper 281. 46 pp. This paper deals with the inductance of electrical resistances of less than one ohm, suitable for use in new methods of measuring alternate current that require small resistances for the laboratory tests.

Sensitivity and Magnetic Shielding Tests of a Thomson Galvanometer for Use in Radiometry. W. W. Coblentz, Scientific Paper 282. 23 pp. This paper describes an investigation made to improve the sensitivity and design of a specialized galvanometer for use in radiometry. By using a lighter suspension in a vacuum, the sensitivity has increased tenfold. The results will be of great value in the study of stellar radiation since the recent advances in this field called for the increased sensitivity which has been now obtained. The paper gives details as to construction and results of tests.

Volume Effect in the Silver Voltameter. E. B. Rosa and G. W. Vinal. Scientific Paper 283. 11 pp. This paper is a continuation of the Bureau's researches on the silver voltameter which is the primary standard for the measurement of the international ampere. It has been found that when the electrolyte for the voltameter is not sufficiently pure that the deposits in the large voltameters are in excess of those in the small voltameters in series with them. This phenomenon has been called the "volume effect." The present paper shows that this effect is due to the impurities of the electrolyte and not to other causes as was thought by several previous observers. It is also shown that the effect is the same in all forms of the silver voltameter which the Bureau has tested. A theory to account for the effect is given. This phenomenon affords a valuable criterion of the purity of the electrolyte used in the voltameter.

Constants of Spectral Radiation of a Uniformly Heated Inclosure or So-called Black Body—II. W. W. Coblentz. Scientific Paper 284. 19 pp.

Strength and Other Properties of Concretes as Affected by Materials and Methods of Preparation. R. J. Wigg, G. M. Williams and E. R. Gates. Technologic Paper 58. 172 pp. This paper describes the effect of variation in composition, proportions, methods of handling, etc., upon compressive strength of these materials. Conclusions are drawn from 20,000 tests of about 300 different mixtures.

Data on Oxidation of Automobile Cylinder Oils. C. E. Waters. Technologic Paper 73. 20 pp. This gives a study of carbonization when heated for different lengths of time at given temperatures and for equal periods at different temperatures. Significance of data for oil testing is pointed out.

Determination of Volatile Thinner in Oil Varnish. E. W. Boughton. Technologic Paper 76. 7 pp. Describes method satisfactory for practical purposes, though only approximate for precise values. Methods tried were based on steam distillation, evaporation at 100° C. and from thin film at room temperature.

Standard Methods of Gas Testing. Circular 48, 2nd Ed. 202 pp. This circular contains suggestions as to location and equipment of gas-testing laboratories, description of accepted forms of apparatus, directions for making tests, and recommendations as to interpretation of experimental results. For this second edition a thorough revision has been made to correct minor errors, to incorporate suggestions of value, and to take account of recent investigations at the Bureau and elsewhere.

Further Experiments on Volatilization of Platinum. G. K. Burgess and R. G. Waltenberg. Scientific Paper 280. 10 pp. This is a continuation of the report on experimental results showing the loss of weight on heating platinum crucibles and the conditions under which this loss may be reduced to a minimum. It is shown that the loss of weight increases rapidly with rise of temperature.

BUREAU OF MINES

Effects of Temperature and Pressure on the Explosibility of Methane-Air Mixtures. G. A. Burrell and I. W. Robertson. Technical Paper 121, 13 pp. "The results are important in that they show that pressure and temperature conditions may vary over rather a wide range without affecting the explosibility of methane-air mixtures. Inconsistent results that have been obtained in the laboratory by different investigators on the limits of inflammation of methane-air mixtures cannot be explained on the basis of slight variations in temperatures and pressures. They depend rather on the nature of the source of ignition, method of ignition, size and shape of the containing vessel, and in some cases inaccuracies in mixing and analyzing the gases."

Sensitiveness to Detonation of Trinitrotoluene and Tetranitromethylanilin. GUY B. TAYLOR AND WILLARD C. COPE. Technical Paper 145. 9 pp. Paper, 5 cents. "TNT (trinitrotoluene) is much less sensitive to detonation than tetryl (trinitromethylnitramine, or tetranitromethylanilin). The sensitiveness of the former is increased by admixture of the latter."

Quantity of Gasoline Necessary to Produce Explosive Conditions in Sewers. G. A. BURRELL AND H. T. BOYD. Technical Paper 117. 13 pp. Paper, 5 cents. "In this report are shown the quantities of gasoline that must be introduced into sewers in order to produce explosive mixtures of gasoline vapor and air under certain conditions. Many different factors govern explosibility, such as size of the sewer, velocity of the sewage, temperature of the sewer air, volatility and rate of inflow of the gasoline, so that only under identical conditions of tests would duplicate results be obtained." (See THIS JOURNAL, **5** (1915), 750.)

Production of Explosives in the United States during the Calendar Year 1915. With Notes on Coal-Mine Accidents Due to Explosives and List of Permissible Explosives, Lamps, and Motors Tested Prior to May 1, 1916. ALBERT H. FAY. Technical Paper 159. 18 pp. Paper, 5 cents. "The total production of explosives, excluding exports, in the United States during the calendar year 1915, according to figures that the Bureau of Mines has received from manufacturers, was 460,900,796 lbs. (230,450 short tons), as compared with 450,251,489 lbs. (225,126 short tons) in 1914.

"The production for 1915 is segregated as follows: Black powder, 197,722,300 lbs.; "high" explosives other than permissible explosives, 235,828,587 lbs.; and permissible explosives, 27,349,909 lbs. These figures represent a decrease of 8,377,400 lbs. of black powder, an increase of 17,374,616 lbs. of high explosives and 1,652,091 lbs. of permissible explosives, as compared with figures for 1914."

BUREAU OF THE CENSUS

Cotton Production in the United States in 1915. Unnumbered pamphlet. 28 pp. This reports on the statistics of cotton ginned from the crop of 1915 and is a preliminary statement which will be incorporated with the full annual report which is published about October 1.

GEOLOGICAL SURVEY

Some Paleozoic Sections in Arizona and their Correlation. FREDERICK LESLIE RANSOME. Professional Paper 98-K, from Shorter Contributions to General Geology. pp. 133-166. Published July 15, 1916.

Possibilities of Oil and Gas in North-Central Montana. EUGENE STEBINGER. Bulletin 641-C, from Contributions to Economic Geology, 1916, Part II, pp. 49-91. Published July 17, 1916. "The purpose of the report here presented is to summarize all the available data concerning the possible occurrence of oil and gas in a considerable area in the north-central part of Montana, extending from the latitude of Great Falls northward to the international boundary.

"The facts observed seem to warrant the statement that considerable gas territory, on a scale comparable with the Alberta fields, may be found, and also that the area shows some probability of yielding oil. It cannot be too strongly emphasized, however, that a rational search for oil and gas in the State should begin with operations in the areas where the rocks are most strongly arched."

Asphalt, Related Bitumens, and Bituminous Rock in 1915. JOHN D. NORTHROP. Mineral Resources of the United States, 1915, Part II, pp. 135—150. Published July 18, 1916. "The natural asphalt of all varieties sold at the sources of production in the United States in 1915 aggregated 75,751 short tons, valued at $526,490, a decrease of 4,137 tons, or 5 per cent, in quantity and of $15,633, or 2 per cent, in value from the corresponding totals in 1914.

"The statistics of output of the native bitumens, gilsonite and grahamite, in 1915, record slight increases over the output in 1914 and indicate a sufficient expansion of the home markets to compensate largely for the loss of foreign customers as a consequence of the European war.

"The sales in 1915 of manufactured asphalt obtained from petroleum of domestic origin amounted, at the sources of production, to 664,503 short tons, valued at $4,715,583, an average of $7.10 a ton, an increase of 303,820 tons, or 84 per cent in quantity, and of $1,698,614, or 56 per cent, in market value, but a decrease of $1.26, or 15 per cent, in average price per ton, as compared with the output in 1914."

The asphalt imported for consumption in the United States in 1915 was:

	Quantity (short tons)	Value
Crude	135,276	$661,356
Bituminous limestone	2,976	19,001
Total	138,252	$680,357

The occurrence and distribution of asphalt, details of various sources, and the activity of the market in various districts, is discussed together with sections on ozokerite and ichthyol.

PUBLIC HEALTH REPORTS

Artificial Purification of Oysters. WILLIAM F. WELLS. Public Health Reports 31, 1848-52. This is a report on experiments upon purification of polluted oysters by placing them in water to which calcium hypochlorite has been added. It is concluded that a remarkable degree of purification occurs within a period of 24 hrs. and the character of the results suggests the commercial applicability of this procedure for the purification of oysters otherwise entirely unsuitable for food purposes.

Court Decisions Pertaining to Public Health. JASON WATERMAN. Public Health Reports, **31**, 1834-48. This is a digest of judicial decisions which were published by title in the Public Health Reports previous to January 1.

COMMERCE REPORTS—JULY, 1916

A company is being organized in Japan to manufacture **soda** electrically from the surplus salt which has accumulated from lack of transportation. (P. 6.)

The price of **soap** in Germany is now 2 to 10 times that of two years ago. (P. 10.)

Arrangements are being made to develop the **oil**-bearing lands of Bolivia. (P. 50.)

The prices of **drugs** in Germany for the last three years are given. Advances are in some cases over tenfold. (P. 36.)

Study of the **iron ore** deposits near Kuznetsk, Siberia, indicate the presence of over 27,000,000 tons of ore, much of which contains 54 to 58 per cent iron. (P. 61.)

Large **manganese** deposits are reported from Thunder Bay, Ontario. (P. 68.)

The Census figures for the United States **fertilizer** industry are given in detail. (P. 70.)

A new **iodine** factory is to be erected in Vladivostok, to secure iodine from seaweed, which is to be harvested in such a way as not to destroy the roots. (P. 87.)

The principal **tanning** materials used in the Philippines are mangrove and camanchili bark. Modern methods are being gradually introduced. (P. 88.)

The deposits of **bauxite** in both British and Dutch Guiana are very promising. (P. 92.)

The fruit of the "vijao" plant is used in Porto Rico as a source of a valuable **red dye** and **red ink.** (P. 110.)

"Humogen" or bacterized peat is not on the market in England. (P. 111.)

Efforts are being made to develop the cultivation of **sisal** in the Philippines. (P. 132.)

Steps are being taken to start a **beet-sugar** industry in Siberia. (P. 147.)

A United States **paper** company is to erect a 200 tons news print paper mill in Canada. (P. 148.)

The output of **tungsten** ores in Argentine consists chiefly of wolframite with some scheelite. (P. 163.)

Experiments in Germany upon the use of alcohol-benzene mixtures instead of **gasoline** as automobile fuels, showed that a mixture of equal parts of alcohol and benzene gives best results. An ordinary carbureter was used, but it was found necessary to install a supplementary reservoir containing gasoline or ether, to be used in starting the car. (P. 171.)

Owing to the scarcity of **manganese** in Germany, iron ores rich in manganese are being shipped from Brunswick to other parts of Germany. (P. 183.)

The **petroleum** industry of Ecuador is very promising. While at present the small output is secured by seepage into shallow excavations, it is believed that deep drilling will prove profitable. At present little refining is done, most of the product being used for asphalt. (P. 186.)

In spite of the high prices, **potassium carbonate,** and potash **soft soap** are still preferred in England for wood scouring. (P. 190.)

Efforts being made in Canada to substitute **pepsin** for **rennet** in cheese making appear promising. (P. 201.)

Extensive **coal** deposits have been found in Iceland. (P. 205.)

The output of **tungsten** and **iron ores** from Chosen (Korea) is increasing. (P. 206.)

In an effort to solve the **iron** and **steel** problem of Spain, orders have been published prohibiting the exportation of iron or steel until domestic needs are met. Efforts will be made to increase the manufacture of iron and steel instead of as at present, exporting over 90 per cent of the ores mined.

The United States continues to be the largest importer of **rubber** from Java with Great Britain second, and Netherlands third. (P. 241.)

An English report on **oil-producing nuts** and **seeds,** shows that palm kernel cake is a valuable cattle and hog food. (P. 246.)

Raffia wax, obtained in Madagascar from the leaves of the raffia palm, is proposed as a substitute for carnauba wax, to which it is very similar. (P. 259.)

Hemlock bark is again being used in and exported from Canada as a source of **tannin.** (P. 260.)

Iron mines in China, containing 60,000,000 tons of 65 per cent ore, are to be operated by Japanese interests. (P. 282.)

The Chinese methods of **salt** production are all primitive. Much of the salt is obtained from gypsum quarries which are allowed to lie idle intermittently. Large quantities of sea salt are also obtained principally by solar evaporation. (P. 313.)

The **extract of "babul" pods,** the fruit of the tree that produce gum arabic, can be used for **tanning** in India only if a small amount of carbolic acid be added to prevent fermentation. (P. 315.)

The wild Philippine plant "datura alba" is a promising source of **atropine** and **hyoscyanine.** (P. 317.)

Switzerland has only one **sugar** factory, and is now almost entirely dependent upon the United States for sugar, which they have difficulty in importing. (P. 324.)

The **sand-lime brick** industry of Germany has fallen off during the war. (P. 329.)

An extended British report on the **palm-kernel** industry advocates its entire British control. Formerly over three-fourths of the palm kernels, grown on English or French soil, were sent to Germany for extraction. An export duty on palm kernels from West Africa, to countries other than British, is urged. (P. 330.)

Scarcity of **coal** has caused a great shortage of **gas** in Venice, thus crippling the **glass** industry. (P. 335.)

In an investigation of the **waterproofing of concrete,** the Bureau of Standards plans to erect a number of concrete tanks along the Potomac. (P. 339.)

The principal supply of **asbestos** from Russia is of the serpentine variety, found principally in the Ural Mountains. (P. 342.)

Arrangements are being made to supply **cyanide** for South Africa from Glasgow and other British plants. (P. 373.)

A plant for making **nitrates** and **nitric acid** from the atmosphere, under hydroelectric power, is being constructed in Spain. Supplement 15*b*. (P. 14.)

SPECIAL SUPPLEMENTS ISSUED DURING AUGUST ARE AS FOLLOWS:

DOMINICAN REPUBLIC—26*a*
ARGENTINA—38*a* and 38*b*
GERMANY—6*a* and 6*b*
SPAIN—15*b* and 15*c*
NETHERLANDS—9*a*
IRELAND—19*h*
BRAZIL—40*b*
CANADA—23*d*
CUBA—25*a*
HAITI—30*a*

STATISTICS OF EXPORTS TO THE UNITED STATES

QUEBEC DISTRICT—Sup. 23*d*
Aluminum
Antimony
Asbestos
Balsam gum
Bones
Bronze powder
Arc lamp carbons
Calcium acetate
Asparin
Carbolic acid
Nitric acid
Oxalic acid
Tartaric acid
Wood alcohol
Ammonium sulfate
Anilin
Barium chloride
Bone-black
Calcium carbide
Creosote oil
Glycerine
Gum arabic
Gum camphor
Gum gambier
Gum kauri
Chloride of lime
Magnesite
Menthol
Potassium chlorate
Sodium nitrate
Soda ash
Chrome ore
Coal
Copper ore
Ammonium nitrate
Potassium chloride
Glue
Vegetable tallow
Hides
Ferromanganese
Lead
Mercury fulminate
Cod oil
Castor oil
Cottonseed oil
Palm oil
Paints
Paper
Paper stock
Silver
Sulfur ore
Tar
Tin
Zinc ore

DOMINICAN REPUBLIC—Sup. 26*a*
Hides
Sugar
Molasses
Copper ore
Rosin
Wax
Fustic
Logwood

GERMANY—Sup. 6*a* and 6*b*
Aluminum
Carbon electrodes
Lactic acid
Dextrin
Glycerin
Lanolin
Thorium nitrate
Earthenware
Glassware
Enameled ware
Glue
Hides
Rubber
Tungsten
Paints
Paper
Artificial silk
Tin
Epsom salts
Ergot
Ichthyol
Thymol
Magnesite
Vienna lime
Gums
Fusel oil
Palm-kernel oil
Sesame oil
Copper ore
Manganese ore
Beeswax
Mineral wax
Dyestuffs
Bleaching powder
Quinine
Sodium cyanide
Zinc dust
Beet seed
Potash

BRAZIL—Sup. 40*b*
Cottonseed
Carnauba wax
Gold
Hides
Manganese ore
Monazite
Rubber
Sugar

CUBA—Sup. 23*a*
Hides
Sugar
Molasses
Asphalt
Copper ore
Iron ore
Manganese ore
Beeswax

HAITI—Sup. 30*a*
Beeswax
Bone
Fustic
Guano
Hides
Logwood

LONDON—161
Rubber
Tin
Hides
Indigo
Creosote oil
Platinum
Copper

AMSTERDAM—Sup. 9*a*
Cinchona bark
Quinine
Cocoa butter
Copal gum
Drugs
Earthenware
Hides
Kapok
Magnesite
Milk sugar
Paraffin
Paint
Paper
Rags
Rubber
Tin

SPAIN—Sup. 15*a* and 15*b*
Antimony
Beet pulp
Cork
Argols
Fusel oil
Glycerin
Licorice
Calcium tartrate
Potassium carbonate
Hides
Paper stock
Soap stock
Essential oils
Iron ore
Pyrites
Copal gum
Rubber
Copper
Copper ore
Manganese ore
Saffron
Beeswax
Gayuba leaves
Ursi-uva leaves

ARGENTINA—Sup. 38*a* and 38*b*
Bones
Quebracho extract
Glycerine
Hides
Rubber
Casein
Crude tartar
Tankage
Glue stock
Linseed
Oleo and stearin oil
Tungsten ore
Tallow

BOOK REVIEWS

Outlines of Industrial Chemistry. By Frank Hall Thorp, with Assistance in Revision from Warren K. Lewis. Third Revised and Enlarged Edition. xxv + 665 pp., 137 figures. The Macmillan Company, New York, 1916. Price, $3.25.

"The great progress which has been made in chemical industry since the publication of the second edition of this work in 1905 has necessitated entire rewriting of many sections of the book, with elimination of much obsolete matter and the introduction of much new material."

A careful examination of this third edition of "Thorp" has convinced the reviewer that in general it presents a clear and concise, yet comprehensive, view of the domain of chemical technology, and that it will serve its purpose of imparting to students "some knowledge of the plant and methods employed in the more important manufacturing operations based upon chemical changes." It will be found to be a useful textbook, but the opportunity for decided improvement is still apparent.

In the first place, a criticism of a work of this size which attempts to cover so large and progressive a field, is that certain of the sections are likely to be so indefinite that they are misinforming. An illustration in point in the present case is the account of the petroleum industry, wherein the author endeavors to describe the refining of crude petroleum without enlightening the student regarding the varieties of crudes and the several distinct processes used for each. Foreign texts do not supply the desired information on present-day American practice in refinery technology, and it is unfortunate that the author did not avail himself of recent literature of the type of F. C. Robinson's paper in *Proc. Eng. Club Phila.*, April, 1913. Moreover, the work could be improved by the inclusion of brief accounts of the technology of hydrogen and the important rarer metals (tungsten, vanadium, thorium, etc.) and by presenting available statistics of production. The importance of chemical economics is not adequately appreciated by teachers of industrial chemistry. Then, too, one is disappointed to observe that the author gives no space to the turpentine industry of the United States and that he has omitted consideration of carbon dioxide, sulfur dioxide, sulfur chloride, sodium silicate, natural gas gasoline, ethyl ether, formaldehyde, and oxalic acid.

In general, the descriptive matter is accurate, although the following oversights have been noted by the reviewer: No mention is made of the important Koppers oven (p. 36); the account of gas producer practice (p. 42) requires modernization; the author states (p. 206) that "in some cases window glass * * * is machine-blown," while, as a matter of fact, at least 80 per cent of the sheet glass now produced in this country is mechanically blown; providing care is exercised, hydrochloric acid gives just as stable a hydrogen dioxide as phosphoric acid (p. 273); the Smith process for making carbon chlorides is not mentioned (p. 298); "326" on p. 518 should read *362;* petroleum (p. 343) is also made from "B. S." and rod-wax; the continuous system of distillation is used not only in Russia (p. 343), but largely in our own country; the oil-shales of Scotland are not "permeated with bitumen" (p. 345), but contain a bituminous substance, kerogen; in connection with asphalt (p. 347), mention should have been made of byerlyte and Dubbs' asphalt; the use of silicate of soda in refining cottonseed oil is not referred to (p. 360); "musk, Baur" is a nitro-derivative of tertiary butyl-xylene (p. 395); and bauxite is not a "hydrated oxide of alumina" (p. 639). The lists of references do not include many recent contributions of importance, which could have replaced a number of the old citations; and then the author has been careless in his bibliographic notes. It is unfortunate that American writers on chemical subjects have not more generally adopted the logical journal abbreviations of *Chemical Abstracts.*

Owing to the fact that Dr. Thorp's book has demonstrated its general excellence by appearing in a third revised edition, the reviewer has been inclined to refrain from critical comment thereon. However, the desire to be helpful and coöperative has induced him to indicate whereby its established usefulness might be further augmented.

W. A. Hamor

Organic Agricultural Chemistry. (The Chemistry of Plants and Animals.) By Joseph Scudder Chamberlain, Ph.D., Professor of Organic and Agricultural Chemistry in the Massachusetts Agricultural College. 319 pp. The Macmillan Company, New York, 1916. Price, $1.60.

The present volume, as stated by the author in his preface, was written as an elementary textbook with the aim of giving "students of practical agriculture enough general scientific instruction in chemistry to enable them to understand and correlate the broad problems of agricultural practice."

In the first, or systematic, section of the book seven chapters are devoted to a presentation of the simpler facts of organic chemistry in their relationship to the problems of plant and animal life. The second, or physiological, section (seven chapters) discusses the subject of enzymes, composition of plants and animals, the living cell and its food, animal food and nutrition, and plant physiology. In the third section upon crops, foods and feeding, two chapters are devoted to the occurrence and uses of important constituents of agricultural plants and a concluding chapter to animal foods and feeding.

The author's presentation of his subject, which is in the lecture style, is clear and direct. A series of interesting experimental studies are included at intervals in the text. These laboratory exercises, which are carefully selected, advance the student towards obtaining a practical first-hand knowledge of the chemistry of plant and animal life.

In the physiological section of his book the author makes a unique departure from usual custom in presenting the chemistry of animal life before that of plants. This innovation will no doubt come as a shock to those who believe that the subject of agricultural chemistry must be unfolded in the supposedly logical sequence of mineral, plant and animal. Dr. Chamberlain's belief that a previous acquaintance with animal chemistry will help the student to gain a more correct view of the laws of plant life has much to recommend it. To work back from the higher to the lower is sometimes the more rational method. Liebig in his "Natural Laws of Husbandry" discussed the plant before he took up the soil.

The reviewer, after a careful perusal of this new work, has found but little to criticize. While a few statements—as that polarized light is light which has passed through a double crystal of quartz (p. 70), or that the one carbohydrate which does not contain the elements hydrogen and oxygen in the proportion H_2:O is a pentose sugar, known as rhamnose (p. 110), or that cellulose is hydrolyzed by enzymes to maltose (p. 164)—are incorrect or incomplete, such minor defects in a book not written for specialists are unnoticeable amid the many excellent qualities which Dr. Chamberlain's "Organic Agricultural Chemistry" possesses.

The book contains a good index and is well printed. It is cordially recommended to all who are interested in the subject.

C. A. Browne

Organic Chemistry or Chemistry of the Carbon Compounds. By VICTOR VON RICHTER. Edited by PROF. R. ANSCHÜTZ and PROF. G. SCHROETER. Newly translated and revised from the German original (after Prof. Edgar F. Smith's 3rd American Edition) by DR. PERCY E. SPIELMANN. Vol. I (Aliphatic Series), xvi + 677 pp. P. Blakiston's Son & Company, Philadelphia. Price, $5.00 net.

The advent of this new translation of this standard work will be welcomed by the chemical profession, since it is highly desirable that a reference book of this character should be up to date. Unfortunately, the second volume, dealing with the aromatic series, has not appeared as yet, but is promised for the near future. The original plan of the former editions has been followed. Some minor changes from the original German edition have been made, such as arrangement of some of the formulae to emphasize more clearly certain points under discussion. Only a few errors were noticed by the reviewer and the workmanship is very good.

J. M. NELSON

Steam Boilers and Combustion. By JOHN BATEY. Vol. XV, The Broadway Series. 211 pp., 18 diagrams. Scott, Greenwood & Son, London. Price, 4 s. 6 d.

In the preface of this book the author explains his addition to the literature on a branch of engineering which has already been the subject of many treatises by the statement that "most of the books published are highly technical works dealing with what has been done and not with the possibilities of future development." He emphasizes the necessity of improvement in steam boiler operation and implies that in this volume he has laid the way for such improvement by making clear the theory involved. About one-third of the book is given up to the description of different types of boilers and the remainder to the explanation of the phenomena of combustion, heat transfer and steam generation. A careful study of this work has convinced the reviewer that it can be of no possible value to American engineers because most of the boilers described are of types no longer used in this country, and the theories advanced concerning combustion and steam generation are absolutely opposed to those accepted by the engineering profession. The technically trained engineer can but disagree with the author upon almost every subject considered, and the man without a technical education may be led very far astray.

HARRY L. PARR

The American Fertilizer Handbook. Ninth Annual Edition, 1916. 400 pp. Ware Bros. Company, Philadelphia. Price, $1.00.

The ninth annual edition of this Handbook follows the form of the previous editions and contains the standard reference statistics and directories of the fertilizer industry and allied trades. The directories of fertilizer manufacturers, allied fertilizer trades, cottonseed oil mills, and packers and renderers have been carefully revised up to date. The subject list of this edition is as follows:

National Fertilizer Association and Southern Fertilizer Association (Officers, Committees and Members); Agricultural Experiment Stations; State Fertilizer Officials; Fertilizer Materials Statistics, covering the production, imports, consumption and prices of Sulfate of Ammonia, Atmospheric Nitrogen, Blood, Guano, Potassium Salts, Bones, Pyrites, Sulfuric Acid, Fish Scrap, and Nitrate of Soda; State Fertilizer Tonnage; Soil Improvement Committees of the National and Southern Fertilizer Associations; Potash Salts; Cottonseed Oil and Meal; Rank of States in Crop Values; Reference Library—an index of the important articles in the previous editions of the Handbook; Reference Index—a list of the important articles in *The American Fertilizer* from January 1, 1915, to May 15, 1916; Directory of Fertilizer Manufacturers; Directory of Allied Fertilizer Trades; Phosphate Rock Section; Fertilizer Machinery, Factory Construction Equipment and Supplies Section; Fertilizer Materials Section; Brokers, Exporters, Importers, Commission Merchants and Forwarding Agents Section; Chemists, Assayers, Engineers, Contractors, Leadburners, Samplers and Laboratory Equipment Section; Cottonseed Oil Mill Directory and Machinery Section; Packers and Renderers Directory and Machinery Section.

In addition the following special contributions are included: "Fertilizers: What They Are—How to Apply Them," by H. G. Bell, J. W. Henceroth and C. A. Waugh; "The Sulfuric Acid Industry," by A. M. Fairlie; "Possible Sources of Potash in America," by F. K. Cameron; "Potash Salts—1914," by W. C. Phalen; "Preventable Losses in Fertilizer Plants," by S. J. Martenet; "Sulfur and Pyrite in 1914," by W. C. Phalen; "The Cyanamid Industry—World Status," by E. J. Pranke; "The Production of Phosphate Rock in 1914," by W. C. Phalen; "The Cottonseed Oil Industry," by T. C. Law; "The Western Animal Ammoniate Market," by J. H. Schmaltz.

The British Coal-Tar Industry. A series of papers edited by WALTER M. GARDNER, Bradford Technical College. 437 pages. Williams and Norgate, London. Price, $2.25.

This volume is a collection of the more important papers and addresses on the coal-tar industry of England which have appeared from time to time during the past forty odd years. The first paper in the collection is naturally the original Cantor Lecture of Sir William H. Perkins given in 1868, and entitled "The Aniline or Coal-Tar Colors." Other important papers marking the progress of this branch of chemistry are "The Artificial Production of Alizarine" by Prof. H. E. Roscoe (1870); "The Synthesis of Indigo" by Prof. R. Meldola (1901). These earlier articles dealing with the chemical development of the coal-tar colors are really quite interesting reading even at the present date. The later articles in the book, however, appearing from 1908 on to 1915, are chiefly of a polemical or retrospective character, and their keynote is one of mournful self-recrimination for allowing Germany to run away with all the dyestuff business which should have by right belonged to England. The chief reason from the English point of view as to why England should have controlled the manufacture of coal-tar products appears to be the fact that Perkin discovered and manufactured the first real coal-tar dyestuff. The English chemists also acknowledge that they are equal, if not superior, to their German confrères, and consequently the industry should have remained in England. But sad to relate it did not. There are many reasons, or rather excuses given for this circumstance. The manufacturers of England were not alive to the advantages of painstaking chemical research, they did not sufficiently encourage the chemist in his pioneer work; the Government did not lend its power and influence to the proper development of the industry; and the Universities maintained a supercilious disregard of the technical sciences, and in so far as chemistry was concerned, seemed to have no interest beyond laboratory experiments.

Some of the authors in this volume also are very insistent in putting forth the argument that the character of the British patent laws worked an unfair advantage in favor of the German competitor. While this makes a good hook on which to hang an argument, I doubt if it has much real weight of reason behind it. As a matter of fact the English, both as manufacturers and chemists, were more interested in other things than the making of dyestuffs, and neglected this branch to follow others which they considered more profitable.

J. MERRITT MATTHEWS

NEW PUBLICATIONS

By Irene DeMatty, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Batteries: Starting and Lighting Batteries; Upkeep, Care and Repair of Storage Batteries. 8vo. 47 pp. Price, $1.00. American Bureau of Engineering, Chicago.

Bridge Engineering. J. A. L. Waddell. 8vo. 2177 pp. Price, $10.00. John Wiley & Sons, Inc., New York.

Chemistry of Familiar Things. S. S. Sadtler. 2nd Ed. 8vo. 320 pp. Price, $1.75. J. B. Lippincott Co., Philadelphia.

Coal-Tar and Ammonia. Georg Lunge. 3 vol. 1718 pp. Price, 63 s. Gurney & Jackson, London.

Diesel Engines, Land and Marine. Giorgio Supino. 2nd Ed. 8vo. 309 pp. Price, $3.75. J. B. Lippincott Co., Philadelphia.

Dynamo and Electric Motor Building. A. H. Avery. 12mo. 152 pp. Price, $0.50. Funk & Wagnalls, New York.

Food Values. M. McKillop. 12mo. 136 pp. Price, $0.60. E. P. Dutton & Co., New York.

Gases: Industrial Gases, Including the Liquefaction of Gases. Geoffrey Martin. 8vo. 158 pp. Price, 7 s. 6 d. Crosby, Lockwood & Son, London.

Gold: Metallurgy of Gold. T. K. Rose. 6th Ed. 8vo. 601 pp. Price, $6.50. J. B. Lippincott Co., Philadelphia.

Highway Engineers' Handbook. W. G. Harger and E. A. Bonner. 2nd Ed. 16mo. Price, $3.00. McGraw-Hill Book Co., New York.

Hydraulic Flow Reviewed. A. A. Barnes. 8vo. 158 pp. Price, $4.50. Spon & Chamberlain, New York.

Mechanical Handling and Storing of Material. (American Edition.) G. F. Zimmer. 4to. 752 pp. Price, $12.50. D. Van Nostrand Co., New York.

Microbiology: Manual in General Microbiology. 8vo. Price, 10 s. 6 d. Chapman & Hall, London.

Mineralogy: Elements of Mineralogy. F. Rutley. 19th Ed. 12mo. 394 pp. Price, $1.25. D. Van Nostrand Co., New York.

Mining Hand-Sketching and Drawing. F. Mawson. 8vo. 47 pp. Price, $0.60. Spon & Chamberlain, New York.

Oils: A Practical Treatise on Friction, Lubrication, Fats and Oils; Including the Manufacture of Lubricating Oils, Leather Oils, Paint Oils, Solid Lubricants and Greases. E. E. Dieterichs. 2nd Ed. 12mo. 137 pp. Price, $1.25. H. C. Baird & Co., Philadelphia.

Organic Chemistry: Theoretical Organic Chemistry. Julius B. Cohen. New Ed. 12mo. 588 pp. Price, $1.60. The Macmillan Co., New York.

Ozone; Its Manufacture, Properties and Uses. A. Vosmaer. 8vo. 197 pp. Price, $2.50. D. Van Nostrand Co., New York.

Reagents and Reactions: Reattivi e Reazioni. Edgardo Tognoli. xii + 277 pp. Price, L. 3,50. Ulrico Hoepli, Milano.

Steel: The Physico-Chemical Properties of Steel. C. A. Edwards. 8vo. 229 pp. Price, $3.50. J. B. Lippincott Co., Philadelphia.

Tables for Calculating the Cubic Contents of Excavations and Embankments. F. H. Gross. 8vo. 93 pp. Price, $2.50. F. H. Gross & Co., Beardstown, Ill.

Turbines: The Marine Steam Turbine. J. W. M. Sothern. 8vo. 561 pp. Price, $6.50. D. Van Nostrand Co., New York.

Vinegar; Its Manufacture and Examination. C. A. Mitchell. 8vo. 218 pp. Price, 8 s. 6 d. Chas. Griffin & Son, London.

Waterworks Handbook. A. D. Flinn and Others. 8vo. 824 pp. Price, $6.00. McGraw-Hill Book Co., New York.

RECENT JOURNAL ARTICLES

Acid Bessemer Process. H. H. Campbell. *Iron Age*, Vol. **98** (1916), No. 6, pp. 302–304.

Bakelite Micarta-D Gears and Pinions. T. D. Lunch and R. E. Taley. *The Electric Journal*, Vol. **13** (1916), No. 8, pp. 368–371.

Belt Drive: Where Belt Drive is Superior. H. H. Suplee. *Engineering Magazine*, Vol. **51** (1916), No. 5, pp. 697–704.

Bituminous Materials Tests for Sheet Asphalt. F. P. Smith. *Engineering News*, Vol. **76** (1916), No. 5, pp. 205–209.

Bronze Alloys for Automobile Work. W. M. Corse and G. F. Comstock. *Iron Age*, Vol. **98** (1916), No. 5, pp. 251–254.

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Chemistry in the Brass Foundry. E. P. Later. *The Foundry*, Vol. **44** (1916), No. 8, pp. 317–319.

Chemistry of Minerals. J. E. Pogue. *Engineering and Mining Journal*, Vol. 102 (1916), No. 6, pp. 255–259.

Coffee: Microscopy of Coffee. Andrew L. Winton. *Tea and Coffee Trade Journal*, Vol. **31** (1916), No. 1, pp. 23–28.

Engle Furnace for Redistilling Spelter. R. H. Engle. *Engineering and Mining Journal*, Vol. **102** (1916), No. 5, pp. 213–215.

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Irrigation: Slow Rate of Utilization of Irrigation Works. R. P. Teele. *Engineering News*, Vol. **76** (1916), No. 5, pp. 202–203.

Lead Salts, Alkalinity and Solvent Power of Cyanide for Gold. H. R. Edmands. *Mining and Scientific Press*, Vol. **113** (1916), No. 5, pp. 161–162.

Motor Drive: Why Motor Drive Is Best. W. H. Easton. *Engineering Magazine*, Vol. **51** (1916), No. 5, pp. 687–696.

Oxy-Acetylene Process. Henry Cave. *Engineering Magazine*, Vol. **51** (1916), No. 4, pp. 521–527.

Oxygen: The Effect of Oxygen on Pure Iron. Wesley Austin. *Iron Trade Review*, Vol. **59** (1916), No. 4, pp. 177–178.

Paper: Spun Paper and Some of Its Uses. *Paper*, Vol. **18** (1916), No. 20, pp. 16–18.

Plastic Flow Phenomena. W. Trinks. *Blast Furnace and Steel Plant*, Vol. **50** (1916), No. 8, pp. 362–363.

Platinum and the Standard of Light. H. E. Ives. *Lighting Journal*, Vol. **4** (1916), No. 7, pp. 150–152.

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Reinforced Concrete Ore Dock at Ashland, Wis. W. E. King. *Engineering News*, Vol. **76** (1916), No. 6, pp. 242–245.

Slags: Conditions and Causes of Iron in Slags. W. G. Imhoff. *Blast Furnace and Steel Plant*, Vol. **50** (1916), No 8, pp. 359–361.

Soils: Testing Various Soils for Drainage Properties. J. R. Haswell. *Engineering News*, Vol. **76** (1916), No. 5, pp. 211–214.

Spelter: Its Grades and Uses. G. C. Strong and Others. *The Foundry*, Vol **44** (1916), No. 8, pp. 326–327.

Stamped and Enameled Ware. C. C. Lynde. *Steel and Iron*, Vol. **50** (1916), No. 7, pp. 211–215.

Steam: Making the Steam Plant Adequate for Both Power and Heating. C. L. Hubbard. *Engineering Magazine*, Vol. **51** (1916), No. 5, pp. 716–723.

Steam Heat for Melting the Softer Metals. Robert Cramer. *American Machinist*, Vol. **45** (1916), No. 5, pp. 177–179.

Steel: An Investigation Dealing with the Occurrence of Alumina Inclusions in Steel. Albert Sauveur. *Metallurgical and Chemical Engineering*, Vol. **15** (1916), No. 3, pp. 149–151.

Steel: Making Copper Clad Steel. *Iron Age*, Vol. **98** (1916), No. 6, pp. 296–297.

Steel: Testing Malleable and Cast Steel. Andrew Harley. *Iron Trade Review*, Vol. **59** (1916), No. 3, pp. 121–128.

Steels: Heat Treatment for Drop Forged Steels. W. C. Peterson. *Steel and Iron*, Vol. **50** (1916), No. 7, pp. 215–218.

Sulfur Elimination in By-Product Coking. C. C. Campbell. *Blast Furnace and Steel Plant*, Vol. **59** (1916), No. 8, pp. 368–374.

Thermalene: Production, Properties and Use of Thermalene. *American Machinist*, Vol. **45** (1916), No. 6, pp. 221–225.

Tin: The Bolivian Tin Industry. Howland Bancroft. *Mining and Scientific Press*, Vol. **113** (1916), No. 4, pp. 119–125.

Tin: A Review of the Tin Situation. L. Addicks and W. A. Cowan. *The Foundry*, Vol. **44** (1916), No. 8, pp. 327–328.

Welding: How to Make Oxy-Acetylene Welds. Henry Cave. *Engineering Magazine*, Vol. **51** (1916), No. 5, pp. 724–733.

Welding: Power Plant Welding Outfit. E. S. Fitz. *Power*, Vol. **44** (1916), No. 3, pp. 93–95.

Welding Tubing by Oxy-Acetylene. *Iron Trade Review*, Vol. **59** (1916), No. 3, pp. 117–119.

MARKET REPORT—AUGUST, 1916

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON AUGUST 21.

INORGANIC CHEMICALS

Acetate of Lime,	100 Lbs.	7.00	@	7.05
Alum, lump ammonia	100 Lbs.	6.00	@	7.00
Aluminum Sulfate, high-grade	Ton	65.00	@	100.00
Ammonium Carbonate, domestic	Lb.	9½	@	10
Ammonium Chloride, gray	Lb.	10	@	15
Ammonium Phosphate, commercial, 98–100%	Lb.	—	@	—
Aqua Ammonium, 26°, drums	Lb	5½	@	6
Arsenic, white	Lb.	5⅞	@	6
Barium Chloride	Ton	100.00	@	105.00
Barium Nitrate	Lb.	18	@	19¼
Barytes, prime white, foreign	Ton	—	@	—
Bleaching Powder, 35 per cent	100 Lbs.	4½	@	4¾
Blue Vitriol	Lb.	8¾	@	9½
Borax, crystals, in bags	Lb.	7¾	@	8
Boric Acid, powdered crystals	Lb.	11¾	@	12½
Brimstone, crude, domestic	Long Ton	30.00	@	30.50
Bromine, technical, bulk	Lb.	1.30	@	1.40
Calcium Chloride, lump, 70 to 75% fused	Ton	30.00	@	35.00
Calcium Chloride, granulated	Ton	20.00	@	25.00
Caustic Soda, 74 per cent	Lb.	3¾	@	4
Chalk, light precipitated	Lb.	4½	@	5¼
China Clay, imported	Ton	18.00	@	30.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered	Ton		$35.00	
Glauber's Salt, in bbls	100 Lbs.	65	@	70
Green Vitriol, bulk	100 Lbs.	1.25	@	1.50
Hydrochloric Acid, commercial, 18°	Lb.	1⅞	@	2
Hydrochloric Acid, C. P., conc., 22°	100 Lbs.	2	@	2¼
Iodine, resublimed	Lb.	4.25	@	4.30
Lead Acetate, white crystals	Lb.	15⅝	@	15⅞
Lead Nitrate	Lb.	15½	@	16
Litharge, American	Lb.	9¼	@	9¾
Lithium Carbonate	Lb.	1.02	@	1.05
Magnesium Carbonate	Lb.	19	@	22
Magnesite, "Calcined"	Ton		$75.00	
Nitric Acid, 36°	Lb.	6¾	@	7
Nitric Acid 42°	Lb.	7	@	7½
Phosphoric Acid, sp. gr. 1.750	Lb.	29½	@	30
Phosphorus yellow	Lb.	80	@	—
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, casks	Lb.	38	@	40
Potassium Bromide (granular)	100 Lbs.	2.90	@	3.00
Potassium Carbonate, calcined, 80 @ 85%	Lb.	75	@	80
Potassium Chlorate, crystals, spot	Lb.	47	@	48
Potassium Cyanide, bulk, 98–99 per cent	Mixture	37	@	38
Potassium Hydroxide	Lb.	86	@	90
Potassium Iodide, bulk	Lb.	3.70	@	3.80
Potassium Nitrate	Lb.	—	@	—
Potassium Permanganate, bulk	Lb.	1.50	@	1.75
Quicksilver, flask, 75 lbs.		72.00	@	74.00
Red Lead, American, dry	Lb.	9¾	@	—
Salt Cake, glass makers'	Ton	10.50	@	12.00
Silver Nitrate	Oz.	41½	@	—
Soapstone in bags	Ton	8.00	@	12.00
Soda Ash, 48 per cent	100 Lbs.		3	
Sodium Acetate	Lb.	12	@	14
Sodium Bicarbonate, domestic	100 Lbs.	1.80	@	2.00
Sodium Bicarbonate, English	Lb.	3½	@	3⅝
Sodium Bichromate	Lb.	30	@	32
Sodium Chlorate	Lb.	23	@	25
Sodium Fluoride, commercial	Lb.	—	@	—
Sodium Hyposulfite	100 Lbs.	1.35	@	1.60
Sodium Nitrate, 95 per cent, spot	100 Lbs.	3.00	@	3.10
Sodium Silicate, liquid	100 Lbs.	1.00	@	1.25
Sodium Sulfide, 30%, crystals, in bbls	Lb.	1⅞	@	2
Sodium Bisulfite, powdered	Lb.	4⅞	@	5½
Strontium Nitrate	Lb.	48	@	50
Sulfur, flowers, sublimed	100 Lbs.	2.30	@	2.70
Sulfur, roll	100 Lbs.	1.95	@	2.25
Sulfuric Acid, chamber, 66°	Ton	$25.00	@	—
Sulfuric Acid, conc., sp. gr. 1.842	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming)	Ton	60	@	70
Talc, American white	Ton	9.00	@	12.00
Terra Alba, American, No. 1	100 Lbs.	75	@	80
Tin Bichloride, 50°	Lb.	13½	@	14
Tin Oxide	Lb.	42	@	44
White Lead, American, dry	Lb.	8¾	@	—
Zinc Carbonate	Lb.	24	@	28
Zinc Chloride, commercial	Lb	13	@	15
Zinc Oxide, American process XX	Lb.	10	@	11
Zinc Sulfate	Lb.	6½	@	7¼

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls	Lb.	65	@	70
Acetic Acid, 60 per cent, in bbls	Lb.	12	@	13
Acetic Acid, glacial, 99½%, in carboys	Lb	30	@	32
Acetone, drums	Lb.	40	@	—
Alcohol, denatured, 180 proof	Gal.	47	@	48
Alcohol, grain, 188 proof	Gal.	2.64	@	2.66
Alcohol, wood, 95 per cent, refined	Gal.	64	@	66
Amyl Acetate	Gal.	5.25	@	5.50
Aniline Oil	Lb.	30	@	32
Benzoic Acid, ex-toluol	Lb.	7.50	@	8.00
Benzol, 90 per cent	Gal.	63	@	65
Camphor, refined in bulk, bbls	Lb.	60	@	61
Carbolic Acid, U. S. P., crystals, drums	Lb.	50	@	55
Carbon Bisulfide	Lb.	6	@	6½
Carbon Tetrachloride, drums, 100 gals	Lb.	17½	@	18
Chloroform	Lb.	48	@	50
Citric Acid, domestic, crystals	Lb.	64	@	67
Cresol, U. S. P.	Gal.	70	@	75
Dextrine, corn (carloads, bags)	100 Lbs.	3.50	@	3.55
Dextrine, imported potato	Lb.	12	@	13
Ether, U. S. P., 1900	Lb.	15	@	20
Formaldehyde, 40 per cent	Lb.	11	@	11½
Glycerine, dynamite, drums included	Lb.	35	@	36
Oxalic Acid, in casks	Lb.	59	@	61
Pyrogallic Acid, resublimed bulk	Lb.	2.80	@	2.85
Salicylic Acid	Lb.	2.10	@	2.20
Starch, cassava	Lb.	3¾	@	4½
Starch, corn (carloads, bags) pearl	100 Lbs.	2.55	@	2.61
Starch, potato	Lb.	6	@	6½
Starch, rice	Lb.	8	@	10
Starch, sago	Lb.	3½	@	4
Starch, wheat	Lb.	5	@	6
Tannic Acid, commercial	Lb.	62	@	64
Tartaric Acid, crystals	Lb.	66	@	68

OILS, WAXES, ETC.

Beeswax, pure, white	Lb.	37	@	39
Black Mineral Oil, 29 gravity	Gal.	13½	@	—
Castor Oil, No. 3	Lb.	14	@	15
Ceresin, yellow	Lb.	10	@	14
Corn Oil, crude	100 Lbs.	7.75	@	7.85
Cottonseed Oil, crude, f. o. b. mill	Gal.	71	@	72
Cottonseed Oil, p. s. y.	Lb.	10¾	@	—
Creosote, beechwood	Lb.	3.00	@	3.25
Cylinder Oil, light, filtered	Gal.	21	@	—
Fusel Oil, crude	Lb.	4.50	@	4.60
Japan Wax	Lb.	14	@	14½
Lard Oil, prime winter	Gal.	1.05	@	1.10
Linseed Oil, raw (car lots)	Gal.	72	@	—
Menhaden Oil, crude (southern)	Gal.	49	@	50
Naphtha, 68 @ 72°	Gal	36¾	@	37½
Neat's-foot Oil, 20°	Gal.	1.08	@	1.10
Paraffine, crude, 120 m. p.	Lb.	7	@	—
Paraffine Oil, high viscosity	Gal.	29½	@	30
Rosin, "F" Grade, 280 lbs.	Bbl.		6.75	
Rosin Oil, first run	Gal.	29	@	31
Shellac, T. N.	Lb.	30	@	31
Spermaceti, cake	Lb.	25	@	26
Sperm Oil, bleached winter, 38°	Gal.	80	@	82
Spindle Oil, No. 200	Gal.	24	@	25
Stearic Acid, double-pressed	Lb.	12½	@	13½
Tallow, acidless	Gal.	80	@	81
Tar Oil, distilled	Gal.	40	@	41
Turpentine, spirits of	Gal.	45	@	—

METALS

Aluminum, No. 1, ingots	Lb.	58	@	59
Antimony, ordinary	Lb.	13	@	15
Bismuth, N. Y.	Lb.	3.05	@	3.10
Copper, electrolytic	Lb.		26½	
Copper, lake	Lb.		27	
Lead, N. Y.	100 Lbs.	6.50	@	6.75
Nickel, electrolytic	Lb.	45	@	—
Nickel, shot and ingots	Lb.	50	@	—
Platinum, refined	Oz.	60.00	@	65.00
Silver	Oz.		66¼	
Tin	Lb.	38¼	@	38¾
Zinc, N. Y.	Lb.		10	

FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs.	3.45	@	3.50
Blood, dried F O B Chicago	Unit		2.90	
Bone, 4½ and 50, ground, raw	Ton	—	@	—
Calcium Cyanamid	Unit of Ammonia		2.55	
Calcium Nitrate, Norwegian	100 Lbs.		—	
Castor Meal	Unit		—	
Fish Scrap, domestic, dried, f. o. b. works	Unit	3.25	&	10
Phosphate, acid	Unit	80	@	86
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 78–80 per cent	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent	Ton	350.00	@	400.00
Pyrites, furnace size, imported	Unit	16	@	—
Tankage, high-grade; f. o. b. Chicago	Unit	2.50	&	10

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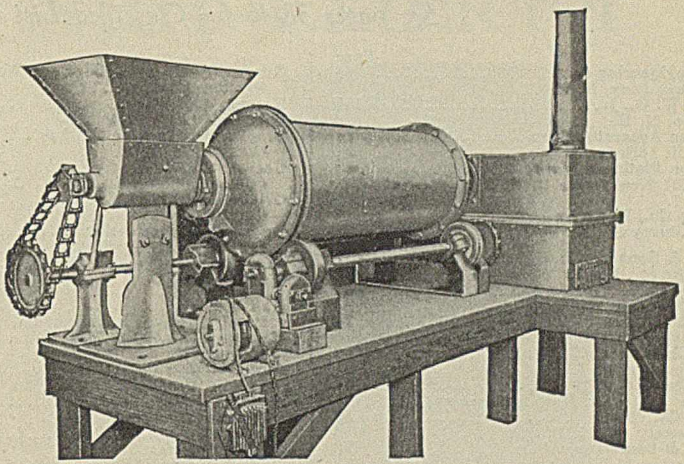

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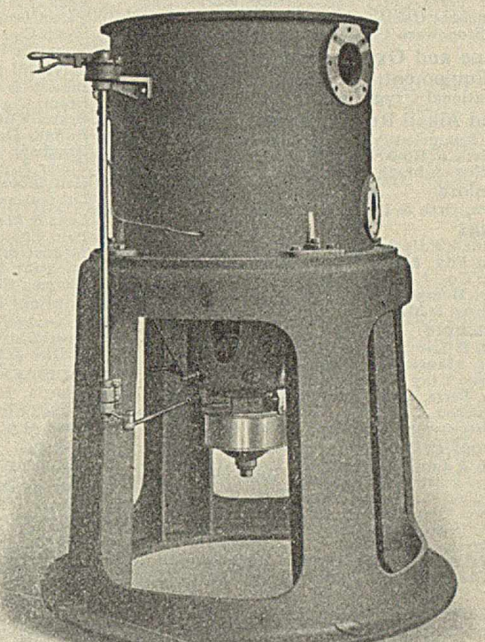

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District Office:
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Duriron Castings Co., N. Y. C.
German-American Stoneware Wks., N. Y. C.
Knight, Maurice A., Akron, Ohio.
Lummus Co., The Walter E., Boston, Mass.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.
Robinson Clay Product Co., Akron, O.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.
U. S. Stoneware Co., The, Akron, O.

Acetylene and Oxy-Acetylene Generators and Equipment
International Oxygen Co., N. Y. C.

Acid and Alkali Resistant Apparatus
Elyria Enameled Prod. Co.,Elyria,O., & N.Y.C.
Pfaudler Co.,Rochester,N.Y., Detroit, & N.Y.C.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Acid Colors
Marden, Orth & Hastings Co., Inc., N. Y. C.

Acid Eggs
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Jacoby, Henry E., N. Y. C.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Acid Pitchers
Bausch & Lomb Optical Co., Rochester, N. Y.
Knight, Maurice A., Akron, Ohio.
Robinson Clay Product Co., Akron, O.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.
U. S. Stoneware Co., The, Akron, O.

Acid Proof Brick
Bausch & Lomb Optical Co., Rochester, N. Y.
German-American Stoneware Works, N. Y. C.
Knight, M. A., Akron (East Side), Ohio.
Robinson Clay Product Co., Akron, O.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.
Thermal Syndicate, Ltd., New York City.
U. S. Stoneware Co., The, Akron, O

Acids
Herman & Herman, Inc., N. Y. C.
Marden, Orth & Hastings Co., Inc., N. Y. C.

Acid: Acetic
Carbolic
Citric
Hydrochloric
Hydrofluoric
Lactic
Mixed
Nitric
Oleum
Marden, Orth & Hastings Co., Inc., N. Y. C.

Acid, Oxalic
Marden, Orth & Hastings Co., Inc., N. Y. C.
Wiarda, John C. & Co., Brooklyn, N. Y.

Acid, Sulphuric
Marden, Orth & Hastings Co., Inc., N. Y. C.
Wiarda, John C. & Co., Brooklyn, N. Y.

Acid, Tartaric
Wiarda, John C. & Co., Brooklyn, N. Y.

Acid Ware (Vitrified Clay)
Robinson Clay Product Co., Akron, O.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.

Acid Valves
Chadwick-Boston Lead Co., Boston, Mass.
Cleveland Brass Mfg. Co., The, Cleveland, O
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C
York Manufacturing Co., York, Pa

Agitators, or Mixers
Devine Co., J. P., Buffalo, N. Y.
Dorr Co., The, Denver, Col. & N. Y. C.
General Filtration Co., Inc., Rochester, N. Y
Pfaudler Co., Rochester, N.Y., Detroit & N.Y.C
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C
Werner & Pfleiderer Co., Saginaw, Mich

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Abbé Engineering Co., N. Y. City.
Crowell Engineering Co., Brooklyn, N. Y.
General Electric Co., Schenectady, N. Y.
Hubbard's Sons, Norman, Brooklyn, N. Y.

Air Washers
Carrier Engineering Corp., N. Y. C.

Aluminum Compounds
Alum
Aluminum Sulphate
Marden, Orth & Hastings Co., Inc., N. Y. C.

Alum
Wiarda, John C. & Co., Brooklyn, N. Y.

Ammeters
Brown Instrument Co., Philadelphia, Pa.

Ammonia
Unger, John S., Chicago, Ill.

Ammonia, Carbonate
Wiarda, John C. & Co., Brooklyn, N. Y.

Ammonia, Fluoride
Wiarda, John C. & Co., Brooklyn, N. Y.

Ammonia, Muriate
Wiarda, John C. & Co., Brooklyn, N. Y.

Ammonium Compounds — Ammonium Nitrate
Marden, Orth & Hastings Co., Inc., N. Y. C.

Ammonia Fittings and Supplies
York Manufacturing Co., York, Pa.

Analysis—Gas Apparatus
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eberbach & Son Co., Ann Arbor, Mich.
Eimer & Amend, New York City
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sarco Co., Inc., New York City.
Scientific Materials Co., Pittsburg, Pa.

Analytical Apparatus
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Buffalo Dental Mfg. Co., Buffalo, N Y
Eberbach & Son Co., Ann Arbor, Mich
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo
Laboratory Supply Co., Columbus, O.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia Pa.

Analytical Laboratories
Columbus Laboratories, Chicago, Ill.
Dearborn Chemical Co., Chicago, Ill.
Sadtler & Son, Samuel P., Philadelphia.

Antimony, Needle
Wiarda, John C. & Co., Brooklyn, N. Y.

Asphalt Flow Plates
Howard & Morse, N. Y. C.

Bakelite
General Bakelite Co., New York City.

Balances and Weights
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eberbach & Son Co., Ann Arbor, Mich.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Laboratory Supply Co., Columbus, O.
Lenz & Naumann, Inc., N. Y. C.
Mine & Smelter Supply Co., Denver, Salt Lake City, El Paso, N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

Barium Carbonate
Wiarda, John C. & Co., Brooklyn, N. Y.

Barium Chloride
Marden, Orth & Hastings Co., Inc., N. Y. C.
Wiarda, John C. & Co., Brooklyn, N. Y.

Barium Nitrate
Marden, Orth & Hastings Co., Inc., N. Y. C.
Wiarda, John C. & Co., Brooklyn, N. Y.

Basic Colors
Marden, Orth & Hastings Co., Inc., N. Y. C.

Belt Cement
Schieren Co., Chas. A., N. Y. C.

Belt Dressing
Schieren Co., Chas. A., N. Y. C.

Blanc Fixés
Marden, Orth & Hastings Co., Inc., N. Y. C.
Wiarda, John C. & Co., Brooklyn, N. Y.

Blue Vitriol
Wiarda, John C. & Co., Brooklyn, N. Y.

Boilers
Sowers Mfg. Co., Buffalo, N. Y.

Boiler Water Treatment
Dearborn Chemical Co., Chicago, Ill.
Merck & Co., N. Y. C.

Blowers
Abbé Engineering Co., N. Y. C.
Crowell Mfg. Co., Brooklyn, N. Y.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Bolting Cloth
Abbé Engineering Co., N. Y. C.

Bone Ash
Wiarda, John C. & Co., Brooklyn, N. Y.

Boiler Insulation
Kieselguhr Co. of America, Los Angeles, Calif.

Boiler Settings
Kieselguhr Co. of America, Los Angeles, Calif.

Bone Black
Booth Apparatus Co., Syracuse, N. Y.

Books
Blakiston's Son & Co., P., Philadelphia, Pa.
Chemical Publishing Co., The, Easton, Pa.
Longmans, Green & Co., New York City.
Van Nostrand Co., D., N. Y. C.

Borax
Wiarda, John C. & Co., Brooklyn, N. Y.

Brick—Heat Insulating
Kieselguhr Co. of America, Los Angeles, Calif.

Briquette Molds
Howard & Morse, N. Y. C.

Brimstone, Crude
Union Sulphur Co., New York City.

Brinell Machines
Scientific Materials Co., Pittsburgh, Pa.

Brokers (Chemicals)
Herman & Herman, Inc., N. Y. C.

Burners—Gas and Oil
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Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Buffalo Dental Mfg. Co., Buffalo, N Y.
Eberbach & Son Co., Ann Arbor, Mich.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Laboratory Supply Co., Columbus, O.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sargent, E. H. & Co., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.

Burners—Pyrites
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Burners—Sulphur
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Burners—Sulphur (Rotary)
Glens Falls Machine Works, Glen Falls, N. Y.

Calorimeters—Fuel and Gas
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chem. Co., Henry, St. Louis, Mo.
Lenz & Naumann, Inc., N. Y. C.
Palo Company, N. Y. C.
Sarco Co., Inc., New York City.
Sargent, E. H. & Co., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

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Calcium Carbonate
Calcium Hydrate
Calcium Hypochlorite
Calcium Oxide
Calcium Phosphate
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Norton Co., Worcester, Mass.
Thermal Syndicate, Ltd., New York City.

Carboy Stoppers
Bausch & Lomb Optical Co., Rochester, N. Y.
Knight, Maurice A., Akron Ohio.
Lehigh Car, Wheel & Axle Wks., Fullerton, Pa.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.

Car Wheels
Lehigh Car, Wheel & Axle Wks., Fullerton, Pa.

Castor Oils
Marden, Orth & Hastings Co., Inc., N. Y. C.

Castings (Acid and Heat Resisting)
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Buffalo Fdy & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Pacific Foundry Co., San Francisco, Cal.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Castings (Chemical)
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Buffalo Fdy. & Mch Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Duriron Castings Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Pacific Foundry Co., San Francisco, Cal.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.
Stevens-Aylsworth Co., N. Y. C.
Werner & Pfleiderer Co., Saginaw, Mich.

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Devine Co., J. P., Buffalo, N. Y.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

Caustic Soda
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Hooker-Electrochemical Co., N. Y. C.

Cement Filler
Toch Brothers, N. Y. C.

Cement Testing Apparatus
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Centrifugal Engineers
Sharples Specialty Co., The, West Chester Pa.

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Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
International Equipment Co., Boston, Mass.
Schaum & Uhlinger, Inc., Philadelphia.
Sharples Specialty Co., The, West Chester, Pa.
Tolhurst Machine Works, Troy, N. Y.

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Booth Apparatus Co., Syracuse, N. Y.

Chemicals
Badische Company, New York City.
Baker & Adamson Chemical Co., Easton, Pa.
Baker Chemical Co., J. T., Phillipsburg, N. J.
Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Dearborn Chemical Co., Chicago, Ill.
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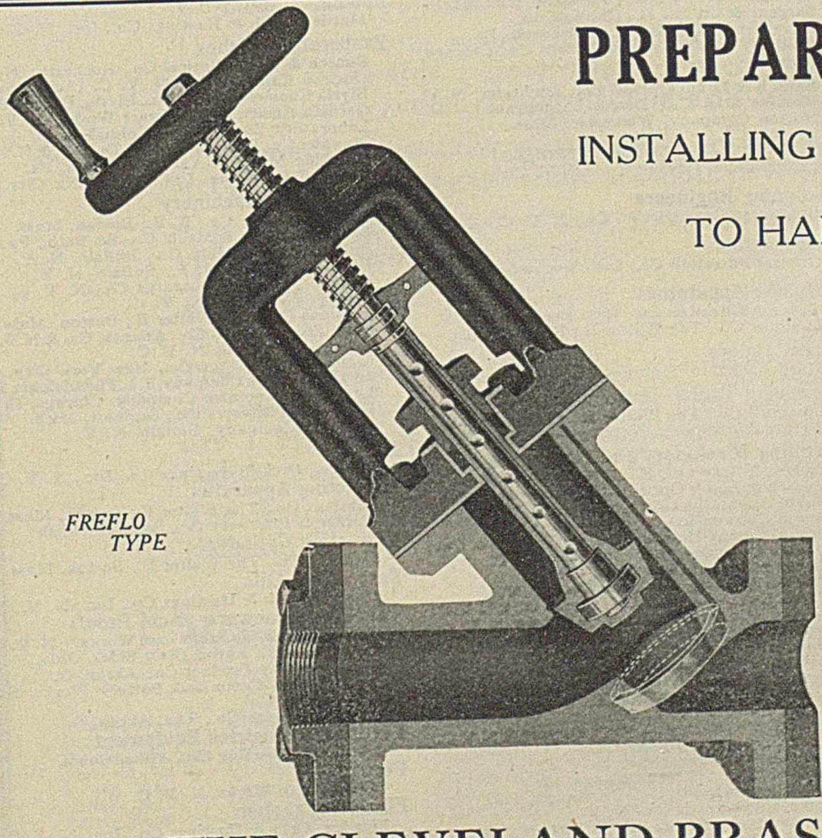

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Corning Glass Works, Corning, N. Y.
Eberbach & Son Co., Ann Arbor, Mich.
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Griebel Instrument Co., Carbondale. Pa.
International Glass Co., Millville. N. J.
Laboratory Supply Co., Columbus, O.
Scientific Materials Co., Pittsburgh, Pa.
Whitall Tatum Co., Philadelphia, Pa.

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Lummus Co., The Walter E., Boston, Mass
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.

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Mallinckrodt Chem. Co., St. Louis, Mo.
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Electro Bleaching Gas Co., N. Y. C

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Chrome Solution
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Beta-Naphthol
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Dinitro-Naphthalene
Dimethyl Aniline
Naphthalene
Picric Acid
Salicylate, Soda
Salicylic Acid
Salol
Toluol
Marden, Orth & Hastings Co., Inc., N. Y. C.

Coal-Tar Products
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National Aniline & Chemical Co., N. Y. C.

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Pratt Eng. & Mach. Co., Atlanta, Ga. &'N.Y.C.
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Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co.,San Francisco, Cal
Eberbach & Son Co., Ann Arbor, Mich.
Eimer & Amend, N. Y. C.
Heil Chem. Co., Henry, St Louis, Mo.
Lenz & Naumann, Inc.. N. Y. C.
Palo Company, N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburg, Pa.
Thomas Co., Arthur H., Philadelphia, Pa.

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National Aniline and Chemical Co., N. Y. C.

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Laboratory Supply Co., Columbus, O
Norton Co., Worcester, Mass.
Scientific Materials Co., Pittsburgh, Pa.
Thermal Syndicate, Ltd., New York City.

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Jacoby, Henry E., N. Y. C.
Lummus Co., The Walter E., Boston, Mass.

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Foster, A. B., Washington, D. C.
Guarantee Construction Co., N. Y. C.
Hall & Paul, Pittsburgh, Pa.
Hersey Co., Ltd., Milton, New York, Montreal, Winnipeg.
Levin, Isaac H., Newark, N. J.
Little, Arthur D., Inc., Boston, Mass.
Munn, W. Faitoute, East Orange, N. J.
Ney, A. H., Inc., N. Y. City.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.
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Spackman Eng. Co., Henry S., Philadelphia, Pa.
Unger, John S., Chicago, Ill.

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General Electric Co., Schenectady, N. Y.

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Copper Oxide
Wiarda, John C. & Co., Brooklyn, N. Y.

Copper Sulphate
Marden, Orth & Hastings Co., Inc., N. Y. C.

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Bucyrus Copper Kettle Works, Bucyrus, O.

Corn Oil (Extracted)
Woolner & Co., Peoria. Ill.

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Kieselghur Co. of America, Los Angeles, Calif.

Critical Point Determination Apparatus
Brown Instrument Co., Philadelphia, Pa.
Scientific Materials Co., Pittsburgh, Pa.

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Baker & Co., Inc., Newark, N. J. (Platinum)
Bausch & Lomb Optical Co., Rochester, N. Y.
Bishop & Co., J., Malvern, Pa. (Platinum)
Buffalo Dental Mfg Co., Buffalo, N. Y
Dixon Crucible Co., Joseph, Jersey City, N. J
Duriron Castings Co., N. Y. C. (Acid Proof).
Heil Chemical Co., Henry, St. Louis, Mo.
Laboratory Supply Co., Columbus, O.
Norton Co. Worcester, Mass. (Alundum).
Thermal Syndicate, Ltd., N. Y. C. (Vitreosil).

Crushers and Grinders (Industrial and Laboratory)
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Bausch & Lomb Optical Co., Rochester, N. Y.
Braun Corporation, Los Angeles, Calif.
Braun-Knecht-Heimann Co., San Francisco, Cal.
Eimer & Amend, New York City.
Heil Chemical Co., Henry, St. Louis. Mo.
Lehigh Car, Wheel & Axle Wks., Fullerton, Pa.
Palo Company, N. Y. C.
Raymond Bros. Impact Pulv. Co., Chicago, Ill.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Williams Patent Crusher & Pulv. Co., Chicago

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Hoskins Mfg. Co., Detroit, Michigan.
Norton Company, Worcester, Mass.

Cylinders (Oxygen and Hydrogen)
International Oxygen Co., N. Y. City.

Designing Engineers
Guarantee Construction Co., N. Y. C.

Diaphragms
General Filtration Co., Inc., Rochester, N. Y.

Diffusion Apparatus
General Filtration Co., Inc., Rochester, N. Y.
Lummus Co., The Walter E., Boston, Mass.

Direct Colors
Marden, Orth & Hastings Co., Inc., N. Y. C.

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Lummus, Co., The Walter E., Boston, Mass.
Werner & Pfleiderer Co., Saginaw, Mich.

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Hodges Water Still Co., Woodbury, N. J.
Laboratory Supply Co., Columbus, O.
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Lummus Co., The Walter E., Boston, Mass.
Palo Company, N. Y. C.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Roos' Sons, August, N. Y. C.
Sanborn Evaporator Co., N. Y. C.
Sargent & Co., E. H., Chicago, Ill.
Scientific Materials Co., Pittsburgh, Pa.
Stevens-Aylsworth Co., N. Y. C.
Stokes Machine Wks., F. J., Philadelphia.
Swenson Evaporator Co., N. Y. C.
Thomas Co., Arthur H., Philadelphia, Pa.
Unger, John S., Chicago, Ill.
Werner & Pfleiderer Co., Saginaw, Mich.
Zaremba Company, Buffalo, N. Y.

Draft Gauges
Brown Instrument Co., Philadelphia, Pa.

Dry Blast Plants
Carrier Engineering Corp., N. Y. C.

Dryers
Lehigh Car, Wheel & Axle Wks., Fullerton, Pa.

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Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine & Company, J. P., Buffalo, N. Y.
Jacoby, Henry E., New York City.
Stokes Machine Co., F. J., Philadelphia, Pa.
Werner & Pfleiderer Co., Saginaw, Mich.

Drying Apparatus and Machinery
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Co., J. P., Buffalo, N. Y.
Jacoby, Henry E., New York City.
Werner & Pfleiderer Co, Saginaw, Mich.

Ductility Machines
Howard & Morse, N. Y. C.

Dyestuffs
Farbwerke-Hoechst Co., New York City
Herman & Herman, Inc., New York City.

Dyewoods
Marden, Orth & Hastings Co., Inc., N. Y. C.

Dynamos and Motors
General Electric Co., Schenectady, N. Y.

Efficiency Instruments
Brown Instrument Co., Philadelphia, Pa.
Scientific Materials Co., Pittsburgh, Pa.

Electrical Instruments
Brown Instrument Co., Philadelphia, Pa.
Thwing Instrument Co., Philadelphia Pa

Electrical Measuring Instruments
Brown Instrument Co., Philadelphia, Pa.
Leeds & Northrup Co., Phila., Pa.

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General Electric Co., Schenectady, N. Y.

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Bausch & Lomb Optical Co., Rochester, N. Y.
Bishop & Co., J., Platinum Works, Malvern, Pa.
Eimer & Amend, New York City.
Engelhard, Chas., New York City.
Heil Chemical Co., Henry, St. Louis, Mo.
Palo Company, N. Y. C.

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Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.

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Toch Brothers, N. Y. C.

Epsom Salts
Marden, Orth & Hastings Co., Inc., N. Y. C.

Evaporating Dishes
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Duriron Castings Co., N. Y. C. (Acid Proof).
Elyria Enameled Prod. Co., Elyria, O.,& N.Y.C.
German-American Stoneware Works, N. Y.
Laboratory Supply Co., Columbus, O.
Pfaudler Co., Rochester, N.Y., Detroit, & N.Y.C.
Scientific Materials Co., Pittsburgh, Pa.
Thermal Syndicate, Ltd., New York City.

Evaporating Machinery
Badger & Sons, Co., E. B., Boston, Mass.
Bethlehem Fd'y & Mach. Co., So. Beth., Pa.
Buffalo Fdy. & Mch. Co., Buffalo, N. Y.
Devine Company, J. P., Buffalo, N. Y.
Electric Heating Apparatus Co., N. Y. C.
Jacoby, Henry E., N. Y. C.
Lummus Co., The Walter E., Boston, Mass.
Pratt Eng. & Mach. Co., Atlanta, Ga. & N.Y.C.
Roos' Son, August, N. Y. C.
Sanborn Evaporator Co., New York City.
Stokes Machine Company, F.J., Philadelphia, Pa.
Swenson Evaporator Company, Chicago, Ill
Werner & Pfleiderer Co., Saginaw, Mich.
Zaremba Company, Buffalo, N. Y.

Extracts
Marden, Orth & Hastings Co., Inc., N. Y. C.

Extracting Apparatus
Lummus Co., The Walter E., Boston, Mass.
Werner & Pfleiderer Co., Saginaw, Mich.

Extraction Cylinders
Lummus Co., The Walter E., Boston, Mass.

Fatty Acid Oils
Marden, Orth & Hastings Co., Inc., N. Y. C.

Faucets (Stoneware—Acid Proof)
German-American Stoneware Works, N. Y. C.
Knight M. A., Akron (East Side), Ohio.
Robinson Clay Product Co., Akron, O.
Steiger Terra Cotta and Pottery Works, San Francisco, Cal.
U. S. Stoneware Co., The, Akron, O.

Fertilizer Industries Equipment
Schutte & Koerting Co., Philadelphia.

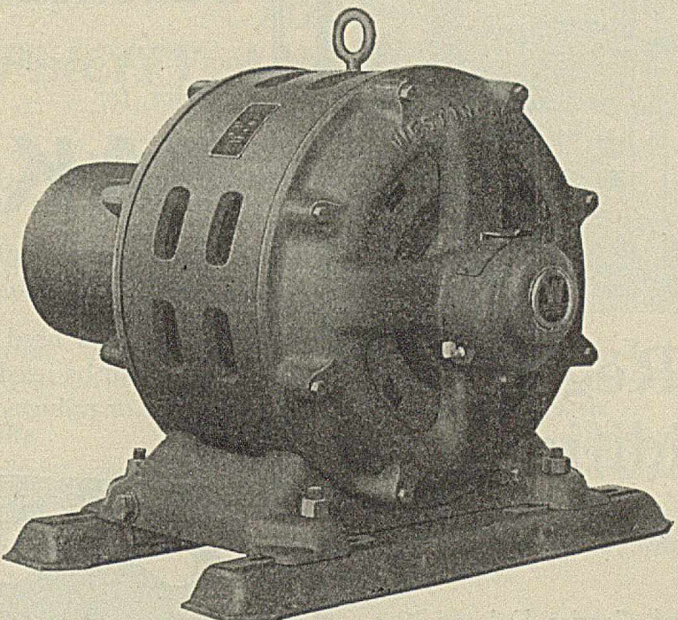
Fertilizers
German Kali Works, N. Y. C.

Fibre Toughener
Marden, Orth & Hastings Co., Inc., N. Y. C.

Filter Cloth (Metallic)
Sweetland Filter Press Co., Brooklyn, N. Y.

Filtering Media
General Filtration Co., Inc., Rochester, N. Y.
Kieselguhr Co. of America, Los Angeles, Cal.

Not Every Motor Is Suitable for



Electrochemical Service

Successful and continuous service in chemical plants is assured with Westinghouse Type CS Motors.

The coils are form wound and impregnated by a special vacuum process, and afterwards treated, which renders the windings impervious to the destructive action of alkaline and acid fumes.

The rotor is practically indestructible. There is nothing to burn out, work loose or deteriorate under the heat developed in service.

The frame and feet are of heavy forged open-hearth steel, thus providing great mechanical strength.

The efficiency and power factor are unusually high, which means low power cost.

The Westinghouse Company gives each and every detail the benefit of its years of experience—maintains a large specialized engineering corps; has a most complete shop equipment; employs only materials of the highest grade, and tests all details and machines carefully before shipment.

The Westinghouse Type CS Motor is the most serviceable for electrochemical Plants.

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Toledo, Ohio
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*W. E. & M. Co. of Texas

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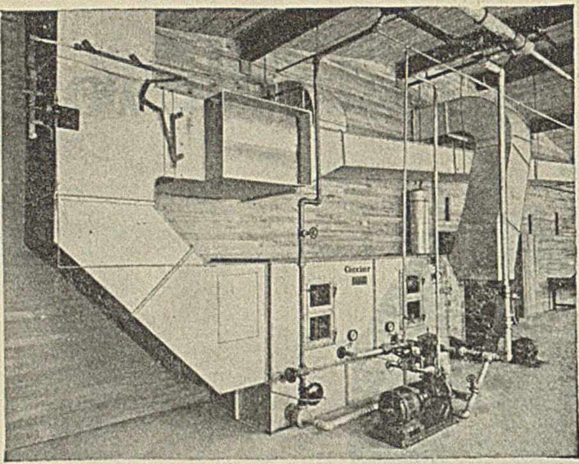

Closely Regulated Dehumidification All Year Around

The above typical Carrier Dehumidifier installation at the plant of the Gathmann Ammunition Co., Texas, Md., uses well water for dehumidifying and is completely equipped for automatic regulation.

This type of dehumidifier can be used even where artificial refrigeration is required to get the water cool enough, provided the cooling is done in some other part of the building and the cooled water is pumped to the dehumidifier.

However, where a very cool temperature is required, the Carrier Self-Contained Dehumidifier, provided with means for cooling the water by refrigeration *within the humidifier*, is more compact and highly efficient under a wide range of conditions.

The exact type of dehumidifier for any particular conditions is a matter concerning which our engineers are always ready to advise. If interested in dehumidification, get our new bulletin, and if you want some helpful suggestions, tell us your requirements.

Carrier

Engineering Corporation

39 Cortlandt St., New York

Chicago:
Transportation Bldg.

Buffalo:
Mutual Life Bldg.

Boston:
176 Federal St.

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Carrier
AIR CONDITIONING AND DRYING EQUIPMENT

33

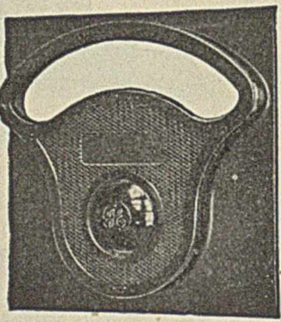
Not a Hard Rubber Substitute—

not if you consider a substitute as something inferior, for

BAKELITE

is vastly superior to hard rubber in every way except possibly flexibility.

Bakelite is used for everything that hard rubber can be used for, and it makes a better product or reduces cost.

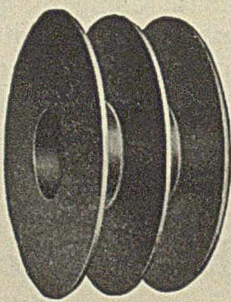


This unique material is used for moulded insulation where hard rubber won't do because of the heat. Bakelite is chemically inert—it won't turn green, nor bloom; it resists oil, water, acids and most solvents.

When metal inserts are needed, Bakelite shows to great advantage, the inserts are moulded in, accurately positioned while moulding; they are more secure than when screwed into hard rubber and the expense of drilling, tapping and fitting is eliminated.

Bakelite moulded pieces are as beautiful as the best polished hard rubber.

Bakelite is not a hard rubber substitute—it's better.



Strength—high heat resistance—imperviousness to moisture and oils—high electrical resistance.

Metal inserts positioned with absolute accuracy—no expense for drilling, tapping or fitting.

GENERAL BAKELITE COMPANY

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Lummus Benzol Stills
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Producing pure white turpentine, free from oils on spot test

Your specifications, advising crudes, quantities and products desired, are solicited

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Schutte Diaphragm

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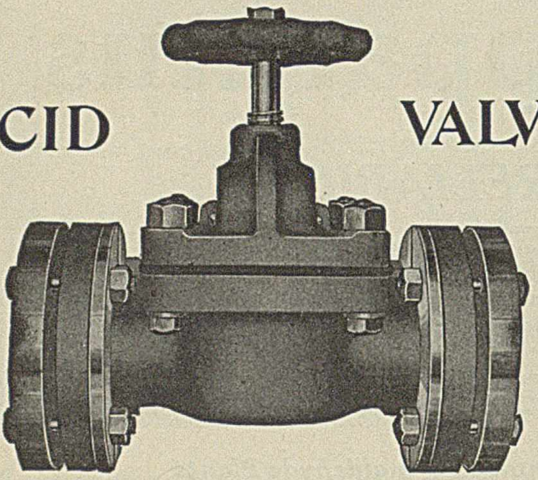

THIS valve does not have the objectionable stuffing box, neither does the stem extend into the acid, but is above the disc which is made of a high grade of hard rubber composition. There is absolutely no tendency to stick. Acid comes only in contact with lead or rubber composition. Write for catalog 8-L.

Schutte & Koerting Co.

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Boston Pittsburg Denver

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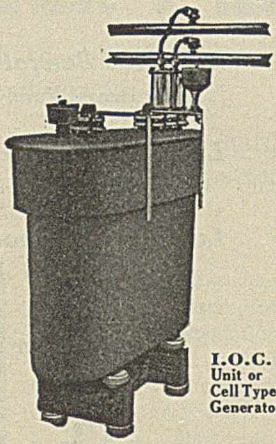
I.O.C. SYSTEM OXYGEN and HYDROGEN GENERATORS

Both our Unit and our Bipolar Generators are rated at 4 cu. ft. of oxygen and 8 cu. ft. of hydrogen per K.W.H. hour. Knowing your current cost, figure for yourself the power cost per cu. ft. of gas, The added cost factors—interest, depreciation, upkeep, attendance (the latter practically nothing)—will increase this slightly. But you will still find that your own I. O. C. plant will save you 50 to 60 per cent over the cost of gas in cylinders. Why—then—persist in wasteful methods? Let us consult with you.



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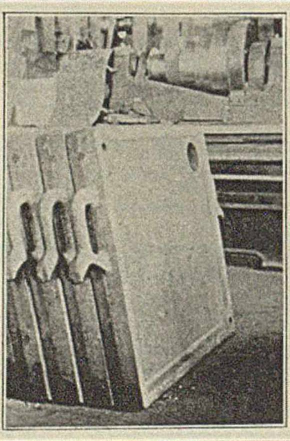

THE SPERRY FILTER PRESS

is built to filter most efficiently the materials it is intended to handle. We are thus prepared to supply Sperry filter presses made of wood, lead, bronze or iron arranged in many different combinations as to feeding, washing, etc.

To the left is shown a cut of the Sperry steam-heated or refrigerated filter plates. These are often used either to prevent or to cause crystallization during filtration.

D. R. SPERRY & CO. Makers of the **Sperry Filter Press, Batavia, Ill.** Near Chicago

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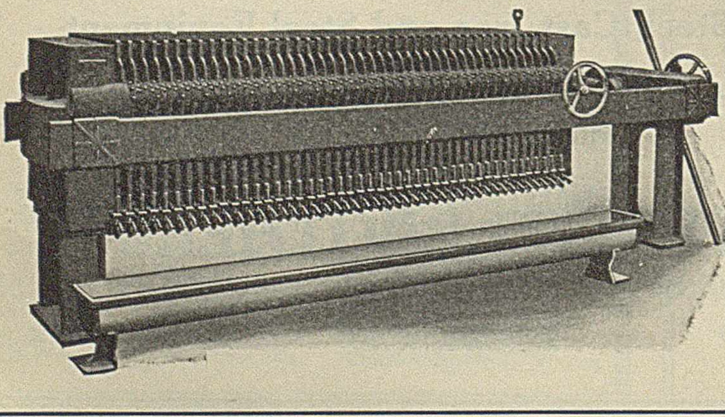

Unusual Operating Efficiency

The Shriver Filter Press is designed in such a manner as to guarantee an unusual volume of efficiency in operation at low cost.

Proper proportioning insures excessive strength. Our pyramid drainage surface construction on the plates gives increased filtering area. The large openings in the frames prevent clogging. We have installed improved outlet cocks which facilitate operation. And our accurate machining throughout prevents leakage.

Made in sizes adaptable to any kind of work
Special presses made to order

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